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COATED EXPLOSIVE COMPRISING AMMONIUM NITRATE

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This invention relates to explosives and more particularly is concerned with a novel process for preparing water-resistant ammonium nitrate based explosives and to novel explosive compositions prepared thereby.

Prilled ammonium nitrate in admixture with liquid paraffinic hydrocarbons, e.g. fuel oil, has enjoyed large scale commercial usage as a blasting agent and explosive. However, the resulting compositions, which ordinarily contain about 6 weight percent oil, have a low density, about 0.8 gram per cubic centimeter, and rapidly and substantially completely are degraded when placed in contact with water because of dissolution of the nitrate prills. These ammonium nitrate-fuel oil explosives (commonly called ANFO in the art) therefore can be used only in water containing bore holes or other wet areas when placed in bags or waterproof containers or otherwise protected from water contact.

Heretofore attempts have been made to upgrade the water resistance of prilled ammonium nitrate by coating the surface of the prills with water repellant materials, e.g. grease, wax or clay. These direct surface treatments are not satisfactory since a substantially uniform and effective water resistant coating cannot readily be realized because of many small openings and irregularities present in the porous prills.

It is a principal object of the present invention to provide a novel process for preparing a water resistant particulate ammonium nitrate and explosive composition based thereon.

It is another object of the present invention to provide a method for forming in situ a water resistant protective coating for particulate porous ammonium nitrate which coating also provides fuel for use in an explosive composition.

It is another object of the present invention to provide an ammonium nitrate based explosive composition wherein prilled, porous ammonium nitrate can exist in the presence of water.

It is another objective of the present invention to provide a method for forming directly a grease within porous ammonium nitrate prills after a liquid fuel hydrocarbon has permeated the prill wherein the hydrocarbon thus transformed into the grease within the pores of the prill is not readily displaced by more dense water or aqueous solutions.

These and other objects and advantages readily will become apparent from the detailed description presented hereinafter.

The present invention comprises treating a porous, particulate ammonium nitrate with a grease-forming soap material, adding a liquid hydrocarbon to the so-treated ammonium nitrate and mixing the fuel and treated particulate ammonium nitrate thereby to provide in situ in the pores of and on the surface of the ammonium nitrate a protective water resistant grease coating.

The resulting grease coated ammonium nitrate can be mixed with an aqueous ammonium nitrate solution in proportions so as to provide either a paste-like or pourable slurry. The resulting explosive composition is substantially water resistant and exhibits good explosive power upon detonation.

More particularly in accordance with the present invention, prilled ammonium nitrate is dusted or otherwise blended with from about 0.5 to about 2 weight percent, based on the weight of ammonium nitrate, of a finely divided alkaline earth or earth metal salt of an aliphatic carboxylic fatty acid having from about 8 to about 24 carbon atoms in the aliphatic group. The mixture of fatty acid salt and porous prilled ammonium nitrate is thoroughly blended so as to provide a substantially uniform dispersion of the fatty acid salt in contact with the particulate ammonium nitrate. A petrolic liquid, preferably a liquid paraffinic oil of relatively low viscosity, such as a No. 2 diesel oil for example, is added to the blended ammonium nitrate and fatty acid salt and this mixture agitated to provide a substantially uniform dispersion of the petrolic liquid throughout the mixture. The amount of petrolic liquid to be employed ranges from about 4 to about 8 weight percent of the total mix of ammonium nitrate, fatty acid salt and petrolic liquid. The resulting hydrophobic grease produced by the interaction of the oil and fatty acid salt in accordance with the present novel process is distributed substantially completely over the surface and within the pores of the particulate porous ammonium nitrate. The resulting grease coated prill provides directly a usable water resistant ammonium nitrate explosive composition. The water resistant grease composition provides fuel for the ammonium nitrate oxidizer in substantially the same manner as does the oil itself in the non-water resistant ANFO explosive composition of the art.

An added advantage of the present invention is that the grease coated porous particulate ammonium nitrate product can be admixed with an aqueous ammonium nitrate solution to provide an explosive wherein discrete particles of ammonium nitrate co-exist in the presence of an aqueous ammonium nitrate oxidizer solution. In preparing this latter composition, grease coated prills produced by the present process are admixed with an aqueous solution of ammonium nitrate ordinarily containing a small amount of a thickening agent, e.g. a natural gum. The ammonium nitrate concentration in the solution ranges from about 60 weight percent, based on total weight of the solution, up to the saturation level of the ammonium nitrate in the aqueous liquid. The total amount of aqueous solution used is such that the amount of water to be employed is at a maximum about 15 weight percent of the explosive composition. Ordinarily the water content ranges from about 3 to about 15 weight percent of the total weight. Pourable slurry explosives result when the water content at a minimum is about 9 weight percent. With water concentrations less than about 9 percent, the resulting product exhibits good explosive power but is not in the form of a pourable slurry. At higher water concentrations than set forth hereinbefore, the resulting explosive product tends to become less sensitive to detonation. Ordinarily, the slurry explosive of the present invention contains on a weight basis from about 9 to about 15 percent water, from about 2½ to about 8 percent liquid hydrocarbon fuel, from about 0.6 to about 1.8 percent alkaline earth metal or earth metal aliphatic carboxylic acid salt, from 0 to about 3 percent thickening agent, and balance ammonium nitrate.

Prilled ammonium nitrate products as produced for use in ANFO compositions, for fertilizers or other uses or other particulate porous ammonium nitrate forms all are suitable as oxidizer source material. This material can be employed in the as prilled condition or can be ground and otherwise treated to provide a predetermined classification of particle size range.

The term "alkaline earth metal" as used herein with respect to the fatty acid metal salts includes magnesium, calcium, strontium and barium. The term "earth metal"

is meant to include aluminum, gallium, indium and thallium.

Specific examples of suitable alkaline earth metal- and earth metal fatty acid salts for use in the present invention are aluminum oleate, aluminum stearate, aluminum tallate, calcium stearate, calcium tallate, calcium oleate and the like.

The liquid fuel to be employed ordinarily is selected from petrolic liquids or fractionated petrolic liquid products. Kerosene fuel oils, lubricating oils and other relatively high flash point crude oil fractions, crude oil itself and the like are particularly suitable hydrocarbons for use in the present process and composition.

Thickening agents particularly suitable for use with the aqueous ammonium nitrate solution in preparing the water resistant prill-aqueous ammonium nitrate composition of the present invention are the natural gums, although other thickeners can be employed. Guar gum and paraya gum are specific examples of suitable gum thickeners.

In the grease coated ammonium nitrate-aqueous ammonium nitrate explosive composition, a portion of the petrolic liquid fuel can be substituted by use of a water soluble oxidizable carbon containing material which can be added to the ammonium nitrate solution. Sugars, monohydric and polyhydric alcohols, amines and amides are examples of such fuel materials. Additionally, if desired, solid inorganic oxidizers such as the light metals, e.g. magnesium, aluminum, and alloys and mixtures of these metals also can be incorporated into the explosive composition. Further, a minor portion, for example up to about 20 weight percent of the ammonium nitrate can be substituted by sodium nitrate or potassium nitrate.

The following examples will serve to further illustrate the present invention but are not meant to limit it thereto.

Example 1.—About 562 grams of ammonium nitrate prills and about 5.9 grams of powdered aluminum oleate were weighed into a flexible plastic bag. The two components were thoroughly blended, as ascertained by visual inspection, by kneading and tumbling the bag. When the finely divided aluminum oleate appeared to be substantially homogeneously dispersed with respect to the ammonium nitrate prills, about 24.1 grams of No. 2 diesel oil was introduced into the bag and the mix procedure repeated. The resulting product exhibited a grease-like coating which appeared to be distributed substantially completely over and in the particulate ammonium nitrate.

In a separate container about 284 grams of ammonium nitrate were dissolved in about 120 grams of water, about 4 grams of a guar gum were added slowly to the aqueous solution with continuous stirring. The grease-containing ammonium nitrate prills, and the ammonium nitrate solution were mixed and about 2 milliliters of ammonium hydroxide (28 percent NH_3) was simultaneously introduced therein. (This latter material acted as a cross-linking agent for the guar gum.) The resulting product was a pourable slurry and had a density of about 1.2 grams per cubic centimeter.

A sample of the resulting slurry was placed in water and observed at intervals over an extended period of time. No apparent visual change in the sample was observed either with respect to the slurry consistency or dissolution of the particulate ammonium nitrate present therein.

An explosive charge (about 1000 grams) was prepared in accordance with the procedure and using the mix components described directly hereinbefore. As a control, a second 1000 gram charge was prepared in a similar manner except that the aluminum oleate compound and correspondingly the aluminum oleate-blending operation was omitted.

Each of the charges was placed in a 5 inch diameter water-proof paper container. The charge filled the container to a height of about 9 inches. An additional 9 inches of water was then placed on top of the charge. Both charges were allowed to stand in the presence of the water for about 1½ hours. After this time, each carton was centered on a 9" x 9" x 0.75" steel plate. The plate in turn was centered on the top of a 3" x 3" cylindrical cast lead block. The lead block was placed on a steel anvil. A 40 gram pentolite wafer was placed just below the upper surface of the charge. The charge was detonated and the decrease in the height of the head block measured. With the water resistant composition of the present invention, the reduction in height of the lead block was found to be 1.31 inches. For the control, the decrease in height of block upon detonation was only 0.63 inch. The marked reduction in explosive power demonstrated by the control is attributed to degradation of the sample from water during the relatively short term storage period prior to detonation.

Example 2.—About 95 parts by weight prilled ammonium nitrate were dusted with about 1 part by weight powdered aluminum oleate to provide a visually homogeneous mixture and about 4 parts by weight fuel oil blended therewith in accordance with the procedure set forth in Example 1.

Separately about 69.5 parts by weight ammonium nitrate was dissolved in about 29.5 parts by weight water and about 1 part by weight guar gum blended therein.

These two mixtures in turn were blended in various proportions to provide explosive compositions having a total water content in the final mixture of from about 3 to about 15 weight percent. About 0.01 part by weight aqueous ammonia solution (28 percent NH_3) was used in all cases as a cross-linking agent for the guar gum.

The resulting compositions were tested for water resistance by immersion in water and all found to exhibit the desired high resistance to physical degradation by water.

The compositions also were tested for detonability using the submerged water lead block deformation test procedure reported in Example 1. Table I presents the composition formulation and explosive results obtained for various combinations of the grease covered ammonium nitrate prills and the aqueous ammonium nitrate solution.

TABLE I

Run No.	Grease Coated Prills (Wt. Percent of Total Composition)	Aqueous Ammonium Nitrate Solution (Wt. percent of Total Composition)	Density, g./cc.	Components, Wt. percent of Total Composition					Explosive Results Lead Block Deformation, Inches	Remarks
				NH_4NO_3	Fuel Oil	Al Oleate	Guar Gum	Water		
1	89.8	10.2	0.95	92.4	3.6	0.9	0.1	3.0	1.87	Thick paste.
2	79.6	20.4	1.06	89.9	3.2	0.8	0.2	6.0	2.25	Paste.
3	69.4	30.6	1.12	87.2	2.8	0.7	0.3	9.0	0.94	Pourable slurry.
4	59.2	40.8	1.20	84.6	2.4	0.6	0.4	12.0	1.06	Do.

Example 3.—In a separate study water resistant slurry explosives were prepared in accordance with the process of the present invention by admixing aluminum oleate-fuel oil treated ammonium nitrate prills with an aqueous ammonium nitrate solution. In these studies, the amount

of fuel oil and ammonium nitrate were varied in the preparation of the water resistant prill component. The composition data and explosive results (lead block deformation test as described in Example 1) are summarized in Table II.

TABLE II

Run No.	Water Resistant Prills Component, Weight percent [1]			Aqueous Ammonium Nitrate Solution Component, Weight percent [1]			Explosive Results Lead Block Detonation, Inches
	NH_4NO_3	Al Oleate	Fuel Oil	NH_4NO_3	Guar Gum	Water	
1	58.4	0.6	0	28.5	0.4	12.1	0.25
2	57.2	0.6	1.2	28.5	0.4	12.1	0.81
3	56.1	0.6	2.4	28.5	0.4	12.1	1.06
4	54.9	0.6	3.5	28.5	0.4	12.1	0.94
5	53.7	0.5	4.7	28.5	0.4	12.1	1.12
6	52.5	0.5	5.9	28.5	0.4	12.1	1.12

[1] Based on total composition weight.
NOTE.—Density of final compositions ranged from about 0.95 to about 1.25 grams per cubic centimeter.

In a manner similar to that described for the foregoing examples, ground porous particulate ammonium nitrate can be blended with calcium stearate and this mixture in turn blended with kerosene to provide a water resistant particulate ammonium nitrate. Similarly aluminum stearate and crude oil can be blended with a prilled fertilizer grade ammonium nitrate to produce a water resistant ammonium nitrate based composition. These and other porous ammonium nitrate- alkaline earth metal- or earth metal carboxylic fatty acid salt-liquid hydrocarbon blends prepared in accordance with the present invention can be admixed with aqueous ammonium nitrate solutions to provide high energy water resistant ammonium nitrate based explosives. Additionally, if desired other solid fuels such as light metals, e.g. particulate magnesium, aluminum, magnesium alloys, aluminum alloys and mixtures thereof can be introduced into the explosive compositions of the present invention. Also water soluble carbon-containing oxidizable materials can be dissolved in the ammonium nitrate solution and used in the preparation of these explosive compositions. These latter materials can be used to replace a part of the liquid hydrocarbon fuel used in the preparation of the water resistant prill.

Various modifications can be made in the present invention without departing from the spirit or scope thereof for it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. A process for preparing a water-resistant ammonium nitrate based explosive composition which comprises,

(a) blending porous particulate ammonium nitrate with a member selected from the group consisting of alkaline earth metal- and earth metal salts of aliphatic carboxylic acids, the amount of said salt ranging from about 0.5 to about 2 weight percent based on the weight of said ammonium nitrate, said salt having from about 8 to about 24 carbon atoms in the aliphatic group,

(b) adding a petrolic liquid to the blend of said fatty acid salt and said ammonium nitrate, the amount of said petrolic liquid ranging from about 4 to about 8 weight percent of the total mixture,

(c) mixing said petrolic liquid and the blend of said fatty acid salt and particulated ammonium nitrate thereby to provide in situ in and on said ammonium nitrate a protective, water resistant coating, and

(d) admixing the so-prepared water resistant coated porous ammonium nitrate with an aqueous solution of ammonium nitrate, said solution ranging in ammonium nitrate concentration from about 60 weight percent of said solution up to the saturation level

and the total amount of water at a maximum is about 15 weight percent of the total explosive composition.

2. A process for preparing a water-resistant pourable slurry-type ammonium nitrate based explosive composition which comprises;

(a) blending porous particulate ammonium nitrate with a member selected from the group consisting of alkaline earth metal- and earth metal salts of aliphatic carboxylic acids, the amount of said salt ranging from about 0.5 to about 2 weight percent based on the weight of said ammonium nitrate, said salt having from about 8 to about 24 carbon atoms in the aliphatic group,

(b) adding a petrolic liquid to the blend of said fatty acid salt and said ammonium nitrate, the amount of said petrolic liquid ranging from about 4 to about 8 weight percent of the total mixture,

(c) mixing said petrolic liquid and the blend of said fatty acid salt and particulated ammonium nitrate thereby to provide in situ in and on said ammonium nitrate a protective, water resistant coating, and

(d) admixing the so-prepared water resistant coated porous ammonium nitrate with an aqueous solution of ammonium nitrate, said solution ranging in ammonium nitrate concentration from about 60 weight percent of said solution up to the saturation level, and the amount of water ranging from about 9 to about 15 weight percent of the total slurry-type explosive composition.

3. A process for preparing a water-resistant, pourable slurry-type ammonium nitrate based explosive composition which comprises;

(a) blending about 100 parts by weight prilled ammonium nitrate with about 1 part by weight powdered aluminum oleate,

(b) admixing about 5 parts by weight fuel oil with the blend of said aluminum oleate and said prilled ammonium nitrate,

(c) mixing said fuel oil with said aluminum oleate-ammonium nitrate blend thereby to provide a water resistant coating in the pores of and on the surface of said prilled ammonium nitrate; and

(d) adding with agitation about 80 parts by weight of an aqueous ammonium nitrate solution to said coated water resistant ammonium nitrate prills, said aqueous solution comprising about 57 parts by weight ammonium nitrate, about 22 parts by weight water and about 1 part by weight gum.

4. A pourable, slurry-type water resistant ammonium nitrate based explosive composition which comprises;

(a) on a weight basis from about 0.6 to about 1.8 percent of a member selected from the group consisting of alkaline earth metal and earth metal aliphatic carboxylic acid salt, the aliphatic group of said salt having from about 8 to about 24 carbon atoms;

(b) from about 2.5 to about 8 percent liquid hydrocarbon fuel,

(c) from about 9 to about 15 percent water,
(d) a maximum of about 3 percent thickening agent, and
(e) balance, porous particulate ammonium nitrate, said composition being further characterized in that a portion of said ammonium nitrate is blended with said aliphatic carboxylic acid salt and said liquid hydrocarbon thereby to form a water resistant coating in and on said particulate ammonium nitrate and the remainder of said ammonium nitrate is dissolved in said water forming a solution ranging from about 60 percent to saturation with respect to said ammonium nitrate, said solution being admixed with said

water resistant coating containing particulate ammonium nitrate.

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