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PROCESS FOR MANUFACTURING GAS-ENTRAINED AQUEOUS GEL EXPLOSIVE

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ABSTRACT OF THE DISCLOSURE

A sensitive gas-entrained water gel explosive is made by mixing at a location convenient to the blasting site a concentrated aqueous solution of ammonium nitrate, nitric acid, sodium nitrate and hexamethylenetetramine and a minor amount of a thickening agent such as guar gum, allowing sufficient time for the gum to become hydrated and give the maximum thickening effect, then, mixing the resulting thickened solution with solid ammonium nitrate and a minor amount of a fuel to yield a thickened slurry, pumping the thickened slurry and injecting into the exit stream from the pump both a substantial quantity of a gas and a solution which has the effect of cross-linking the thickening agent and conducting the resulting thickened slurry through a static mixer.

DESCRIPTION OF THE INVENTION

Ammonium nitrate in the strictest sense is not an explosive substance. However, it is a compound which undergoes thermal decomposition and if sufficient heat is supplied continuously so as to maintain the thermal decomposition reaction, the production of gaseous decomposition products may be made to reach explosive proportions. During about the last two decades, low cost blasting explosive compositions based on ammonium nitrate have gained an increasing proportion of the market for industrial explosives. In recent years a type of composition which has become increasingly popular is a thickened or gelled slurry of ammonium nitrate along with other solid ingredients such as fuels, sensitizers, propellants and high explosives in a saturated aqueous solution of ammonium nitrate. By including in these compositions both ammonium nitrate as an oxidizing agent and solid fuels such as powdered coal, sulfur or finely divided aluminum, it has been possible to cause enough heat to be generated during the decomposition of the major part of the ammonium nitrate so as to drive the thermal decomposition reaction to substantial completion. A problem encountered with these slurry explosives is that of obtaining sufficient sensitivity, so that they are easily initiated. Probably the most common means of obtaining sensitivity has been to include in the composition an extremely flammable fuel such as pigment grade powdered aluminum, or an explosive or propellent substance such as TNT or smokeless powder, which will release enough energy to keep the thermal decomposition going. Paint grade aluminum powder is made by lubricating aluminum particles with a substance such as stearic acid and milling these particles into tiny flakes. It has been known for many years that when this type of aluminum powder is mixed with an oil or a hydrocarbon solvent the particles are readily wetted and disperse rapidly, making fairly stable suspensions. However it has also been well known that

when paint grade aluminum flakes are mixed with water, although they can be dispersed by vigorous mixing because of their small size and relatively low specific gravity, they carry with them into the water tiny bubbles of air, as a consequence of failure of the water to wet the coated solid particles. This grade of aluminum powder is commonly used in aqueous ammonium nitrate slurry explosives to increase the sensitivity. Both the tiny bubbles of air carried by the particles and the readily oxidizable nature of the aluminum are known to contribute to the sensitization. It has been realized for some time that probably the most important property of paint grade aluminum which makes it particularly useful for sensitizing slurry explosives is its ability to disperse tiny bubbles of air throughout the composition. (See, for instance, U.S. Pats. 3,453,158 and 3,249,474.) So far as the extra energy obtainable from oxidization of the metal is concerned, this can be supplied by other fuels. However, attempts to disperse microscopic bubbles of air by other means have met with only partial success. When air is injected into a slurry composition the bubbles are almost invariably too large. Attempts to subdivide air bubbles and reduce their size by mixing nearly always fail. Paint grade aluminum powder therefore remains the commonest sensitizing agent in use, even though it is hazardous to handle and is usually the most expensive ingredient of explosive compositions on a weight basis.

We have discovered a procedure by which sensitive gas-entrained slurry blasting agents may be made without the use of paint grade aluminum powder or other finely divided water repellent substances to carry microscopic bubbles of gas into the dispersion. In the process of the present invention we preferably employ as a starting material a concentrated aqueous solution of ammonium nitrate and hexamethylenetetramine, preferably made by reacting commercial aqueous formaldehyde solution with ammonium nitrate, followed by adding a minor proportion of sodium hydroxide thereto. If used immediately the ammonium nitrate solution prepared by the preferred method is at an elevated temperature, which facilitates mixing therewith a small amount of a water dispersible thickening agent, most conveniently a polysaccharide gum such as guar gum. Preferably the process comprises the following steps:

(a) Mixing a water dispersible thickening agent with a concentrated aqueous solution contaiing ammonium nitrate, nitric acid, sodium nitrate and hexamethylenetetramine and allowing the resulting mixture to stand for a sufficient length of time to obtain a pumpable uniformly thickened solution;

(b) Mixing together the pumpable thickened solution of step (a) with solid particles of ammonium nitrate and a minor proportion of a fuel to yield a thickened slurry;

(c) Pumping the thickened slurry and injecting into the exit stream from the pump a stream of gas and an aqueous solution which effects the cross-linking of the thickening agent, so as to greatly increase the thickening effect; and

(d) Conducting the resulting stream of thickened slurry through a motionless mixer under conditions substantially free from shear to yield a sensitive gas-entrained aqueous gel explosive.

Following is a detailed discussion of the process with illustrative examples.

U.S. Pat. 3,496,040 discloses a class of slurry blasting agents consisting of aqueous solutions of ammonium nitrate, hexamethylenetetramine and a thickening agent, havsuspended therein solid ammonium nitrate and a solid fuel. Typical compositions contain at least 15% water, ammonium nitrate, sodium nitrate, hexamethylenetetramine, a solid fuel such as particulate aluminum and a thickening agent such as guar gum to stabilize the suspension against settling. It is quite feasible to prepare slurry blasting agents of this type by merely mixing the individual ingredients with water, using a major amount of solid ammonium nitrate, solid sodium nitrate and a small percentage of hexamethylenetetramine to prepare the original concentrated solution on which the slurry blasting agent is based. However, during the preparation by this simple procedure heat is absorbed as the ammonium nitrate goes into solution, so that the preparation of a saturated liquor requires a source of heat, thereby increasing the expense. The liquor may be acidic, basic or neutral, the pH being readily adjusted by addition of either nitric acid or sodium hydroxide. Usually sodium nitrate is added to such compositions as a cheap secondary oxidizing agent. A cheaper method of preparing the liquid phase which is used as a base for preparing this class of slurry explosives involves reacting ammonium nitrate with formaldehyde in aqueous solution in a ratio of at least 4 mols of ammonium nitrate per 6 mols of formaldehyde and dissolving therein a quantity of unreacted ammonium nitrate to produce an aqueous solution of ammonium nitrate, nitric acid and hexamethylenetetramine and adding thereto sufficient sodium hydroxide to adjust the pH preferably between 4 and 7 and produce sodium nitrate as a secondary oxidizing agent.

In a specific instance, 411 parts by weight of ammonium nitrate, 138 parts by weight of commercial 37 weight percent aqueous formaldehyde solution and 59 parts by weight of water are charged to a stirred reactor. The minor, varying amount of methanol usually present in commercial aqueous formaldehyde does not appear to interfere with the process and need not be removed. After stirring until reaction is substantially complete, 36 parts by weight of sodium hydroxide pellets is added to the mixture and stirring is continued until a homogeneous solution is obtained. The resulting concentrated aqueous solution of ammonium nitrate, nitric acid, sodium nitrate and hexamethylenetetramine is employed in the manner illustrated below.

(a) Thickening the concentrated solution

To the concentrated solution made by the method described above there is added about 0.9% by weight of a commercial polysaccharide gum solid for the purpose of thickening aqueous slurry explosives or blasting agents. A specific thickener suitable for the purpose is a guar gum solid under the designation GM 492. It is essential to the success of this process that the thickening of the solution be done in a thorough manner. The small amount of thickening gum is preferably distributed uniformly throughout the concentrated solution by pumping through an eductor in to which the gum is slowly introduced at a uniform rate of addition. After addition of the gum to the solution, mixing should be continued, preferably with slowly rotating paddles or mixing blades for a period of several minutes in order to insure that uniform solution is obtained. Ordinarily when a hydroxy substituted polymeric gum is used to thicken aqueous solution the solvation of the gum by water requires a substantial reaction time to go to completion. This should be allowed to occur. If convenient, the solution containing the gum sohuld be allowed to stand overnight so as to allow ample time for hydration of the gum to go to completion, so as to obtain the maximum thickening effect. When this is done the concentrated solution will be thick enough so that it can be easily picked up and held in cupped hands without leaking substantially between the fingers. In this condition the solution, although quite thick, can be pumped and poured readily and can be transported or stored safely and conveniently.

(b) Mixing in the solid ingredients

In this step it is convenient to use mixing apparatus which has been designed to mix together dense slurries such as concrete. In a specific instance there may be charged into a concrete mixer 65.3 parts by weight of the pumpable thickened solution obtained in step (a), 34.7 parts by weight of solid particulate ammonium nitrate and 50 parts by weight of a dry explosive consisting of ammonium nitrate particles impregnated with 6% by weight of diesel fuel. These ingredients are mixed together to form a thickened slurry.

(c) Pumping, gas injection and cross-linking the slurry

The thickened slurry produced in Step (b) may be pumped in suitable apparatus designed for this purpose. For instance, there are slurry pumps which are manufactured for the purpose of pumping oil well drilling muds and also there are pumps specifically designed for pumping concrete and grout slurries of various consistencies. Most of these pumps are designed to minimize wear and malfunction caused by abrasive particles in the slurries, so that they are capable of long service with minimum upkeep. In a specific instance a peristaltic type of concrete pump such as for example a pump of the type disclosed in U.S. Pat. 3,180,272 is employed. This type of pump delivers a slurry stream with pulsating pressure. These pulsations are advantageous in the present process because they make it easier to inject other substances into the slurry stream making it unnecessary to use high injection pressures. In a specific example, immediately following the pump there is injected into the output stream from the pump a stream of gas under a pressure of about 100 p.s.i.g. and through another injection inlet located close to the gas inlet there is injected approximately 1.25 weight percent of a solution made up by combining 100 parts by weight water with 10 parts by weight zirconium sulfate, 3 parts by weight chromium trioxide and 3 parts by weight aluminum sulfate. This solution has the effect of cross-linking the hydrate polysaccharide gum in the thickened slurry blasting agent composition so that the gum takes on a tough elastic character when the cross-linking becomes complete. There is some variation in toughness of the cross-linked slurry, depending upon the gas which is injected. Nitrogen, for example, readily produces a much tougher cross-linked gel than air and carbon dioxide yields cross-linked gels of intermediate toughness.

Suitable cross-linking solutions may be formulated according to the published recommendations of the manufacturers of the gum. The injected gas and cross-linking solutions are not evenly distributed in the explosive composition at this stage, as there is a tendency for more injection to take place during the pressure drops than at the peak pressures of the pump output. Thorough mixing and dispersion of the gas are accomplished in the following step.

(d) Dispersion of the gas

The successful dispersion of gas in the explosive composition in bubbles small enough to obtain the desired sensitivity to initiation and propagation of explosion depends on several factors. It has been found necessary first of all to have the gum fully hydrated and the thickening effect at a maximum prior to mixing in the suspended solids, so as to insure a uniformly thickened slurry with no lumps or thin spots which will permit gas bubbles to move freely and becames coalesced and segregated. It is also necessary to have a stable thickened slurry which does not spontaneously generate heat or gas bubbles on standing. To assure stability, a pH between 4 and 7 is preferred in the concentrated aqueous

phase. A variety of gases may be used, based upon expense and convenience of obtaining a supply of gas under pressure, so as to facilitate injection into the viscous fluid stream. We have found compressed air, nitrogen and carbon dioxide to be cheap, safe and convenient to obtain and use.

It is necessary to obtain thorough mixing and dispersion of the injected gas in the slurry by mixing in some manner. It has been found that any sort of vigorous mixing or chopping of the slurry involving conditions of high shear destroys some of the valuable properties of the slurry without giving the uniform fine dispersion of gas which is desired. There has recently come into use a type of mixing device which assures efficient blending of all the components in a fluid stream without subjecting the various components to high shearing forces, cavitation or some drastic physical treatment. These devices are called motionless mixers. They are essentially chambers containing baffles of a variety of shapes, through which a viscous fluid mixture can be pumped. The baffles effect division, rotation, relative displacement and recombination of portions of the stream of viscous fluids in such a way that the mixture becomes more uniform as it passes through the baffle chamber. Devices of this type are disclosed for example in U.S. Pat. 3,286,992 and U.S. Pat. 3,168,390. The motionless mixers are described in Chemical Engineering magazine, pp. 94–96 of May 19, 1969 and pp. 92 and 93 of the issue of Mar. 22, 1971. We have found that a thickened slurry containing injected gas and cross-linker as described above need only be passed through a sufficient length of static mixer to obtain the desired properties in the final explosive. The pressure drop attributable to the static mixer may be only about 40 to 60 p.s.i. when rate of flow is regulated to obtain mixing conditions substantially free from shear. The diameter of the conduit attached to the pump outlet and the diameter and length of static mixer can be selected to obtain the desired throughput rate, pressure drop and degree of mixing. The sensitive gas-entrained slurry basting agent obtained as described above has been found to be a desirable product for the blasting of rock, particularly for making excavations. A sensitive gel with higher explosive energy, useful for moving harder rock or for wider spacing of charges may be made by charging to the mixer in step (b) for example 65.3 parts by weight of the pumpable thickened solution obtained in step (a), 30.7 parts by weight of solid particulate ammonium nitrate, 50 parts by weight of a dry explosive consisting of ammonium nitrate particles impregnated with 6% by weight of diesel fuel and 4 parts by weight of particulate aluminum (granular aluminum or chopped aluminum foil).

For even higher energy for the purpose of blasting hard rock with smaller charges, as in quarrying or mining, there may be charged to the mixer in step (b) 65.3 parts by weight of the pumpable thickened solution obtained in step (a), 26.7 parts of solid particulate ammonium nitrate, 50 parts by weight of a dry explosive consisting of ammonium nitrate particles impregnated with 6% by weight of diesel fuel and 8 parts by weight of coarse granular aluminum.

Explosive compositions intermediate in makeup between those specifically disclosed may also be made by the method of this invention. All of these compositions are sufficiently sensitive so that explosion is easily initiated with the use of conventional blasting caps and detonating cord in conjunction with cast primers or dynamite. Furthermore, the method of this invention is broadly applicable to manufacture of aqueous ammonium nitrate slurry explosives of the gel type which are sensitized by microscopic gas bubbles and contain no propellant or explosive substance as sensitizer. In application to other formulations, the same principles must be observed, that is; thorough mixing and hydration of the gum in step (a) to obtain a pumpable, uniformly thickened concentrated aqueous ammonium nitrate solution; obtaining a pumpable thickened slurry of stable characteristics in step (b) injecting the gas and the cross-linking solution into the exit stream of the pump in step (c) and conducting the resulting stream through a motionless mixer in step (d).

I claim:

1. A process for manufacturing a sensitive aqueous gel explosive comprising the steps:

(a) mixing a water dispersible thickening agent with a concentrated aqueous solution containing ammonium nitrate, nitric acid, sodium nitrate and hexamethylenetetramine and allowing the resulting mixture to stand for a sufficient length of time to obtain a pumpable uniformly thickened solution;

(b) mixing together the pumpable thickened solution of step (a) with solid particles of ammonium nitrate and a minor proportion of a fuel to yield a thickened slurry;

(c) pumping the thickened slurry and injecting into the exit stream from the pump a stream of gas and an aqueous solution which effects the cross-linking of the thickening agent so as to greatly increase the thickening effect; and

(d) conducting the resulting stream of thickened slurry through a motionless mixer under conditions substantially free from shear to yield a sensitive gas-entrained aqueous gel explosive.

2. A process for manufacturing a sensitive blasting gel comprising the steps:

(a) mixing a water dispersible polysaccharide gum thickening agent with a concentrated aqueous solution containing ammonium nitrate, nitric acid, sodium nitrate and hexamethylenetetramine and allowing the resulting mixture to stand for a sufficient length of time to obtain a pumpable uniformly thickening solution;

(b) mixing together the pumpable thickened solution of step (a) with solid particles of ammonium nitrate, a portion of which particles are impregnated with a hydrocarbon fuel to yield a thickened slurry;

(c) pumping the thickened slurry and injecting into the exit stream from the pump a stream of gas and an aqueous solution which effects the cross-linking of the thickening agent so as to greatly increase the thickening effect; and

(d) conducting the resulting stream of thickened slurry through a static mixer to yield a sensitive gas-entained blasting gel.

3. A process for manufacturing a sensitive blasting gel comprising the steps:

(a) mixing a water dispersible thickening agent with a concentrated aqueous solution containing ammonium nitrate, nitric acid, sodium nitrate and hexamethylenetetramine produced by reacting ammonium nitrate with aqueous formaldehyde and adding sodium hydroxide thereto and allowing the resulting mixture to stand for a sufficient length of time to obtain a pumpable uniformly thickened solution;

(b) mixing together the pumpable thickened solution of step (a) with solid particles of ammonium nitrate and a minor proportion of coarse granular particulate aluminum to yield a thickened slurry containing suspended ammonium nitrate and aluminum particles;

(c) pumping the thickened slurry and injecting into the exit stream from the pump a stream of gas and a solution which effects the cross-linking of the thickening agent so as to greatly increase the thickening effect; and

(d) conducting the resulting stream of thickened slurry through a static mixer to yield a sensitive gas-entrained blasting gel.

4. In a process for manufacturing a gelled aqueous slurry blasting composition which depends upon a dispersed gas for sensitivity and contains no propellant or high explosive sensitizers, the improvement consisting of

(a) pumping a thickened slurry comprising solid ammonium nitrate, a minor proportion of a fuel and a thickening agent and injecting into the exit stream from the pump a stream of gas and an aqueous solution which effects crosslinking of the thickening agent so as to greatly increase the thickening effect and (b) conducting the resulting stream of thickened slurry through a motionless mixer under conditions substantially free from shear to yield a sensitive gas-entrained aqueous gel explosive.

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