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3,713,917

BLASTING SLURRY COMPOSITIONS CONTAINING CALCIUM NITRATE AND METHOD OF PREPARATION

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No Drawing. Continuation-in-part of application Ser. No. 821,095, May 1, 1969. This application Nov. 16, 1970, Ser. No. 90,005

Int. Cl. C06b 1/04

U.S. Cl. 149—20

8 Claims

ABSTRACT OF THE DISCLOSURE

Pumpable slurry blasting compositions of high sensitivity are made up of a liquid phase which is an aqueous solution of powerful inorganic salts, such as ammonium and/or sodium nitrate, including calcium nitrate, plus a liquid fuel such as ethylene glycol. The liquid phase is at least partially thickened before adding particulate solid fuels such as carbonaceous or hydrocarbonaceous solids (coal, gilsonite) and/or heat-producing metals, such as aluminum, magnesium, or boron. Self-explosive particles of TNT, smokeless powder, etc., can be used with or in lieu of other fuels. Proportions of calcium nitrate and total liquid are so selected that, on cooling from an elevated preparation temperature, the calcium salts crystallize out in substantial proportions, thus taking up water of crystallization, in effect increasing viscosity of the slurry to condition such that it is not pumpable by conventional pumping means, and thus improving and maintaining sensitivity and detonability to levels suitable for small diameter charges.

This application is a continuation-in-part of Ser. No. 821,095 filed May 1, 1969, now Pat. No. 3,660,181.

BACKGROUND AND PRIOR ART

Slurry blasting agents, having an aqueous liquid phase containing dissolved ammonium nitrate and/or other powerful oxidizing agents, thickened with a hydratable gum and/or starch, and rendered detonable by inclusion of suspended particulate solid fuel, have come into wide commercial use in recent years. The most widely used blasting slurries are made up mainly of an aqueous solution of ammonium nitrate, to which some sodium nitrate may be added, together with guar gum as a thickener or gelling agent and sensitized by inclusion of suspended particles of TNT, aluminum, or other fuels. Examples of these are described in U.S. patents to Cook and Farnam, Nos. 2,930,685 and Reissue 25,696. Other fuels are often included, such as gilsonite, coal and other hydrocarbons or carbonaceous solids, as in U.S. Pats. 3,367,805 and 3,453,158. Sulfur is often used as a fuel ingredient, as in U.S. Pats. 3,249,477 and 3,282,752. Instead of the nitrates, other powerful inorganic oxidizer salts such as sodium, ammonium and other chlorates and perchlorates may be used, or these may merely supplement the more common ammonium sodium nitrates.

These slurry blasting agents often have important advantages over the more conventional dynamites and other solid explosives. They can be pumped or poured to fill boreholes, completely up to any desired height. Many of them can be made at the blasting site from separate non-explosive ingredients, thus eliminating many safety problems. They can be loaded with minimum labor by pumping them directly from a mixing station into deep boreholes. When properly thickened or gelled, they have high resistance to erosion and/or leaching effect of ground water which is frequently encountered in boreholes; in this

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respect they are usually much superior to dry explosives such as AN/FO or ammonium nitrate sensitized with fuel oil. They may have greater density than AN/FO and are superior in this respect also to most dynamites.

Slurry blasting agents of the prior art, however, also have some deficiencies. Some of the thickening systems based on a guar gum and/or starches, with or without cross-linking agents, are not stable enough for extended storage. They may be subject to syneresis, or may lack stability at warm temperatures or undergo leaching, etc., in the presence of water. For on-site preparation and delivery, it is desirable to have a thickening or gel-forming system which is delayed long enough to permit pumping the agent through a hose without excessive energy or pressure and yet acts rapidly enough to thicken up and hold the composition together with sufficient firmness to prevent gravitational separation of suspended solid particles from the aqueous suspending medium and to resist leaching or penetration and breaking up by the action of ground water, e.g., in boreholes. To some extent, the use of cross-linking agents has been very helpful in this respect. Examples of cross-linking are described in U.S. Pats. Nos. 3,096,223, 3,445,305, 3,485,686 and others. An example of a very successful method for mixing and delivering these slurries is given in U.S. Pat. No. 3,303,738.

Another problem of prior art slurries is that of consistent or controlled sensitivity. Most slurry blasting agents based on aqueous solutions of ammonium nitrate, or of mixtures of ammonium nitrate and sodium nitrate, are quite insensitive and hence require large diameter charges and powerful boosters for reliable detonation. Water, of course, strongly opposes detonation even though, at high temperatures, it can enter actively into the explosive reaction, as described in U.S. Pat. 25,695 mentioned above. Various means have been proposed and used to increase sensitivity in such slurries. The use of self-explosive particles was one of the first, as in U.S. Pat. No. 2,930,686. Finely divided aluminum, as in Reissue 25,695 and 3,367,805, is helpful, especially if it is coated so as to be repellant toward the liquid phase and thus to entrap bubbles of air or other gas to form "hot spots." These assist in both initial detonation and in propagation of the detonation wave through the explosive mass. Combinations of elemental sulfur in the fuel and sodium nitrate in the oxidizer are helpful. See U.S. Pats. Nos. 3,249,477 and 3,282,752, mentioned above. Reduction in bulk density or apparent density by incorporation of gas is helpful in many cases, see U.S. Pat. 3,382,117, and various methods for introducing or generating gas for this purpose have been described in U.S. Pats. 3,288,658, 3,288,661, 3,390,028-32, 3,453,158, and others. The sensitivity of most of the fuel-sensitized blasting slurries, as distinguished from those containing self-explosive sensitizers can be increased by reducing their bulk density but the work potential also may be reduced to an objectionable degree.

It is obviously desirable to increase sensitivity, or to maintain adequate sensitivity for reliable detonation, without losing blasting power. It is also highly desirable to avoid the considerable losses in sensitivity which occur in most slurries as the ambient temperature is lowered. Many blasting slurries which have adequate sensitivity at normal ambient temperatures are failures when placed in cold boreholes or when used in cold weather. To improve sensitivity and to maintain it in spite of substantial temperature reductions is a major object of this invention.

This invention is based, among other things, on the discovery that use of calcium nitrate as a significant ingredient in aqueous ammonium nitrate slurries, particularly, can be extremely helpful in maintaining sensitivity over wide temperature ranges. This is surprising, because calcium nitrate has generally been regarded as a

relatively "dead" oxidizer. Although it has been mentioned frequently as a possible component of blasting compositions, including blasting slurries, there are relatively very few instances where it has actually been used. Calcium nitrate has been suggested as a possible constituent of explosives, including slurry type explosives in various references, including U.S. Pats. 3,249,476, 3,390,029, 3,450,582, 3,459,608, 3,475,238, 3,496,040, and others. However as far as applicants are aware, the concept of using dissolved calcium nitrate in a starting solution, which is heated above ambient temperature during slurry formation, in sufficient proportions to precipitate strongly and tie up part of the water in the slurry as it cools to ambient or borehole temperature, has not previously been known. By this means, according to the present invention, several useful functions not hitherto recognized or known are accomplished. (1) Since commercial calcium nitrate carries with it about 15% by weight of water of crystallization, the quantity of added water or other liquid required to obtain a pumpable or pourable fluid consistency is substantially reduced, compared to slurries made up of salts having no water of crystallization. (2) Calcium nitrate added to a solution containing ammonium nitrate, or containing a mixture of ammonium nitrate and other strong oxidizer salts such as sodium nitrate can form eutectic mixtures of relatively lower crystallization or "fudge" point. That is to say, more total oxidizer of the nitrate, chlorate and/or perchlorate type mentioned above, can be dissolved in a given quantity of water or water mixed with a compatible organic liquid such as a lower alcohol, diol, or similar oxygenated hydrocarbon derivative having fuel value. This makes it possible to reduce the mixing temperature for greater safety. (3) By making the solution at a temperature somewhat above ambient, e.g., 30° C. or higher, solubility of calcium nitrate mixed with other oxidizers such as ammonium nitrate, etc., is very high indeed, making possible the formation of effective suspensions of solid particulate fuels (aluminum, gilsonite, sulfur, TNT, etc.) which can be poured and pumped as liquids, with remarkably small proportions of liquid solvent. (4) After the slurry has thus been mixed, it can be pumped or flowed through conduits to a point of use. By this term it is intended to mean either a blasting site, such as a borehole filled directly by pumping or by pouring, or a package or container such as a bag, tube, can, drum or box. This flowing and filling, or delivery, is accomplished before the slurry composition has cooled to its crystallization or "fudge" point. (5) As further cooling takes place, in a borehole, for example, or in a container, the crystallization of the calcium nitrate takes up substantial amounts of water of crystallization, about four mols of water per mol of salt. This tends to stabilize as well as to increase slurry viscosity, drying up excess water and converting the composition at least directionally to a firmer (though still pliable) mass which is very resistant to gravitational segregation of suspended solid particles. The liquid phase is pre-thickened appreciably before the suspended solid particles are added. This stabilizing or relative rigidification fixes in place numerous small bubbles of air or other gas contained in the slurry. Such a gas may be air, temporarily entrapped when solids are added to the viscous liquid phase, or it may be other gas introduced or generated in situ in the slurry, e.g., by decomposition of nitrites, hydrides, carbonates, etc. The amount of calcium nitrate should be sufficient to cause fixation or stabilization of the gas bubbles widely distributed throughout the firm gel structure. According to an accepted "hot spot" theory, numerous small but widely distributed bubbles contribute very substantially to sensitization of the slurry. The dehydrating effect of the calcium nitrate thus helps to assure good sensitivity of the cooled slurry, even at temperatures where comparable mixtures containing ammonium nitrate without calcium nitrate would fail.

Objects of the present invention therefore include (a) making possible use of less aqueous solvent to obtain a pourable, pumpable (through viscous) slurry; (b) reducing the fudge point and thereby avoiding unnecessary heating of the solution to obtain a desired concentration of oxidizer salt; (c) accelerating the firming up or rigidification of the slurry after it is delivered or packaged, thereby to (d) hold suspended particles in the slurry against segregation; (e) improve water resistance, and (f) improve sensitivity by fixing previously entrapped or otherwise incorporated gas bubbles against migration and escape, thus enhancing sensitivity of the cooled slurry to detonation. The firming up of the slurry also tends to prevent wetting of coated particles of paint grade aluminum commonly used as a fuel and sensitizer. This helps aluminum sensitized slurries to retain their sensitivity during long time periods of storage. By the expression "sensitizing to detonation," it is always intended to mean so affecting the composition that it will detonate more readily on initiation by a primary explosive such as a cap or a booster. The invention will be better understood by reference to the preferred embodiment and specific examples shown below.

SUMMARY

An explosive slurry blasting composition is improved in its sensitivity, particularly, and also in its stability, in presence of water, and its general reliability, by incorporating in the solution enough calcium nitrate, at least 5% and preferably 10%, more preferably as much as 20% or more, of calcium nitrate as an oxidizer ingredient. The calcium nitrate component is combined with other powerful inorganic oxidizer salts conventionally used in explosives of this character, particularly ammonium nitrate or ammonium nitrate mixed with sodium nitrate. The latter may be used alone with calcium nitrate, under some conditions, and other oxidizers such as the ammonium; also, the alkali metal chlorates and perchlorates and mixtures of any two or more of these may sometimes be substituted wholly or in part for the ammonium nitrate, etc. As a lower limit, calcium nitrate is used in proportions necessary to dehydrate or firm up the slurry, as it passes through the fudge point on cooling, sufficiently to cause a firming up or rigidification, due to taking up water or crystallization, that will positively prevent gravitational segregation of solid particles such as fuel (aluminum, carbonaceous or hydrocarbonaceous particles such as gilsonite or coal, TNT, etc., or oxidizer crystals, flakes, granules, or pellets, and the like). Further, the lower limit should preferably be enough calcium nitrate to hold the fudge point of the oxidizer solution below 50° C. while using only enough liquid to produce a smooth pourable and pumpable slurry at that temperature. The maximum proportion of calcium nitrate is about 40% by weight, based on the final total slurry, and preferably not substantially more than the weight of other oxidizer salt present, such as AN, etc. Preferred proportions are between about 20 and 35% by weight of calcium nitrate. Particulate fuels, such as aluminum, carbon containing particles, etc., may comprise 5 to 30% by weight of the total. Added water, as distinguished from that present as water of crystallization in the calcium nitrate used, is between 2 and 15% by weight, preferably combined with an inorganic compatible liquid fuel value selected from the lower alcohols and polyols, such as ethylene glycol, propylene glycol, glycerol. Preferably, ethylene glycol is used in proportions of 3 to 20%, more preferably 5 to 12%. The solution, which forms the liquid phase of the slurry when the slurry is first formed by suspending the particulate solids (which solids may comprise both fuels and oxidizers) is thickened enough, prior to adding the solids, to entrap at least enough air or other gas, which may be introduced with the solids or otherwise, to effect a lowering of bulk

density of the slurry. Gelling or thickening agents, preferably cross-linkable, such as galactomamans, farinaceous or argillaceous materials, preferably guar gum, are used in proportions of 0.05 to 4% for this purpose. These include the thickener added to the solution before the fuels or other solid and undissolved particles are added thereto.

DESCRIPTION OF PREFERRED EMBODIMENT

To illustrate the range of ingredients and proportions thereof which can be used in the present invention, a number of compositions were prepared and tested. These are described, along with test results, in specific examples described below. The invention is not limited to these examples, however.

Example I

Two solutions were prepared at 55° C., using the following ingredients in percentage by weight (A shows water added, whereas B shows total water, including water of crystallization present, deducted from calcium nitrate):

Comp.	AN	SN	CN	H ₂ O	Guar	ThioU	E.G.	Total
A.....	41.2	3.0	43.2	3.0	0.15	0.1	9.35	100
B.....	43.8	3.0	33.9	9.7	0.15	0.1	9.35	100

These compositions were prepared by mixing the three salts, ammonium nitrate (AN), sodium nitrate (SN) and calcium nitrate (CN) together and adding them to the water and glycol (E.G.). The guar (gum) and thiourea ("ThioU") were added to the oxidizer salts before dissolution. The guar gum was a rapid gelling prehydrated commercial product added after all salts and thiourea had dissolved at an elevated temperature. As the salts commenced to dissolve, water of crystallization in the calcium nitrate was released and the whole mass liquified quite rapidly. Due to the guar gum thickener or gelling agent, the liquid solution was rather viscous and syrupy. Solution A at a temperature of 53° C., had a viscosity of about 1000 cp. or 5000 Saybolt seconds and a density of 1.54 grams per cc. Its fudge point, i.e., the temperature at which the salts precipitated rapidly, was 48° C. This solution was used later for making up explosive slurries by adding finely divided aluminum and other particulate fuels which were suspended in the aqueous-glycol fluid phase. Further data are given below.

Example II

A series of compositions were made up by first making solutions in the same general manner as above. In general, the three nitrates, water and a guar gum thickener dispersed in ethylene or propylene glycol, were mixed at elevated temperatures to form a viscous solution, as above and the various particulate fuels, pelletized TNT, gilsonite, aluminum and/or smokeless powder, were added to the liquid. Proportions are shown as proportions by weight and the data for four compositions are tabulated in Table I below:

TABLE I

	A	B	C	D
Proportions by weight:				
Ammonium nitrate.....	42	45	45	55.2
Sodium nitrate.....	9	10	10	-----
Calcium nitrate.....	37	36.5	36.5	36.8
Water.....	12	8.5	8.5	8.0
Guar gum thickener.....	0.1	0.1	0.1	0.25
Ethylene glycol.....	0.2	-----	-----	0.5
Propylene glycol.....	-----	1.0	1.0	-----
TNT ("Pellitol").....	16	-----	-----	-----
Gilsonite.....	3.7	6.0	6.0	-----
Aluminum, coarse.....	-----	9.0	9.0	-----
Aluminum, fine.....	-----	1.0	1.0	-----
Smokeless powder.....	-----	-----	-----	28
Density, g./cc.....	-----	1.40	1.34	-----

¹ At 54° C.

Composition A was prepared by dissolving the sodium nitrate first in warm water, 70° C., then adding the ammonium nitrate and calcium nitrate together. In these tests a Norwegian calcium nitrate was used. This composition was not tested for detonation, but would be expected to be detonable and it had a good consistency. In compositions B and C test charges were made up in 2", 2½", and 3" diameters, in lengths six times the diameter. The 2" charges failed to detonate completely but the larger charges were all fired successfully with a standard 2A booster (160 g. pentolite). For composition D the proportions starred made up 100% of the solution. For sensitizer, 28 parts of SPCG double base smokeless powder was used. This product had a solution density (before addition of smokeless powder) of 1.61. Density after addition of the SP was not determined. This product fired in a 2-inch column with a standard "2A" booster.

Example III

Another series of tests were made, starting with a standard oxidizer solution which was made up of the following ingredients, parts by weight.

	Percent
Ammonium nitrate (AN)	35.9
Calcium nitrate (CN)	40.8
Sodium nitrate (SN)	6.06
Water	6.06
Ethylene glycol	11.03
Guar gum, commercial	0.22

The sodium nitrate was dissolved first in the water and then the calcium nitrate and ammonium nitrate were added together to the solution which finally became entirely liquid. Temperature of this liquid was about 70° C. Water of crystallization released from the calcium nitrate helped maintain liquidity. This solution had a pH of about 4.5 and an oxygen balance of about +30%.

The guar gum was dispersed in the ethylene glycol and the resulting dispersion added to the oxidizer mixture. The resulting composition was a solution having somewhat higher viscosity than an ordinary aqueous solution of the same salts. It was cooled down to about 50° C. before adding particulate fuel or sensitizer ingredients in the form of various "pre-mixes" mentioned below. This solution had a "fudge" point (congelation temperature) of about 35° C.

In order to cross-link the gum to get higher viscosity and thus prevent segregation of suspended fuel particles, etc., various cross-linking agents, or in some cases a combination of oxidizer-reducer cross-linking agents, were used. A typical cross-linking agent, of oxidizer type, designated "A," was a 50/50 aqueous solution of potassium or sodium dichromate. Gallic acid or potassium antimony tartrate were used as reducing agents in a number of tests. In one test, 0.3% borax and 0.2% hexamethylene tetramine showed better cross-linking than the same amount of borax alone. In some tests, tapioca flour was substituted in proportions of 0.75% by weight in lieu of guar gum (0.15%) but guar gum was better. However, the tapioca flour is a useful supplement thickener.

In some of these compositions gassing agents, such as nitrous acid or nitrites of ammonia, sodium or potassium were added in very small proportions, sometimes with melamine or thiourea to accelerate decomposition and thus provide aeration. Hydrogen peroxide was used in some cases, along with traces of potassium iodide or manganese dioxide to catalyze decomposition. In some cases it was found to be difficult to thicken slurries with pH above 3.0. In these cases, a small amount of nitric acid was used to lower the pH slightly and thereby help thicken the slurry. Thus, 0.55 cc. of 58% nitric acid per 100 g. of slurry as in Table I, composition A, brought pH down to 3.0 and 2.0 cc. brought it to a level between 1.0 and 2.0 Thiourea speeded up the thickening and also increased the gassing rate when ammonium, potassium,

or sodium nitrite were used. Gassing agents are useful not only to reduce density but also to increase sensitivity. Numerous gassing agents are available, as will readily be understood by those skilled in the art.

Slurries were made up also using ground pitch or gilsonite alone, or finely divided aluminum alone, as dry fuel. The gassing rate of such slurries, using KNO_3 , did not change significantly with either fuel but initial thickening was somewhat better with aluminum. Gassing and reasons therefor are discussed further below. A self-cross-linking guar gum was a satisfactory thickener, as long as pH was not too high. So was potato starch. As little as 1% potato starch gave good initial thickening but for increased gel stability needed for prolonged storage, 3% was used. With lesser quantities of potato starch, the gelled slurries seemed to break down after standing a few days. In general, any of the strongly cross-linked polysaccharides, i.e., gums and starches, may be used as thickeners or gelling agents.

Several examples were made up starting with the above solution of Example III, using about 0.16 cc. of concentrated (58% or 70%) nitric acid per 100 grams to reduce the pH, and adding to the final slurry about 0.2% of KNO_3 as a gassing agent. Potato starch (PS) was used as a supplemental thickener. In some cases, extra ethylene glycol (EG) was added. Results are shown in Table II.

TABLE II

Example	Percent solution	Added thickener	Fuels	Modifiers
II-E.....	94	3% PS..	3% ground pitch..	0.05% thiourea, 0.06% KNO_3 , 0.3 cc. "A."
II-F.....	87.2	3% PS..	3% ground pitch, 6% EG.	0.2% thiourea, 0.12% KNO_3 , 0.3 cc. "A."
II-G.....	80.2	3% PS..	10% fine atomized aluminum, 6% EG.	0.05% thiourea, 0.12% KNO_3 , 0.3 cc. "A."

Composition E had a density of 1.14 g./cc. and was fired successfully in 3-inch, 2½-inch, and 2-inch diameter columns at 0° C., using a standard booster. A similar composition having higher density, 1.22, failed in a 2-inch column at the same temperature. Example F, with a density of 1.19, fired successfully under similar conditions as did Example G with a density of 1.06. Critical density for a 2½-inch column of this particular composition appears to be about 1.20. Hence, where a column of slurry explosive is tall, and where its own hydrostatic head, plus stemming, compresses it, supplemental aeration or gassing may be needed. The sensitivity at 0° C. is considered quite remarkable for a slurry explosive containing no self-explosive and no paint grade aluminum powder. For use in deep holes, it is often desirable to add enough gassing agent to keep density below 1.2 under pressure of as much as 50 p.s.i.g.

The compositions of Examples E, F, and G were treated with 0.2, 0.1 and 0.3 cc., respectively (per 100 grams), of concentrated (58%) nitric acid to reduce the pH to where thickening could be accomplished successfully with potato starch. Additional experiments were made to obtain a thickening system that would be effective without reducing the pH by use of acid.

Using solution of Example III as above, and cross-linking the thickener by an oxidation-reduction combination of agents, i.e., 0.2% to 0.3% agent "A" ($\text{K}_2\text{Cr}_2\text{O}_7$ in water) and gallic acid (GA) in proportions of 0.02 to 0.5, good thickening was realized in slurries of high pH (4.3 to 5.0). In some of these, aluminum was used as a fuel, to supplement the ethylene glycol in the solution. In others, a guar meal (GM) was used. Significant data are given in Table III. Each of these contained 3% by weight of potato starch as a supplemental thickener. Penetration (in mm./10) of the slurry as an indication of its viscosity was measured by use of a specially designed cone-shaped penetrometer. These readings were taken after 5 minutes and after 10 minutes, shown in this order;

likewise, densities are given after 5 minutes, 30 minutes and 24 hours to show effectiveness of gassing. Proportions shown are parts by weight.

TABLE III

Ex.	Sol.	Fuel	X-link agents	pH	KNO_3	Pen.	Density, g./cc.
III-H..	87.5	8.5 Al	0.05 GA	4.6	0.4	250 180 170	1.14 1.02 0.78 0.89
III-J..	86.9	8.5 Al	0.05 GA	-----	1.0	240 180	0.75 0.43 0.82 0.73
III-K..	89.8	9.6 GM	0.05 GA	4.8	0.4	250 180	0.57 0.87 0.75 0.60
III-L..	88.4	{5.0 Al 6.0 GM}	0.05 GA	5.0	0.4	230 180	0.90 0.77 0.60 0.82
III-M..	87.9	{8.5 Al 3.0 GM}	0.05 GA	4.8	0.4	300	0.69
III-N..	86.15	10 Al	0.5 GA	-----	0.6		

Blasting slurries must be at least reasonably stable in composition, consistency and density, particularly when they are packaged or are to be used in boreholes where they may stand 24 hours or more before use. If the gel breaks down (or viscosity decreases) so as to permit segregation of the suspended fuel or sensitizer particles, the composition may become worthless. If it loses its aeration or entrapped gas, it may become so insensitive that it will not detonate. Likewise, if placed in deep boreholes, the lower part of the explosive column may be under sufficient hydrostatic or super-imposed pressure that the charge will not detonate, or at least, will not detonate all the way. A particular object, realized in this invention, was to obtain stable gassed slurries that can be detonated in 2½-inch columns or larger, at temperatures as low as 5° C. and under pressures up to 50 p.s.i. The products described in Table III above meet these requirements. Many, perhaps most, of the blasting slurries of the prior art fall far short of the latter requirement.

The use of ethylene glycol with its fuel value and its low temperature solvent properties, as a significant ingredient, is one important feature. Another is the use of calcium nitrate which makes it possible to use higher total proportions of oxidizer for a given fudge point. A mixture of oxidizers containing ammonium nitrate and sodium nitrate with calcium nitrate is usually preferred. As noted above, a fudge point as low as 35° C. or lower is quite remarkable for a slurry having a small quantity of added water and some of these products have such. The use of an effective cross-linking system, such as dichromate-gallic acid or other oxidation-reduction combinations, which are reasonably independent of pH is important. Slurries of low pH (high acidity) are excessively corrosive to mixing and pumping equipment. In situ mixing and pumping of blasting agents has many advantages. Hence, a thickening system not dependent on low pH is advantageous. Separate ingredients which are non-explosive individually can be combined at the mine and pumped directly to the borehole before they get too viscous for pumping through hoses. Hence, controlled viscosity, which builds up slowly enough to permit mixing and pumping but rapidly enough to prevent segregation of solids or borehole water intrusion in the gel, is important.

Example IV

A solution was made up of 22.6 parts by weight of calcium nitrate, 6.5 parts of sodium nitrate, 7.6 parts of water, 24.3 parts of ammonium nitrate, 0.3 part of guar gum and 6.1 parts of ethylene glycol. 0.07 part of thiourea were added also. This solution was the basis for several slurries to be described next. It was found desirable to dissolve the calcium nitrate and the sodium nitrate first, followed by adding the ammonium nitrate with enough heat to overcome its endothermic solution characteristics. The following slurries were made up, using the

solid particulate fuels listed. Parts are by weight on the same basis as the solution which, in each case, was 67.5% of the total:

TABLE IV

	IV-A	IV-B	IV-C
Parts by weight:			
Paint grade Al.....	3.5	3.5	3.5
Atomized Al.....		3.5	6.5
Gilsonite.....	2.1	1.0	
Tapioca flour.....	3.1	3.1	3.1
Sodium thiosulphate.....	0.2	0.2	0.2
Ammon. nitrate, dry.....	23.23	20.83	18.83
Density of slurry, g./cc.....	1.18	1.22	1.25

In addition, 0.2% of sodium dichromate, in an equal amount of water, was added as a cross-linking agent. The solution had a specific gravity of 1.64 and a pH of about 5.1 before the solids were added, at a temperature of about 37° C. All of these three compositions were detonated in unconfined charges of 3/4-inch diameter with #6 blasting caps at 5° C.

Example V

Using solution A of Example I, in the weight percentage proportions indicated, slurries were made up as indicated in the following tabulation:

TABLE V

Composition	Solu- tion	"Pre- mix"	AN	Gassing agent	X-linker	Ox. bal. percent
V-A.....	60	16.5	23.5	0.2	0.25	-2.1
V-B.....	60	8.1	25.9	0.3	0.25	-1.5

Composition V-A had a total water content of 10.2% and composition V-B had 11.2%. Bulk densities before adding the gassing agent were 1.30 and 1.17 g./cc., respectively. When the gassing agent became effective, these dropped to 1.00 and 0.89 g./cc., respectively. Such low densities are not desirable in slurries intended for use under water, but may be useful in other cases. When the slurry is used in a deep borehole of small diameter, the compression in the column under the static head may increase the apparent or bulk density enough to render detonation difficult. In other tests, composition V-A had a density of 1.40 which dropped to 1.14 when 0.2% of gassing agent (nitrite in this case) was added. These slurries showed penetrometer readings of 270 after 5 minutes and 210 after 10 minutes for the ungassed slurry, and 240 after 5 minutes and 180 after 10 minutes for the gassed slurry. Densities after 10 minutes were 1.4 and 1.14, respectively.

Composition V-B had a higher penetration, greater than 300 (mm./10) after 5 minutes and still above 300 after 10 minutes when gassing agent was not used. Its density after 10 minutes was 1.26 which dropped to 0.99 when gassing agent was included. With gassing agent, penetrations were 240 and 200, respectively. In these two compositions, the AN was in cracked prill form. Penetrations were determined by the depth of penetration of a conical plastic contact member into the slurry.

Using the liquid solution of Example V, in proportions of 67.5%, three more compositions were made. These are tabulated below; percentages are by weight.

TABLE VI

Composition	Sol.	PG Al	Atom. Al	Pitch	TF	TS	X-link	AN
V-C.....	67.47	3.50		2.1	3.1	0.2	0.4	23.23
V-D.....	67.47	3.50	3.50	1.0	3.1	0.2	0.4	20.83
V-E.....	67.47	3.50	6.50		3.1	0.2	0.4	18.83

These three compositions had bulk densities, ungassed, of 1.19, 1.22 and 1.24 g./cc., respectively. The solution, as noted above, contained its own thickener. By the expression "ungassed" it is meant that no gassing agent was added deliberately. All of these slurries contained entrained air or other gas in substantial quantities as is evidenced by their apparent or bulk densities which were considerably below their theoretical or true (unaerated

or ungassed) densities. The latter were in excess of 1.5 g./cc. in all cases. "TF" signifies a tapioca flour, used as a supplemental thickener. "TS" is a thiosulphate.

The use of ethylene glycol is particularly preferred because it minimizes added water. It has good solubility in the slurries of this invention also for the oxidizer salts, and is an effective sensitizing fuel. Proportions of at least 3% are preferred. In combination with the calcium nitrate, it has particular value where high sensitivity at low temperatures or in small diameters of charge are desired. Ethylene glycol probably takes up water vapor from the tiny gas bubbles, further enhancing their activity as "hot spots" for propagating the detonation wave. By adding dry ammonium nitrate to the slurry and then bringing it near its fudge point, although still liquid enough to pour and/or to pump freely, the slurry thickens and rigidifies very rapidly as it cools. When pumped into a borehole having a temperature of a few degrees below the slurry fudge point, congelation to a much more viscous or rubbery consistency is very rapid. The hardening, thickening, or stabilization of this slurry is accelerated markedly by the crystallization of the calcium nitrate from the liquid phase. As noted above, the calcium nitrate takes up 4 moles of water for each mole of crystallized salt. This effectively stabilizes entrained gas as well as suspended particles in the slurry. It firmly fixes the particles against settling or migration. The slurry, if cross-linked, firms up to a rubbery, tough consistency, becoming highly resistant to intrusion or leaching by ground waters. It is still a slurry, however, in the sense that it has an essentially continuous though viscous liquid phase in which undissolved solid particles are suspended.

A very important aspect of the invention is the property conferred by the calcium nitrate of firmly fixing the widely disseminated though very small bubbles of gas in the slurry. Whether such gas is introduced in the mixing or generated in situ, it is effective to contribute to sensitivity. This factor appears to contribute in large measure to the exceptional and unexpected high level of sensitivity obtainable in the slurries of this invention. It makes it possible to reduce and in some cases to eliminate entirely requirements for the more expensive sensitizers, such as paint grade aluminum, where economics require lower cost explosives. Reliable detonability in small diameter charges can be assured with very small amounts and sometimes without any aluminum of paint grade quality. This also opens up the potential for wide use of aqueous slurries in packaged stick form, analogous to sticks of dynamite. Such use, though known in the past, has hitherto been quite limited.

The proportions of calcium nitrate, for the purposes of this invention, must be enough to effectively firm up or rigidify the slurry sufficiently to stabilize the tiny gas bubbles entrained in or diffused through the numbers and distribution required for good sensitivity.

In order further to make sure that gas bubbles of adequate number and distribution are present in the liquid phase, the liquid phase must itself be thickened or rendered viscous or gel-like before the solid particulate matter, especially the solid fuel, is incorporated. Hence, an-

other important requirement is that sufficient thickening or gelling agent be added to and effective in the liquid phase to entrap and hold the tiny gas bubbles when and as they are incorporated. Many of them are brought in when dry, particulate solids, especially the fuel particles, are added. Furthermore, the fuel must be in a form that oxidizes readily. If part of the fuel is in solution and hence in a state of molecular subdivision, this is very helpful.

This is another reason for using ethylene glycol or equivalent water miscible fuel.

The composition, when completed, must be firmly gelled and crosslinked so as to maintain the conditions of gas entrapment and distribution and good fuel availability which are essential for high sensitivity. Control of density by suitable gas incorporation is desirable in order to exercise full control of sensitivity. This may be particularly important where the slurry composition is used in very deep boreholes and hence is compressed under a heavy pressure head. However, density control is often less critical with the blasting slurries of this invention than with many prior art compositions.

It is preferred that at least one-fourth, by weight of the oxidizer salt in the solution be calcium nitrate, or at least 10% of the total composition. In some respects, however, the advantage of the invention can be with less, to as little as 5%. In many cases, calcium nitrate can comprise more than half the total oxidizer present, or up to about 40% or more, by weight of the total slurry composition.

Preferably, the slurries of this invention include at least 3% by weight of ethylene glycol as a fuel and liquid extender, at least 10% of calcium nitrate, a stable thickening system, and preferably enough gassing agent or included gas to keep the slurry at a density such that it can be detonated under 50 p.s.i. or more of applied or hydrostatic pressure. Particularly preferred are slurries containing at least 5% by weight of ethylene glycol, at least 20% but not more than about 40% of calcium nitrate, and less than 8% added water. This does not include the water of crystallization brought in by the calcium nitrate, which is an important factor in (a) reducing the amount of added water and (b) stabilizing the composition and particularly, its gas content and distribution, thereby promoting and maintaining sensitivity even during extended storage.

Variations in particular ingredients used and in their respective proportions, including use of self-explosive fuel or sensitizer particles, in some cases, and the addition of other types and varieties of fuels, can be made to the blasting slurries described above, and all within the scope of this invention, as will be obvious to those skilled in the art.

What is claimed is:

1. A free flowing storage stable blasting composition in slurry form and capable of a high degree of solidification in a borehole which comprises a thickened and strongly cross-linked liquid phase holding in stable suspension solid particulate matter, said liquid phase comprising a mixture of 5 to 12% by weight, based on the total composition, of ethylene glycol and 2 to 15% of water aside from any water of crystallization which may be present in other ingredients, an oxidizer component comprising about 20 to 40%, by weight, based on the total composition, of calcium nitrate and a substantial proportion of ammonium nitrate, said oxidizer component being at least partially dissolved in the liquid phase, particulate fuel suspended in said liquid phase, said composition including a small quantity, sufficient to increase sensitivity and to appreciably reduce bulk density, of a gas generating agent which is decomposable, and a small amount of an accelerator for decomposing the generating agent.

2. Composition according to claim 1 wherein the slurry contains sufficient gassing agent to hold its density within detonable limits under an applied pressure of as much as 50 p.s.i.g.

3. Composition according to claim 1 which contains 3.5

to 10% by weight, based on the total composition, of finely divided aluminum as fuel.

4. The method of preparing and delivering an aerated gas-containing blasting slurry composition, which comprises in combination the following steps:

(a) forming a liquid phase at a temperature above ambient by dissolving a combination of calcium nitrate and at least one other powerful inorganic oxidizer salt selected from the group which consists of nitrates, chlorates and perchlorates, in an aqueous solvent so that the water of crystallization of the calcium nitrate contributes to the total liquid present, the liquid solution of salts thus formed having a fudge point above ambient temperature.

(b) prior to addition of particulate solids, as herein-after stated, thickening said liquid phase sufficiently to entrap small gas bubbles incorporated in the liquid phase, as hereinafter stated, by including a cross-linkable gelling agent,

(c) adding a gas generating agent and particulate solid matter including fuel to said liquid phase, to produce a free-flowing slurry of viscous character holding said solids in suspension, and including an accelerator to promote gas generation by said generating agent in situ in the slurry,

(d) delivering the slurry through a flow line to a site where it is to be detonated, before substantial fudging or rigidification of the slurry occurs, and

(e) permitting the delivered slurry to cool through its fudge point in the site and thus to set up firmly, the proportions of calcium nitrate and its tendency to dehydrate the slurry by taking up water of crystallization being sufficient to fix the suspended particulate matter and the generated gas bubbles to insure detonability.

5. Method according to claim 4 which includes cross-linking the thickened slurry.

6. Method according to claim 4 which includes pumping the gel or slurry to a borehole where it sets up and remains sensitive at borehole temperature.

7. Method according to claim 4 which includes deliberately incorporating a decomposable gas generating substance and a decomposition accelerator in said composition to reduce its bulk density substantially below its theoretical or true value.

8. Method according to claim 4 in which the slurry includes ammonium nitrate, sodium nitrate and calcium nitrate and in which ammonium nitrate is dissolved in the liquid phase only after the calcium nitrate has been completely dissolved therein.

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U.S. Cl. X.R.

149—41, 60, 61, 87, 109