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SHAPED EXPLOSIVES CONTAINING FIBROUS POLYOXYMETHYLENE

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The present invention relates to explosive compositions, and more specifically to a novel binder for explosive compositions which normally have a low degree of mechanical strength.

It is frequently desired to produce shaped, i.e., pelletized, briquetted or cast, explosives having a relatively high degree of mechanical strength. These high strength materials do not flake or chip in handling and for certain purposes are more convenient to use than their plastic or particulate counterparts.

Heretofore, organic waxes have been widely used as binders in the formation of shaped explosive compositions. Waxes possess the advantage of being relatively inexpensive and are easily adapted to shaping techniques which include extrusion, pressing, and melt-casting of explosive materials. It is sometimes found, however, that the addition of organic waxes to explosives detracts from the detonation velocities thereof and therefore alters its characteristics.

It is therefore an object of the present invention to provide a novel binder for shaped explosives.

It is another object to provide an explosive composition which may be readily shaped by conventional extrusion, pressing, and melt-casting techniques.

It is a further object to provide a novel binder system for explosives which does not alter the detonation velocity of the explosives.

These and still further objects of the present invention will become readily apparent to one skilled in the art from the detailed description and specific examples which follow.

In general, the present invention contemplates explosive compositions which contain as a binding agent from about 1% to about 15% by weight based on the weight of the explosive of a finely divided fibrous polyoxymethylene polymer, the fibers of which possess a maximum major dimension, i.e., length of less than 50 microns and a length of diameter ratio of at least 10:1.

More specifically, I have found that extremely fine fibrous polyoxymethylene which is obtained by grinding polyoxymethylene produced by the solid state polymerization of trioxane, is a highly efficient binder for high explosive compositions which are to be shaped by conventional extrusion, pressing, or melt-casting techniques. The explosives containing the present fibrous polyoxymethylene binder possess a high degree of mechanical strength. Furthermore, the detonation characteristics of the explosive are not altered by the addition of the presently intended binders.

In general, the explosives to which the present fibrous polyoxymethylene binders are added are those high explosives which possess a rate of detonation of from about 1,000 to about 8,500 meters per second. Furthermore, the high explosives treated in accordance with the present invention should be of the generally non-initiating type and should possess a melting point in excess of from about 50° C. Explosives falling within this general category may be subjected to shaping techniques without undue danger of detonation. Typical explosives which are used in the practice of the invention are single compound explosives such as cyclotrimethylene-trinitramine (RDX), ammonium nitrate, ethylenedinitramine (EDNA), nitroguanidine, pentaerythritol (PETN), di-

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pentaerythritol (DPEHN), mannitol hexanitrate (MHN), cyclotetramethylenetetranitramine (HMX), metadinitrobenzene, 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (picric acid), ammonium trinitrophenolate (ammonium picrate), 2,4,6-trinitrophenyl methyl nitramine (Tetryl), and hexanitrodiphenylamine (Hexite). Furthermore, the invention may be extended to binary explosives such as Amatol (50-50 ammonium nitrate-TNT), Tritonal (80-20 TNT-flake aluminum), Tetrytol (70-30 tetryl-TNT), Pentolite (50-50 PETN-TNT), Picratol (50-50 TNT-ammonium picrate), and Cyclotol (60-40 cyclonite-TNT).

The polyoxymethylene fibers used as a binder in the present invention are obtained by the solid state polymerization of trioxane. This is conveniently done by subjecting solid trioxane to high energy ionizing irradiation to form active polymerization sites therein, polymerizing the initiated trioxane at a temperature in excess of about 30° C. to obtain polymerization, and subsequently removing non-reacted trioxane from the polymerization mass.

In general, from about 0.001 to about 10 megarads of high energy ionizing irradiation may be used to form the active polymerization sites in the trioxane. The high energy ionizing irradiation may be electrons, deuterons, positrons, alpha particles, X-rays and gamma rays having sufficient energy to induce active sites in the trioxane. The trioxane is irradiated in the solid state, that is, at a temperature below the melting point of the trioxane. Conveniently, the irradiation may be conducted at room temperature.

Subsequent to irradiation, the trioxane is heated to a temperature in excess of 30° C., and preferably from about 55 to about 62° C. to achieve polymerization. The polymerization temperature must not exceed the melting point of the trioxane in order to obtain the desired fibrous structure. The trioxane is maintained at the polymerization temperature for a period of from about 0.5 to about 10 hours during which time 50% conversion of trioxane to polymer may be readily obtained.

Subsequent to polymerization, non-reacted trioxane is removed by evaporation or by extraction with a solvent for the trioxane such as water, methanol or acetone. The non-reacted trioxane may be subsequently recycled into the initial polymerization step.

The polyoxymethylene polymers obtained in accordance with the present invention possess a novel fibrous crystalline structure. X-ray diffraction pattern studies indicate that the present polyoxymethylene polymers possess an identity distance of 14 Å. measured along the fiber axis. This differs from the normal 17 Å. identity period observed in polyoxymethylene formed by non-solid state polymerization methods. The polymers possess a melting point of from about 185 to about 200° C. The reduced specific viscosity (RSV) of the polymer as determined at 135° C. using 0.1 gram of polymer in 100 milliliters of gamma butyrolactone range from about 0.3 to about 3.0 deciliters per gram.

Subsequent to isolation of the polymer from the polymerization mass the polymer is subjected to a grinding procedure to produce the small size fibers required for the practice of the invention. Practically any commercial grinding or milling apparatus may be used to achieve the desired degree of fiber size reduction. Grinding apparatus such as high speed rotary shearing devices, and fluid energy mills may be used. In general, however, it is preferred that the latter mentioned fluid energy mill be used to obtain an optimum degree of fiber size reduction. It is found the milling conditions which are set up in the conventional fluid energy mills provide the degree of fiber separation and breaking action required for the production of the desired product.

In general, it is found that the degree of fiber size reduction is dependent on the amount of milling. Satisfactory milling will produce a product which contains fibers having a maximum length of about 50 microns and a maximum diameter of about 5 microns. Such a ground product will also contain a large amount of material which is in the sub-micron range. That is, the diameter of some of the fibers will be considerably less than 1 micron and the length thereof will frequently be less than about 1 micron. These smaller size particles produce a high degree of binding effect, however, it is not required that the entire product may be reduced below the sub-micron size range. So long as the fibers generally fall below the 50 micron length and the 5 micron diameter set forth above, it is found the product will produce a satisfactory binding effect.

The fine size fibrous material is added to the present explosives in amounts ranging from about 1 to about 15% by weight of the explosive. It is generally found, however, that as little as 2 to 4% will frequently produce the increase in mechanical strength required for satisfactory shaping of the explosive charge.

Mixing of the present fibrous binder is done in a conventional manner. Frequently, the fibers may be added at any step in the processing of the explosive where the explosive is in a plastic or molten stage.

Shaping of the presently intended binder-explosive compositions is conducted in a normal manner by extrusion, pressing, or melt-casting. Furthermore, it is contemplated that the explosive compositions treated in accordance with the present invention may contain auxiliary agents such as fillers or sensitizing agents in addition to the presently intended binders. The presence of these additional materials in no way effects the binding action induced by the present fibrous materials. The shaped explosives prepared in accordance with the present invention may be used as propellants, blasting materials, explosion metal shape-forming means, and so forth.

Having described the basic elements of the present invention, the following detailed specific examples are given to illustrate embodiments thereof.

Example I

Commercial trioxane crystals are spread in thin layers on trays and subjected to an irradiation dosage which comprised 0.5 megarad of 2 mev. electrons as delivered from a Van de Graaff accelerator. A total of 20 kilograms of the irradiated crystals are placed in 16 oz. screw top glass jars. The jars are sealed and submerged in a water bath heated to 55° C. The heating is continued for 5 hours, whereupon the product is removed from the jars and extracted with water to remove the non-reacted trioxane. Subsequent to drying, it is found that 5 kilograms of polymer is obtained which represents 25% conversion of trioxane to polymer. The RSV of the product as determined at 135° C. in gamma butyrolactone using 0.1 gram of polymer in 100 milliliters of solvent is 0.79.

The dried polymer is milled in a fluid energy mill using compressed air as the grinding medium. Upon grinding the material at grinding rates ranging from 20 to 40 grams per minute using an injection pressure of approximately 200 p.s.i.g. and a grinding pressure of approximately 250 p.s.i.g., a fine size particulate material is obtained which falls within the required particle size range.

Example II

The fine size particulate polyoxymethylene obtained in Example I is admixed with cyclotrimethyltrinitramine (RDX) in varying amounts. These samples are compressed to densities in the range of 1.29 to 1.47 g./cc. using a hydraulic press. Pressed samples containing the present fibrous binders are detonated along with others which contained conventional wax binders, and the deto-

nating velocities are determined. The results of the detonation velocity tests are tabulated below:

Run	RDX (percent)	POM (percent)	Wax (percent)	Density (g./cc.)	Detonation Velocity (m./sec.)
1	98	2	---	1.29	7,050
2	98	2	---	1.37	7,520
3	96	4	---	1.29	7,090
4	96	4	---	1.37	6,990
5	96	4	---	1.47	7,390
6	97	---	3	1.37	6,850
7	100	---	---	1.29	7,120
8	100	---	---	1.37	7,410
9	100	---	---	1.47	7,770

It is seen from the above that the pressed charges containing 2 and 4% of the present polyoxymethylene fibrous binder produce substantially the same detonation velocity as a pure sample. Furthermore, it is seen the samples containing the present binder possess a higher detonation velocity than those containing a conventional wax binder. It is also found that the pressed charges containing the fibrous polyoxymethylene binder when compressed to a density of 1.29 grams/cc. are solid and can be easily handled without breaking. On the other hand, those prepared with 3% wax are fragile and are easily broken. Differential thermal analysis of the polyoxymethylene-RDX mixture indicates that there is substantially no reaction between the polyoxymethylene and the RDX.

Example III

Numerous conventional explosives are compounded with varying percentages of the present fibrous polyoxymethylene fiber. The charges are pressed with just enough pressure to form a cohesive mass, and then detonation rates are determined. The table below indicates that the detonation rate for the explosive with the binder is substantially the same as that without the binder.

Explosive	POM (percent)	Detonation Rate (m./sec.)
EDNA	10	7,700
EDNA	---	7,750
Nitroguanidine	8	7,625
Nitroguanidine	---	7,650
PETN	2	8,300
PETN	---	8,300
DPEHN	5	7,400
DPEHN	---	7,410
MHN	4	8,200
MHN	---	8,260
m-dinitro benzene	3	6,090
m-dinitro benzene	---	6,000
TNB	2	7,400
TNB	---	7,440
TNT	6	6,850
TNT	---	6,900
Picric acid	5	7,325
Picric acid	---	7,350
Ammonium picrate	7	7,100
Ammonium picrate	---	7,150
Hexite	12	7,050
Hexite	---	7,150
Amatol (50-50)	8	6,300
Amatol	---	6,400
Tritonal (80-20)	6	6,500
Tritonal	---	6,600
Tetrytol (70-30)	4	7,250
Tetrytol	---	7,350
Pentolite (50-50)	1	7,400
Pentolite	---	7,450
Picratol (50-50)	7	6,900
Picratol	---	6,900
Cyclotol (60-40)	11	7,775
Cyclotol	---	7,800
Tetryl	10	7,800
Tetryl	---	7,850

In the compositions set forth in the above table, it is found that in all cases mechanically strong shaped elements are formed. The shaped element containing the fibrous polyoxymethylene possess considerably more mechanical strength than those prepared with wax or not containing any binder.

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The above specific examples clearly indicate that the present fibrous polyoxymethylene binders may be used as a valuable adjunct to commercial explosives. The binder increases the mechanical strength of the shaped charges, but in no way detracts from the detonation rate thereof.

I claim:

1. An explosive composition which comprises (1) a normally solid non-initiating high explosive possessing a detonation rate of from about 1,000 to about 8,500 meters per second, and (2) from about 1% to about 15% by weight based on the weight of the high explosive of a fine size fibrous polyoxymethylene polymer, the fibers of which possess a length of under 50 microns, and a length to diameter ratio of at least 10:1, said fibrous polyoxymethylene being further characterized by possessing an identity distance of 14 A. units as measured along the fiber axis by X-ray diffraction pattern means.

2. A method for forming shaped explosives which comprises admixing from about 1% to about 15% by weight of the finely divided fibrous polyoxymethylene polymer, the fibers of said polymer possessing a length of under 50 microns, and a length to diameter ratio of at least 10:1,

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said fibrous polyoxymethylene being further characterized by possessing an identity distance of 14 A. units as measured along the fiber axis by X-ray diffraction pattern means, with non-initiating explosive capable of being subjected to mechanical forming, and forming said explosive mixture to a shape of desired configuration.

3. The method of claim 2 wherein the mixture is formed by means of mechanical pressing under sufficient force to obtain a self-supporting shape retaining mass.

4. The method of claim 2 wherein said explosive possesses a rate of detonation of from about 1,000 to 8,500 meters per second, and a melting point in excess of about 50° C.

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