United States Patent Office 3,347,722 Patented Oct. 17, 1967

3,347,722

THICKENED AMMONIUM NITRATE BLASTING COMPOSITION CONTAINING ALUMINUM AND UREA

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No Drawing. Filed Apr. 29, 1966, Ser. No. 546,190
12 Claims. (Cl. 149—41)

ABSTRACT OF THE DISCLOSURE

A blasting agent in the form of a cohesive mass and detonatable in the absence of any molecular explosive. The blasting agent comprises ammonium and sodium nitrates, urea, and aluminum in water containing sufficient thickening agent to make a cohesive mass in which a portion of the nitrates and urea are in solution. This high explosive can be conveniently introduced into a borehole, such as may be drilled in hard rock mining.

Explosive compositions may be broadly classified as molecular or "fixed" explosives, heterogeneous explosives, and hybrid explosives. A molecular explosive contains both fuel and oxidizer within the same molecule and usually consists of CH-type groups linked with NO-type groups. Examples of molecular explosives are nitroglycerin and trinitrotoluene. A heterogeneous explosive is a mixture of separate macroscopic particles (or sometimes films) of oxidizer and fuel. A mixture of ammonium nitrate and fuel oil is a good example of a heterogeneous explosive. A hybrid explosive is a mixture of a molecular explosive and a heterogeneous explosive. The hybrid explosives constitute the most common class of commercial explosives—that is, the nitroglycerin dynamites. The molecular explosive portion in the hybrid explosive is nitroglycerin, and the heterogeneous portion consists of ammonium nitrate and/or sodium nitrate together with wood pulp and other carbonaceous substances.

A major objective in the explosive art has been to increase the proportion of the oxidizer, generally ammonium nitrate, and reduce the proportion of high cost, impact- and friction-sensitive molecular explosive ingredients in hybrid explosives. A further objective has been to develop a heterogeneous explosive composition that is free of molecular explosive ingredients and less hazardous than either a molecular explosive or a hybrid explosive while retaining the desirable properties of the latter. Some degree of success has been achieved in this last objective in that mixtures of petroleum oil and particulate ammonium nitrate in the form of prills are now in use as a blasting agent in strip mining applications. This heterogeneous explosive, while very inexpensive, is often variable in composition and physical state. Factors such as oil distribution and particle size are difficult to control: the oil tends to drain off or segregate or it is unevenly absorbed, giving a product of non-uniform composition; also the ammonium nitrate particles tend to sometimes disintegrate because of temperature-induced phase changes and sometimes the ammonium nitrate has a tendency to fuse or set up because of moisture, or because of certain crystalline transformations brought on by temperature cycling. Since the strength of the mixture and its ability to support detonation in the borehole are critically dependent on oil concentration and particle size, the simple "oil-prill" heterogeneous explosive blasting agents, for reasons like those just mentioned, often give variable and unsatisfactory results.

It would therefore be desirable to have available an

inexpensive blasting agent which was stable over long periods of storage, essentially insensitive to moisture, or even the presence of water in the borehole, and which could be readily handled and used. Ideally, such a blasting agent should be pourable, relatively insensitive to shock, but yet be capable of being set off either with a blasting cap or with the use of ordinary initiators such as tetryl pellets.

Wet blasting agents have been disclosed which include mixtures of ammonium nitrate, aluminum and water (see U.S.P. 3,024,727 and Re. 25,695); mixtures of ammonium nitrate, urea and water (see U.S.P. 3,052,578); and ammonium nitrate, urea, a freezing-point depressant, and a molecular explosive such as nitroglycerin or RDX (see U.S.P. 2,548,693). Those wet blasting agents which contain only alumnium in an ammonium nitrate water slurry are limited to about 12% in the amount of water which can be added; and if it is desirable to use more water, a molecular explosive such as TNT must be added. Those wet blasting agents consisting essentially of urea, water and ammonium nitrate apparently require mixing or blending just prior to use and must be used in a borehole substantially free of voids.

Thus, to the desirable characteristics previously set forth for a blasting agent may be added the requirements that it should be free from molecular explosive components, that it does not need to be blended or mixed just prior to use, and that it can be used in boreholes over a wide range of size, shape and configuration.

In accordance with this invention, I have now discovered that it is possible to make a new type of explosive, which may be termed a "simulated molecular explosive." This new type of explosive, which in the strictest sense remains a heterogeneous explosive, exhibits performance characteristics which approach or equal those of comparable true molecular explosives, but it does not possess their sensitivity to shock. This in turn means that they can be readily formulated, handled and shipped. These so-called "simulated molecular explosives" are formed by achieving molecular-scale mixing of at least a portion of the ammonium nitrate and urea, thereby breaking down the normal physical barriers between the oxygen atoms in the ammonium nitrate and carbon and hydrogen atoms in the urea. This in turn materially reduces the length of the reaction zone as evidenced by the ability of these simulated molecular explosives to exhibit detonation velocities approaching theoretical. The wet blasting agents of this invention are made by combining ammonium nitrate, urea, aluminum, water and a thickening agent, along with one or more modifying agents (e.g., bulking agents and catalysts) if desired. The resulting wet blasting agents have relatively high detonation velocities and they can be made in consistencies ranging from putty to a pourable gel-like cohesive or adhesive paste. The actual character of the consistency is controlled by the amount of water and by the thickener used; and the paste-like consistency achieved through the use of the thickener is apparently responsible for maintaining the uniform distribution of the components, even over long periods of storage. An important aspect of this invention lies in the fact that at least a portion of the ammonium nitrate and urea are mixed in what might be termed a "molecular scale" thus giving rise to the simulated molecular explosive without incorporating the inherent dangers associated with the use of a true molecular explosive such as RDX, TNT or nitroglycerin. One or more secondary fuels in addition to the aluminum may also be added in minor amounts.

It is therefore a primary object of this invention to provide an improved wet blasting agent which comprises

ammonium nitrate, urea and aluminum and which, without containing any molecular explosives, approaches or attains the performance of those blasting agents which contain molecular explosives.

It will be evident to those familiar with the subject that many ancillary advantages follow from the substitution of a heterogeneous explosive for a hybrid explosive that contains true molecular explosive ingredients in any proportion. Thus, another object of this invention is to reduce hazards to health and safety resulting from the presence of molecular explosives such as nitroglycerin, trinitrotoluene, tetryl and the like in explosive compositions, by the substitution for such compositions materials that are very insensitive to stimuli of impact, heat and friction, and which are not injurious to health in either manufacture or use. It is still a further object of this invention to eliminate the added cost of molecular explosives by providing heterogeneous explosives that use only inexpensive, readily available, fuel components in conjunction with a major portion of a low cost oxidizer.

It is yet another primary object of this invention to provide a wet blasting agent in which the ammonium nitrate, as well as the urea in the role of a primary fuel, and the aluminum as a secondary fuel, remain uniformly distributed throughout the explosive over long periods of storage and hence one which exhibits uniformity in performance over a wide range of storage and use conditions. Other objects of the invention will in part be obvious and will in part be apparent hereinafter.

The invention accordingly comprises a composition of matter possessing the characteristics, properties, and the relation of components which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

Physical mixtures of ammonium nitrate with a fuel such as urea present reaction zone lengths which are always considerably greater than in the case of molecular explosives. This, in turn, means that these physical mixtures always exhibit burning rates and detonation velocities lower than the true molecular explosives containing essentially the same atomic ratios. This is, of course, a simplified statement of the theory but it may be summarized by saying that if it were possible, in some way, to mix the ammonium nitrate and the fuel on a "molecular scale" so that the molecules of the oxidizer and the fuel are in more intimate contact than in physical mixtures, the detonation velocity would approach the ideal detonation velocity for the combination. Such a simulated molecular explosive can then be used with aluminum which burns to produce large quantites of heat.

I have now found it possible to make a wet blasting agent with ammonium nitrate, urea and aluminum in which mixing of the ammonium nitrate with the urea attains or approaches the desired molecular scale of mixing. The resulting wet blasting agent is an explosive which may be characterized as one which contains at least a portion of the ammonium nitrate and the urea in the form of an association complex as evidenced by n.m.r. spectra measurements. This association complex is present over a very wide range of ammonium nitrate-urea ratios.

The aluminum used is in a finely divided form and may be any grade usually used in explosive formulation. It may be in the form of flakes or it may be the so-called "atomized" aluminum.

The ammonium nitrate suitable for use in the wet blasting agent of this invention may be of any commercial grade ammonium nitrate. It may be completely dry or it may contain up to about 3 percent water, which means that the highly concentrated ammonium nitrate solutions can be taken from the high pans in the ammonium nitrate manufacture and used directly in the compounding of the explosive of this invention. Sodium nitrate may be used to replace up to about 25% by weight of the ammonium nitrate.

Any secondary fuel materials other than aluminum, if used, may be substances which are water-soluble, such as sugar and other carbonaceous materials; or they may be particulate material which are dispersed in the water slurry. This latter type of secondary fuel includes sulfur, carbon, and fuel oil. The primary requirement of the secondary fuel is that it be capable of oxidation under the conditions of the explosion with the yield of a large quantity of heat and also preferably of a large amount of gas. Most carbonaceous materials can fill this function.

The thickeners used may be any of those materials which are capable of setting up the aqueous mixture in a gel-like consistency or in the form of a relatively thick cohesive paste. Normally, these thickeners will be one of the well-known gums such as guar, okra, or locust bean. They may be supplemented by other thickeners such as wood flour, cellulose ester gum and the like. As indicated previously, one or more thickeners is required to impart the desired consistency (whether described as paste-like, gel-like, or otherwise) to the explosive. The consistency is preferably one which maintains all solid materials (undissolved ammonium nitrate, aluminum, bulking agents, other secondary fuels, etc.) uniformly distributed in the blasting agent over an extended period of time.

In addition to these compounds, other modifiers may be used. Among these are the so-called bulking agents such as wood pulp, perlite or urea-formaldehyde microballoons which reduce the density of the wet blasting agent. The microballoons typically have diameters between 20 and 40 microns and may be used to provide a multitude of tiny air pockets intimately distributed throughout the wet blasting agent. These microballoons, in addition to serving as bulking agents, may also serve as heat centers in the shock wave and improve the properties of some forms of the explosive. Other suitable bulking agents may, of course, be used. Other modifiers include such materials as sodium bicarbonate to generate gas and create voids in the wet blasting agent to reduce its density; catalysts such as one of the chromates, e.g., potassium dichromate, and the like. The use of such modifiers will depend upon such factors as the manner in which the blasting agents are to be employed, the performance desired (e.g., more or less brisance) and the conditions under which they are to be initiated.

In the wet blasting agents of this invention the water dissolves a portion of the ammonium nitrate and the urea and there is formed in the resulting solution an association complex of the ammonium nitrate and the urea to effect a molecular-scale mixing. This may be shown by n.m.r. spectra data.

Proton nuclear magnetic resonance (n.m.r.) measures the structural environment around protons; and the spectra obtained, in terms of position, intensity and band width, are indicative of the structural surroundings of the proton (as used in organic structure interpretation) and its exchange rate with other protons. The half-width of an absorption peak is related to the kinetics of the exchange process (see for example J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., N.Y., 1963) such that observing the effect of external variables such as temperature or of internal variables such as the addition of a reactant allows one to calculate and formulate the kinetics of the exchange processes and the reactions involved in these exchange processes.

Solutions of ammonium nitrate and urea were examined in H_2O solvent. These solutions were made up to contain increasing concentrations of ammonium nitrate and into them were added successively increasing concentrations of urea. The half-widths of the water peaks were measured and the disappearance of the urea peak with increasing ammonium nitrate was noted. The observations are summarized in the following table wherein concentrations are given in gram/milliliter of the water solvent and $\Delta\delta_{1/2}$ is used to designate the width of the water absorption peak at half-height in cps. at 37° C.

n.m.r. SPECTRA FOR AMMONIUM NITRATE/UREA SOLUTION

g Urea	g AN	AN/Urea	$\Delta\delta_{1/2}H_2O$	Urea Peak
0	0	--------	0.55	
0	0.19	--------	10	
0	0.38	--------	18	
0	0.77	--------	33	
0	1.15	--------	38	
0	1.54	--------	43	
0.128	0	--------	0.75	Distinct.
0.128	0.19	1	7	Distorted.
0.128	0.38	2	12	Gone.
0.128	0.77	4	18	Do.
0.128	1.15	6	20	Do.
0.128	1.54	8	20	Do.
0.256	0	--------	0.75	Distinct.
0.256	0.19	0.5	8	Distorted.
0.256	0.38	1	11	Observable.
0.256	0.77	2	15	Do.
0.256	1.15	4	16	Gone.
0.256	1.54	6	16	Do.

The half-width ($\Delta\delta_{1/2}$) of the water peak is related to the kinetics of an exchange process such as

$$H_2O + H'_2O \overset{K}{\rightleftharpoons} H'_2O + H_2O$$

by

$$\frac{1}{\tau} \doteq K$$

where

$$\frac{1}{\tau} = \pi\Delta\delta_{1/2}$$

Consequently, the rate of the exchange processes

$$NH_4^+ + H'_2O \rightleftharpoons NH'^+_4 + H_2O$$

$$CO(NH_2) + H'_2O \rightleftharpoons CO(NH'_2)_2 + H_2O$$

are related to the water half-width,

The data demonstrate that ammonium nitrate has a large effect on $\Delta\delta_{1/2}$ while urea has only a small effect. When urea, in a fixed amount, is added to the AN series, the exchange rate (as measured by $\Delta\delta_{1/2}$) is affected considerably.

In addition, an absorption peak due to urea itself (—NH_2 protons) is clearly visible in aqueous solutions and gradually disappears as increasing amounts of ammonium nitrate are added.

The data quite clearly support the existence of a complicated exchange process by which all of the species interact on a molecular basis through the formation of some sort of association complex. The overall process might best be represented as

$$CO(NH_2)_2 + NH_4NO_3 + H_2O \rightleftharpoons CO(NH_2)_2 + NH_4NO_3 + H_2O$$

which must certainly be made up of such equilibria as

$$NH_4NO_3 + H_2O \rightleftharpoons NH_4NO_3 + H_2O$$

$$CO(NH_2)_2 + H_2O \rightleftharpoons CO(NH_2)_2 + H_2O$$

$$NH_4NO_3 + CO(NH_2)_2 \rightleftharpoons NH_4NO_3 + CO(NH_2)_2$$

and one might reasonably expect the following species to be involved as intermediates in these exchange processes:

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

$$NH_4^+ + CO(NH_2)_2 \rightleftharpoons NH_3 + C(NH_2)(NH_3^+)$$

Although I do not wish to be bound by the following theory, it seems reasonable to postulate that in the water solution portion of the wet blasting agent, there is formed a mixture on a molecular scale of the ammonium nitrate with the urea. That there is a solution having an association complex is evidenced by the n.m.r. data. It may be further concluded that in this solution the normal physical barriers between the oxygen atoms in the ammonium nitrate and the carbon and hydrogen atoms in the urea are removed or substantially minimized. Thus, the water medium sets up the required molecular contact between the components to make the mixture of ammonium nitrate and urea the equivalent or near equivalent of a true molecular explosive in performance. The thickening agent maintains the undissolved and dispersed portion of the wet blasting agent uniformly held in the solution portion and thus forms an explosive which remains stable.

The wet blasting agent of this invention may be described further with reference to the following examples which are meant to be illustrative and not limiting.

Examples

In preparing the wet blasting explosive examples of this invention, the components were divided into three groups as follows:

	Weight Percent		
	Ex. 1	Ex. 2	Ex. 3
Group A:			
Ammonium nitrate	50.9	49.0	43.5
Sodium nitrate	16.5	13.0	14.0
Guar gum	1.0	1.4	1.5
Perlite (volcanic glass)	6.5	5.2	5.6
Group B:			
Water	10.9	20.2	23.2
Urea	9.8	7.8	8.4
Group C:			
Aluminum:			
Flake	0.55	1.7	1.9
Atomized	1.65		
Sulfur (rubbermakers grade)	2.2	1.7	1.9
Anhydrous sodium borate	--------	--------	0.5

The components of Group A were carefully dry blended in a Hobart food mill. If desired, the dry blending may be done in a steam-jacketed vessel to warm these components. The urea was dissolved in boiling water and the Group B components in a boiling condition were slowly added to the Group A dry components while a slow blending action was continued. A portion of the ammonium nitrate and sodium nitrate dissolved in the aqueous urea solution while the remaining nitrates and perlite remained dispersed. The resulting dispersion was then subjected to a very thorough mixing by continuing the blending at an increased blending rate for 20 minutes. Then the Group C components were gradually added while blending was continued for ten more minutes to insure uniform distribution of all of the components throughout the mass.

The wet blasting agents of Examples 1 and 2 exhibited a ropy consistency, while that of Example 3, to which the anhydrous sodium borate had been added during final blending, was a gel-like, cohesive material. A very small quantity of sodium borate is desirable to impart this gel-like consistency.

The resulting blasting agents were then loaded warm into a heavy cardboard tube 4 inches in diameter and 24 inches long and fired warm, e.g., about 50° C. The cartridges were primed with a one-inch tetryl pellet and initiated with a No. 6 electric blasting cap.

A detonation velocity of 9,300 feet/second across a 12-inch gap using Du Pont target type probes was determined by a counter chromagraph reading for Example 1 loaded to a density of 1.24 grams/cc. Example 2, loaded to a density of 1.08 grams/cc. and Example 3, loaded to a density of 1.17 grams/cc., both fired under these conditions.

The quantity of water in the wet blasting agent may be as little as 4 or 5% or as much as about 25%. With the exception of a few percent by weight of aluminum and sulfur, a very few percent of any additives used and a minor amount any other secondary fuel, if added, the remainder of the explosive is ammonium nitrate and urea, preferably present in a weight ratio to provide a substantially oxygen-balanced oxidant-fuel mixture. (As previously noted, a minor amount of the ammonium nitrate, e.g., up to about 25%, may be replaced with sodium nitrate.) The amount of finely divided aluminum used will

depend upon the detonation characteristics or brisance desired in the explosive. While aluminum contributes heat and lifting power it also decreases detonation velocity. Thus, the quantity of aluminum may be adjusted to control these parameters. However, the amount of aluminum should range between 1 and 5% by total weight. When other secondary fuels, e.g., sulfur, sugar, carbon or fuel oil, are added, then the quantity of aluminum plus these secondary fuels should not exceed about 5% by weight.

The quantity of thickener should be that which imparts the desired consistency to the wet blasting agent and at the same time maintains the undissolved material uniformly distributed throughout the mass. The final consistency is preferably one which gives a cohesive, but pourable, mass. The effectiveness of thickeners varies greatly and it is within the skill of one familiar with their performance characteristics to use an appropriate amount consistent with the amount of water incorporated in the wet blasting agent. If a bulking agent is added, it may amount to a few percent, i.e., 0 to about 8%; and a catalyst may be used up to a few-tenths to about one percent. As noted in connection with Example 3, a small quantity of sodium borate (up to about 0.5–1.0%) may be added to adjust the physical consistency of the wet blasting agent.

It has been shown from the above description and examples that there is provided a wet blasting agent which is stable, effective, and free from molecular explosives and their inherent disadvantages.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in the above method and composition of matter without departing from the scope of this invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A detonatable wet blasting agent in the form of a cohesive mass, comprising
   (a) a mixture of ammonium nitrate and sodium nitrate, in which said sodium nitrate is present in an amount up to about 25% by weight of said mixture, as an oxidizer;
   (b) urea as a primary fuel;
   (c) aluminum as a secondary fuel;
   (d) water; and
   (e) a thickening agent;

characterized in that at least portions of said ammonium nitrate-sodium nitrate mixture and of said urea are in solution in said water whereby they form an association complex, and the undissolved portion of said blasting agent is retained substantially uniformly distributed throughout the cohesive mass.

2. A wet blasting agent according to claim 1 wherein the amount of said ammonium nitrate-sodium nitrate mixture is present in a quantity sufficient to provide a substantially oxygen-balanced mixture with said urea.

3. A wet blasting agent according to claim 1 wherein said water is present in an amount ranging from about 4 to about 25% by weight of said blasting agent.

4. A wet blasting agent according to claim 1 wherein said thickening agent comprises a gum present in an amount up to about 2% by weight of said blasting agent.

5. A wet blasting agent according to claim 4 wherein said gum is guar gum.

6. A wet blasting agent according to claim 1 including a bulking agent, present in an amount up to about 8% by weight of said blasting agent.

7. A wet blasting agent according to claim 1 including up to about 3% by weight of sulfur.

8. A wet blasting agent according to claim 1 including a small amount of sodium borate as a gelling agent.

9. A detonatable wet blasting agent in the form of a cohesive mass, comprising
   (a) from 10 to 25% by weight water;
   (b) up to 5% by weight of a secondary fuel at least one-half of which is finely divided aluminum;
   (c) up to 8% by weight of a bulking agent;
   (d) up to 2% by weight of a thickening agent; and
   (e) as the remainder a substantially oxygen-balanced mixture of urea and an ammonium nitrate-sodium nitrate mixture wherein said sodium nitrate is present in an amount up to 25% by weight of said nitrate mixture; the blasting agent being further characterized in that at least portions of said ammonium nitrate-sodium nitrate mixture and said urea are in solution in said water whereby they form an association complex and the undissolved components of said blasting agents are retained substantially uniformly distributed throughout the cohesive mass.

10. A wet blasting agent in accordance with claim 9 wherein a portion of said secondary fuel is sulfur.

11. A wet blasting agent in accordance with claim 9 wherein said thickening agent is guar gum.

12. A wet blasting agent in accordance with claim 9 including a small amount of sodium borate not in excess of one percent by weight as a gelling agent.

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