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METHOD OF IMPROVING THE WATER-RESISTANCE OF AMMONIUM NITRATE EXPLOSIVES

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The present invention relates to a method of forming an explosive composition possessing advantageous properties, and, more particularly, it relates to a method of improving the water resistance of an ammonium nitrate explosive composition.

For years, ammonium nitrate has been employed in explosive compositions and in fact today it is the principal power-producing ingredient present in most commercial explosives, for example, it is employed in the so-called ammonia dynamites in which ammonium nitrate in granular form, usually both as coarse and fine particles, is associated with a sensitizing material, for example, nitroglycerine, and with a solid carbonaceous fuel. Ammonium nitrate is a water-soluble salt and difficulties have been encountered in the past in ammonium nitrate-containing explosives due to these properties. Thus, since such explosives are often used under moist or wet conditions, the absorption of water tends to desensitize the explosive and, if sufficient water comes into contact with the explosive, it causes the ammonium nitrate to lose its desired granular characteristics, and in extreme cases, the ammonium nitrate may actually be leached from the explosive product.

Several methods for improving the water-resistance of explosive compositions containing ammonium nitrate have heretofore been used with various degrees of success, for example, nitro cotton has been included in the compositions; the salt has been coated with water-repellent materials such as paraffin, petrolatum, and rosin; and various water-dispersible starch materials, which form a protective gel with water, have been included in the compositions.

One object of the present invention is to provide a method of forming a water-resistant explosive composition containing ammonium nitrate and possessing advantageous properties.

A more specific object of the present invention is the provision of a method of forming an ammonia dynamite characterized by resistance to the moisture and water with which the product will come in contact during the normal use thereof.

Still another object is to provide a method of forming an ammonium nitrate-containing explosive composition rendered water-resistant by

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the inclusion therein of an additive material which does not decrease the sensitiveness or stability of the explosive or otherwise affect the desired properties thereof.

Other objects will be apparent from a consideration of this specification and the claims.

In accordance with the present invention, the explosive composition comprises ammonium nitrate in granular form having admixed therewith and uniformly distributed throughout the mass thereof, a finely divided solid, hydrophilic urea-formaldehyde type reaction product. In addition to the ammonium nitrate and urea-formaldehyde type reaction product, there will also be present in the explosive composition such other ingredients as are usually employed, depending upon the type of explosive desired.

The term "solid, hydrophilic urea-formaldehyde type reaction product" as used herein includes the solid hydrophilic reaction products of formaldehyde and at least one of the amino compounds selected from the group consisting of urea, thiourea, and melamine. As is well known, such reaction products may be obtained as simple chemical products which may be crystalline, such as dimethylolurea, using the urea-formaldehyde reaction products as typical; or they may be obtained as resinous solids, in which case the reaction products are partially condensed or polymerized but still possess hydrophilic properties (hereinafter referred to as "partially polymerized"). Preferably, a reaction product is selected which is completely soluble in water.

The reaction product employed is convertible into a hydrophobic product and when converted the resin is substantially infusible and insoluble in the usual solvents. This characteristic of convertibility from the hydrophilic to the hydrophobic state is possessed both by the simple chemical products and by the partially polymerized resinous products, used in carrying out the method of forming an explosive composition in accordance with the present invention. As is well known, the hydrophilic products are converted into the hydrophobic resin by the use of a catalyst providing acid, with or without the application of heat, depending upon the particular catalyst and reaction product. Examples of catalysts are acids, acid salts, ammonium salts of strong acids, and the like. The convertibility

of the product indicates its applicability for use in carrying out the method of forming an explosive product in accordance with the present invention and, as discussed hereinafter, the water-resistance provided may be due to the conversion of the reaction product.

The reaction product may be a conjoint reaction product of two or more of the amino compounds with the formaldehyde, for example, a reaction product between urea, melamine, and formaldehyde or between urea, thiourea, and formaldehyde. Of the products available for use, a partially polymerized water-soluble urea-formaldehyde or melamine-formaldehyde or urea-melamine-formaldehyde product is preferred. The reaction product may or may not contain a catalyst and satisfactory water-resistance is imparted to the explosive composition in both instances. In addition, the reaction product may contain finely divided fillers such as wood flour or starch, but the use of a reaction product free from such materials is preferred.

The ratio of amino compound to formaldehyde in the reaction product is immaterial so long as the reaction product is obtainable as solid material capable of being subdivided, possesses hydrophilic properties and is convertible to a hydrophobic resinous product, and the adjustment of the ratios of the formaldehyde and the amino compound or compounds used in the preparation of the reaction products is within the skill of the art. Usually, the mol ratio of formaldehyde to urea employed will vary from 1.05 to 1 through 2 to 1 (the ratio in dimethylolurea) to about 2.7 to 1, and in the preferred embodiment, the mol ratio of formaldehyde to urea will be between about 1.2 to 1 and about 1.5 to 1. When thiourea is used, the same ratios are applicable. In the case of melamine, the mol ratios of formaldehyde to melamine may be between somewhat above 1, preferably above 2, to 1 and about 6 to 1, and in the preferred embodiment the ratio will be between about 2 mols of formaldehyde to 1 of melamine and about 3 mols of formaldehyde to 1 of melamine. In the case of urea-melamine-formaldehyde reaction products, the amounts will also be adjusted to obtain a reaction product of the stated properties.

Examples of the partially polymerized resinous products which may be used in carrying out the method of forming an explosive composition in accordance with the present invention are the dry, powdered, water-soluble urea-formaldehyde, melamine-formaldehyde or urea-melamine-formaldehyde resinous products sold on the market as resin glues for use in adhesives particularly for the binding of plywood, veneers, furniture, and the like. Typical of such products are "Uformite" (Resinous Products Chemical Company); "Plaskon Resin Glue" (Plaskon Division of Libbey-Owens-Ford Glass Company); "Cascamite" (Casein Company of America); and "Melmac" and "Melurac" (American Cyanamid and Chemical Corporation). Likewise commercial hydrophilic, convertible molding compositions sold by the stated or other companies may be used, if desired.

The reason why water-resistance is provided by the reaction product is not fully understood, and it may be due merely to the fact that, when moisture or water comes into contact with the product, the hydrophilic reaction product absorbs the moisture or water and possibly swells to protect the ammonium nitrate, but there is some indication that there is a conversion of the reaction product from the hydrophilic state to the hydrophobic state. As pointed out above, the desired protection is afforded by a reaction product which does not contain a catalyst, as well as by one that does, and if it is a conversion that provides the desired water-resistance, the ammonium nitrate, or the ammonium chloride usually occluded therewith, serves as the catalyst when a catalyst-free reaction product is employed. Regardless of the reason for the results obtained, the presence of the finely divided reaction product admixed with the ammonium nitrate particles provides the desired water-resistance to the explosive composition as may be seen from the table hereinafter set forth.

As referred to above, the reaction product is employed in solid, finely divided form, for example, the particle size is generally such that the material will pass through a 100 mesh screen, preferably through a 120 mesh screen. In making the explosive composition, care is exercised to assure that the subdivided reaction product is uniformly distributed throughout the explosive composition.

The ammonium nitrate employed may be of any desired particle size, for example, in the case of the explosive composition in an ammonia dynamite, the ammonium nitrate may be present either as coarse and fine particles or both, for example, in the case of coarse ammonium nitrate at least 60% will be retained on a U. S. S. No. 35 screen, whereas in the use of fine ammonium nitrate at least 95% will pass a U. S. S. No. 35 screen. The ammonium nitrate particles may, if desired, be coated with a water-repellent material, for example, wax or a mixture of paraffin and petrolatum.

As stated above, the explosive composition will comprise, in addition to the ammonium nitrate and the reaction product, other usual ingredients depending upon the type of explosive composition desired. So far as the other components of the explosive composition and the proportions thereof are concerned, the usual practices of the art may be employed. Likewise, the explosive composition may be of any desired density and may be packaged in any suitable casing or shell. In view of the fact that except for the inclusion of the water-resistance-imparting reaction product, the composition may be varied in accordance with the skill of the art, it is not necessary to discuss in detail the other components which may be present in the composition. While the use of the reaction product is advantageous in any explosive composition containing ammonium nitrate, it is especially advantageous for use in an ammonia dynamite, and for this reason further reference will be made to the preferred embodiment of the invention wherein the explosive composition is an ammonia dynamite.

Ammonia dynamites, in addition to the ammonium nitrate, contain a sensitizing material and a solid fuel. The sensitizing agent may be an explosive liquid nitric ester typified by nitroglycerine or it may be an explosive nitro aromatic compound such as trinitrotoluene, trinitronaphthalene, and the like or mixtures thereof. In the preferred embodiment of the invention, the explosive composition contains nitroglycerine which may be relatively pure nitroglycerine or may be a nitrated mixture of glycerine, ethyleneglycol, and corn or cane sugar or other nitratable substance, as is usually em-

ployed in the art. The aforesaid nitrated mixture, as well as relatively pure nitroglycerine, is designated in the trade as nitroglycerine, and that term is used herein to include both materials. In an ammonia dynamite, the amount of nitroglycerine will vary, depending upon the properties desired and the other ingredients present, but is usually employed between 5% and 20% by weight of the total weight of the composition. In the preferred embodiment of the invention, the explosive composition will comprise at least about 6% of nitroglycerine.

The solid fuel may be any one or more of a wide variety of materials, for example, wood pulp, bagasse, ivory nut meal, ground walnut shells, apricot pit pulp, a flour such as corn flour, charcoal, coal, sulphur, and the like, and usually the solid fuel will be present in an amount between about 4% and about 15%.

In addition to the sensitizing agent and the solid fuel, ammonia dynamites usually, or at times, contain other materials, for example, nitro cotton, sodium nitrate, and an antacid such as calcium carbonate (chalk), magnesium carbonate, or the like. Any or all of these materials as well as other ingredients may be present in the explosive composition of the invention in proportions to provide an explosive of the desired characteristics, all as is well known in the art.

The reaction product employed will be sufficient to provide the desired water-resistance and usually will be present in an amount between about ½% and about 5%, preferably between about 1% and about 3%, based on the total weight of the explosive composition, although amounts in excess of these figures and over that required for water-resistance may be employed without disadvantageous effects.

The invention will be further described by means of the following specific examples:

Ammonium nitrate explosive compositions were prepared by conventional procedures to each of the formulae listed in the tables hereinafter set forth in which were incorporated, in accordance with the present invention, a reaction product of the type and in the amount specified in said tables.

Each of these explosive compositions were packed in conventional ¼" x 8" paper cartridges. The ends of the cartridges were sealed with tallow. The wrapper of each of the cartridges was perforated with sixteen ¼" holes arranged in four lines parallel to the axis and equidistantly spaced around the cartridge, the holes in adjacent rows being staggered. Each cartridge was placed in a vessel, was covered with sand, and water was poured into the vessel until it stood above the sand. The cartridge was then removed from the sand after a known number of hours, and its detonability with a No. 6 blasting cap was determined. The results are shown in the tables—"D" designating that the composition detonated after the stated number of hours; "F" designating that the composition failed to detonate in the stated number of hours. The data set forth in the tables show that explosive compositions containing the reaction product possessed greatly increased water-resistance.

Table I

	1	2	3	4	5	6
Nitroglycerine, Percent	6.0	6.0	8.0	6.0	6.0	6.0
Wax-coated Fine Ammonium Nitrate, Percent	48.5	48.5	45.7			
Wax-coated Coarse Ammonium Nitrate, Percent				80.4	81.0	80.4
Coarse Sodium Nitrate, Percent	33.2	33.2	32.4	5.0	5.0	5.0
Chalk, Percent	0.5	0.5	0.5	0.5	0.5	0.5
Fine Apricot Pit Pulp, Percent	7.3	6.3	2.9	4.1	3.5	3.1
Wood Pulp, Percent	0.5	0.5	0.5	2.0	2.0	2.0
Ground Sulphur, Percent	4.0	4.0	4.0			
Yellow Corn Flour, Percent			5.3	2.0	1.0	
Water-Soluble Urea-Formaldehyde Reaction Product		[1] 1.0	[1] 0.7		[1] 1.0	[2] 3.0
Water-Resistance	D-7 / F-16	D-144 / F-168	D-168 / F-192	D-1 / F-3	D-168 / F-192	D-24 / F-48

[1] Freshly prepared dimethylolurea in crystalline form.
[2] "Uformite CB 553"—a water-soluble urea-formaldehyde adhesive in the form of a dry powder and containing a room-temperature-setting catalyst, sold by Resinous Products Chemical Company (Rohm and Haas Company).

Table II

	1	2	3	4	5	6	7
Nitroglycerine, Percent	8.0	8.0	11.85	11.85	11.85	9.8	9.8
Nitro cotton, Percent			0.05	0.05	0.05		
Wax-coated Coarse Ammonium Nitrate, Percent	22.4	22.4				36.1	36.1
Wax-coated Fine Ammonium Nitrate, Percent	22.4	22.4	39.00	39.00	39.00	36.1	36.1
Coarse Sodium Nitrate, Percent	33.0	33.0	25.00	25.00	25.00		
Fine Sodium Nitrate, Percent			10.60	10.60	10.60	7.5	7.5
Bagasse, Percent						7.0	6.5
Fine Soft Coal, Percent	6.0	6.0					
Fine Apricot Pit Pulp, Percent	7.7	5.7	3.00	3.00	3.00		
Wood Pulp, Percent						1.0	2.5
Yellow Corn Flour, Percent			6.00	4.00	5.00		
Ground Sulphur, Percent			4.00	4.00	4.00		
Chalk, Percent	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Partially polymerized, water-soluble Urea-Formaldehyde Resin, Percent		[1] 2.00		[1] 2.00	[1] 1.00	[1] 2.00	[1] 1.00
Water-Resistance	D-3 / F-7	D-24 / F-48	D-7 / F-16	D-144 / F-168	D-72 / F-96	[2] D-24 / F-48	[2] D-16 / F-24

[1] "Cascamite"—a water-soluble urea-formaldehyde resin adhesive in the form of a dry powder, sold by Casein Company of America.
[2] The water-resistance of this explosive composition containing no urea-formaldehyde reaction product was: D-3; F-7.

Table III

	1	2	3	4	5
Nitroglycerine, Percent	11.85	11.85	11.85	11.85	11.85
Nitro cotton, Percent	0.05	0.05	0.05	0.05	0.05
Wax-coated Fine Ammonium Nitrate, Percent	39.00	39.00	39.00	39.00	39.00
Coarse Sodium Nitrate, Percent	25.00	25.00	25.00	25.00	25.00
Fine Sodium Nitrate, Percent	10.60	10.60	10.60	10.60	10.60
Fine Apricot Pit Pulp, Percent	3.00	3.00	3.00	3.00	3.00
Yellow Corn Flour, Percent	4.00	5.00	4.00	5.00	4.00
Ground Sulphur, Percent	4.00	4.00	4.00	4.00	4.00
Chalk, Percent	0.50	0.50	0.50	0.50	0.50
Partially Polymerized Water-Soluble Urea-Formaldehyde Resin, Percent	[1] 2.00	[1] 1.00	[2] 2.00	[2] 1.00	[3] 2.00
Water-Resistance [4]	D-168 F-192	D-144 F-168	D-168 F-192	D-144 F-168	D-96 F-120

[1] "Uformite 505"—a water-soluble urea-formaldehyde adhesive in the form of a dry powder and containing no catalyst, sold by Resinous Products and Chemical Company (Rohm and Haas Company).

[2] "Uformite CD 553"—a water-soluble urea-formaldehyde adhesive in the form of a dry powder and containing a room-temperature-setting catalyst, sold by Resinous Products and Chemical Company (Rohm and Haas Company).

[3] "Plaskon Ready-Mixed 250–2 Glue"—a water-soluble urea-formaldehyde adhesive in the form of a dry powder and containing a catalyst, sold by the Plaskon Division of Libbey-Owens-Ford Glass Company.

[4] Compare with No. 3 of Table II.

Table IV

	1	2	3	4	5	6	7	8	9
Nitroglycerine, Percent	11.85	11.85	11.85	6.0	6.0	10.0	10.0	6.0	6.0
Nitrocotton, Percent	0.05	0.05	0.05						
Wax-coated Fine Ammonium Nitrate, Percent	39.00	39.00	39.00	48.5	48.5	42.0	42.0		
Wax-coated Coarse Ammonium Nitrate, Percent						29.5	29.5	80.4	80.4
Coarse Sodium Nitrate, Percent	25.0	25.0	25.0	33.2	33.2	8.0	8.0	5.0	5.0
Fine Sodium Nitrate, Percent	10.6	10.6	10.6						
Fine Apricot Pit Pulp, Percent	3.0	3.0	3.0	6.3	6.3			4.1	4.1
Yellow Corn Flour, Percent	5.0	5.0	4.0			5.0	5.0	1.0	1.0
Ground Sulphur, Percent	4.0	4.0	4.0	4.0	4.0	4.0	4.0		
Wood Pulp, Percent				0.5	0.5			2.0	2.0
Chalk, Percent	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Partially Polymerized, Water-soluble Melamine-Urea-Formaldehyde Resin, Percent	[1] 1.0	[2] 1.0	[2] 2.0	[1] 1.0	[2] 1.0	[1] 1.0	[2] 1.0	[1] 1.0	[2] 1.0
Water-Resistance	[3] D-168 F-192	[3] D-168 F-192	[3] D-168 F-192	[4] D-24 F-32	[4] D-32 F-48	[5] D-48 F-72	[5] D-48 F-72	[5] D-24 F-32	[6] D-96 F-120

[1] A melamine-urea-formaldehyde co-reacted resin containing approximately 18% inert filler material of a mixture of wood flour and walnut shell flour, sold by American Cyanamid and Chemical Corp. under the designation "Melurac 300."

[2] A melamine-urea-formaldehyde co-reacted resin containing no filler, sold by American Cyanamid and Chemical Corp. under the designation "Melurac 301."

[3] Compare with No. 3 of Table II.

[4] Compare with No. 1 of Table I.

[5] The water-resistance of this explosive composition containing no reaction product was: D-3; F-7.

[6] Compare with No. 4 of Table I.

Table V

	1	2	3	4	5	6
Nitroglycerine, Percent	6.0	6.0	8.0	8.0	9.8	9.8
Wax-coated Fine Ammonium Nitrate, Percent	48.5	48.5	45.7	45.7	36.1	36.1
Wax-coated Coarse Ammonium Nitrate, Percent					36.1	36.1
Coarse Sodium Nitrate, Percent	33.2	33.2	32.4	32.4	7.5	7.5
Chalk, Percent	0.5	0.5	0.5	0.5	0.5	0.5
Fine Apricot Pit Pulp, Percent	6.3	5.3	2.9	2.9		
Wood Pulp, Percent	0.5	0.5	0.5	0.5	1.0	1.0
Ground Sulphur, Percent	4.0	4.0	4.0	4.0		
Yellow Corn Flour, Percent			5.0	5.0		
Bagasse, Percent					7.0	7.0
Water-Soluble Melamine-Formaldehyde Reaction Product, Percent	[1] 1.0	[1] 2.0	[2] 1.0	[3] 1.0	[2] 2.0	[3] 2.0
Water-Resistance	[4] D-48 F-72	[4] D-240	[5] D-32 F-48	[5] D-32 F-48	[6] D-48 F-72	[6] D-16 F-24

[1] "Melmac S-77-W"—a water-soluble melamine-formaldehyde reaction product in the form of a dry powder and containing no filler and only a small amount, if any, of catalyst, sold by American Cyanamid and Chemical Corp.

[2] "Melmac 401"—a water-soluble melamine-formaldehyde reaction product in the form of a dry powder and containing no filler and a very small amount, if any, of catalyst, sold by American Cyanamid and Chemical Corp.

[3] "Melmac 405"—a water-soluble melamine-formaldehyde reaction product in the form of a dry powder and containing no filler and a very small amount, if any, of catalyst, sold by American Cyanamid and Chemical Corp.

[4] The water-resistance of this explosive composition containing no reaction product was: D-7; F-16.

[5] The water-resistance of this explosive composition containing no reaction product was: D-7; F-16.

[6] The water-resistance of this explosive composition containing no reaction product was: D-3; F-7.

Considerable modification is possible in the selection of the particular reaction product and the proportions thereof employed, as well as in other ingredients of the explosive composition, without departing from the present invention.

I claim:

1. The method of improving the water-resistance of an explosive composition comprising a mixture of granular ammonium nitrate, a sensitizer and a solid fuel which comprises intimately mixing with and substantially uniformly distributing throughout said mixture of granular ammonium nitrate, sensitizer and solid fuel, a solid, finely-divided hydrophilic reaction product of formaldehyde and at least one of the amino compounds selected from the group consisting of urea, thiourea and melamine.

2. The method of claim 1 wherein said reaction product is a water-soluble partially polymerized urea-formaldehyde resin and is in an amount between about 0.5% and about 5% based on the weight of the explosive composition.

3. The method of claim 1 wherein said reaction product is a water-soluble partially polymerized melamine-formaldehyde resin and is in an amount between about 0.5% and about 5% based on the weight of the explosive composition.

4. The method of claim 1 wherein said reaction product is a water-soluble partially polymerized urea-melamine-formaldehyde resin and is in an amount between about 0.5% and about 5% based on the weight of the explosive composition.

5. The method of claim 1 wherein the said granular ammonium nitrate has a wax coating.

6. The method of improving the water-resistance of an explosive composition comprising a mixture of granular ammonium nitrate, at least one sensitizer selected from the group consisting of an explosive liquid nitric ester and a nitro aromatic compound, and a solid carbonaceous fuel which comprises intimately mixing with and substantially uniformly distributing throughout said mixture of granular ammonium nitrate, sensitizer and solid fuel, a solid, finely-divided hydrophilic reaction product of formaldehyde and at least one of the amino compounds selected from the group consisting of urea, thiourea and melamine.

7. The method of claim 6 wherein the sensitizer is nitroglycerin and is in an amount between about 6% and about 20% based on the weight of the explosive composition; and wherein said reaction product is a water-soluble partially polymerized urea-formaldehyde resin in an amount between about 0.5% and about 5% based on the weight of the explosive composition.

8. The method of claim 6 wherein the sensitizer is nitroglycerin and is in an amount between about 6% and about 20% based on the weight of the explosive composition; and wherein the reaction product is a water-soluble partially polymerized melamine-formaldehyde resin in an amount between about 0.5% and about 5% based on the weight of the explosive composition.

9. The method of claim 6 wherein said granular ammonium nitrate has a wax coating.

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