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CASTABLE EXPLOSIVE COMPOSITION

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This invention relates to moldable explosive compositions and more particularly to a hydrazine nitrate explosive composition that can be cast at atmospheric temperatures into any desired physical configuration and cured at moderately elevated temperatures to form an essentially non-flowable, non-plastic solid structure.

In the art of explosives it is frequently desirable to produce explosive grains having specialized physical configurations. In some cases such special configurations can be achieved by melting the explosive composition, casting the molten material in a suitable mold and cooling to solidify the composition in the desired shape. However some explosive substances cannot be safely heated to their melting points. Moreover in cases where it is desirable that explosive substances be compounded with, for example, combustible organic materials and metal powders, the resulting compositions are commonly incapable of being cast in molten condition. Explosive grains that are molded from explosive materials in powder form generally have little physical strength.

The present invention is concerned with explosive compositions comprising hydrazine nitrate powder and an organic binder therefor. It is an object of the present invention to provide a hydrazine nitrate-containing explosive grain which has high explosive power and is also relatively insensitive to shock, i.e., which has an impact sensitivity greater than 10 pound-inches. It is another object of the invention to provide such an explosive grain which will burn only when in contact with a flame and will not support combustion when the flame is removed. It is still another object of the invention to provide an explosive grain of this type that has good physical strength. It is a still further object of the invention to provide a method of making such an explosive grain in any desired physical configuration. It is a still further object of the invention to provide a fluid hydrazine nitrate-containing mixture including a curable organic material, which mixture can be cast into a desired configuration at atmospheric temperature and cured at a moderately elevated temperature to form an explosive grain having the desirable properties indicated above. Other objects of the invention will be in part obvious and in part pointed out hereafter.

The present invention is predicated on the finding that a hydrazine nitrate grain having improved properties can be achieved by using a cured polyester as a binder therein. Polyesters that are useful for this purpose are carboxyl-terminated linear condensation products of polyhydric alcohols and polybasic acids having molecular weights within the range 500 to 5,000. Polyhydric alcohols that can be used in preparing such linear condensation products include ethylene glycol, diethylene glycol, glycerol, propylene glycol, polypropylene glycols, pentaerythritol, trimethylolpropane, butanediol, polybutylene glycols, castor oil and mixtures of these polyols. Castor oil, which has an oxygen content of about 15% by weight, has the lowest oxygen content of any of the foregoing polyols. Suitable polybasic acids for reacting with the foregoing alcohols to form linear polyesters include oxalic, adipic, sebacic, 6-amino-caproic, phthalic, isophthalic, terephthalic, malonic, succinic, maleic, fumaric, and itaconic acids and mixtures of these acids. 6-amino-caproic acid, which has an oxygen content of about 24% by weight, has the lowest oxygen content of any of the foregoing

acids. Polyesters prepared by reacting a molar excess of adipic acid with diethylene glycol to form a carboxyl-terminated linear polyester have been found especially satisfactory. The alcohols and acids having more than two functional groups are commonly used only in a small proportion in the reaction mixture to produce a slight amount of cross-linking. Since such polyesters are well known in the art, it is deemed unnecessary to describe in detail methods for making them.

In general the present compositions are prepared by mixing hydrazine nitrate in powder form with the carboxyl-terminated polyester and a suitable curing agent therefor to form a fluid composition that can be cast at atmospheric temperature in a mold of the desired configuration, and then heating to a temperature of the order of 100° to 150° F. to cure the polyester polymer to form a solid explosive grain. While any of the curing agents previously employed for the curing of carboxyl-terminated polyesters may be used, good results have been obtained with compounds having two or more heterocyclic groups that are reactive with carboxyl groups i.e., polyepoxides and polyimines. The diglycidyl ether of bisphenol A sold under the name "Epi-rez 510" is typical of the commercial polyepoxide that may be used, and the alkyleneimine tris-1,2-methyl aziridinyl phosphine oxide sold under the trade name "MAPO" is typical of the commercial imine curing agents that can be employed in making the present compounds. Other curing agents include the diglycidyl ether of bisphenol F [diglycidyl ether of bis-(4-hydroxyphenyl)methane]; tris-1,2-methyl aziridinyl phosphine sulfide; hexamethylene-6,6'-dicycloethylene urea; trimethylol propane-tris-B-propylene imine propionate; ethylene glycol-bis-B-propylene imine propionate; toluene dicycloethylene urea; and terephtaloyl-bis-ethylene imine. Curing is effected by reaction of the heterocyclic groups of these curing agents with the carboxyl terminals of the polyester.

As indicated by the specific examples given below, the present compositions may contain various minor constituents in addition to hydrazine nitrate, the polyester and its curing agent. Thus the performance characteristics of the explosive grain can generally be improved by incorporating any of various metal powders in the composition. For example, magnesium, aluminum, titanium, aluminum alloy, silicon, zirconium, tin, zinc and copper powders or combinations of these powders can be utilized. If desired, burning rate modifiers such as ammonium dichromate can be incorporated in the composition. Also additives such as polypropylene glycol and polyethylene glycol can be used to change the consistency of the uncured formulation and to modify the physical properties of the cured formulation. Curing rate modifiers such as magnesium stearate are sometimes useful. The reaction mixture may contain catalysts for the curing reaction such as 4,4'-methylene bis(2-chloroaniline); 4,4'-methylene dianiline; n-phenylene diamine; diamino toluenes; triethylene tetramine; tetraethylene pentamine; diethylene triamine; tri(dimethyl aminomethyl)phenol and mixtures of these amines.

In order to secure the desired explosive effect, a relatively large proportion of hydrazine nitrate should be employed. More particularly, the cured composition desirably contains from 50% to 80% by weight of hydrazine nitrate and from 20% to 50% of the resin binder and minor constituents. In compositions containing metal powder, the metal powder desirably ranges from 5% to 15% by weight of the composition. In the fluid mixture prior to curing the polyester component may range from 10% to 30% by weight of the mixture and the heterocyclic curing agent from 3% to 10% of the mixture. Thus in the cured composition the binder may range from 13% to 40% by weight.

In some cases a hydrazine nitrate-containing explosive composition may be desired having a putty-like consistency. Such a material having good explosive properties can be prepared in accordance with the present invention by mixing the powdered hydrazine nitrate with the polyester and metal powder in the absence of a curing agent. In this way a permanently plastic composition can be obtained which can be molded to a desired configuration just prior to detonation.

In order to point out more fully the nature of the present invention the following specific examples are given of compositions incorporating the concept of the invention.

EXAMPLE 1

The polyester used in this example was prepared by condensing 9.4 mols of adipic acid with 8.94 mols of diethylene glycol. The resulting polyester polymer had an acid number of 60 and a viscosity of 90 poises at 80° F.

A vertical planetary mixer was charged with 16.05 parts by weight of this polyester, 12 parts of aluminum powder (Reynolds 400), 3.95 parts of the diglycidyl ether of bisphenol A (Epi-rez 510), 1.5 parts of 4,4'-methylene dianiline, 0.5 part of magnesium stearate and 1 part of ammonium dichromate. These ingredients were mixed for 15 minutes to insure wetting of the aluminum powder. Thereafter 65 parts of hydrazine nitrate was added and mixing continued for an additional period of one hour.

One portion of this mixture was cast into dumbbell-shaped specimens and cured at 120° F. for 96 hours. Thereafter the specimens were subjected to a tensile test and exhibited a tensile strength of 5 p.s.i. and a strain of 0.1 in./in. The modulus of the material was 71 p.s.i.

Other portions of the mixture were cast into 4-inch long sections of 1-inch O.D. steel pipe and tested for their explosive characteristics. More particularly, a series of these specimens were detonated against 5-inch square by 1-inch thick mild steel witness plates using a standard test procedure developed at the Army Chemical Center in Edgewood, Maryland. In accordance with this procedure the penetration for a series of detonated specimens is measured and averaged. The test measures a combination of brisance and power. The specimens prepared as described above exhibited a penetration of 0.186 inch. This penetration, under the test conditions used, indicates that the present composition is superior to cast TNT. The impact sensitivity of this material was 13.8 pound-inches.

EXAMPLE 2

The procedure of Example 1 was followed except that the proportions of ingredients were changed as indicated below.

Hydrazine nitrate	52.2
Aluminum	9.8
Polyepoxide	6.7
Polyester polymer	27.3
4,4'-methylene dianiline	2.25
Mg stearate	0.75
Ammonium dichromate	1.0

Samples of this formulation were cured as in Example 1 and exhibited in average penetration of 0.179.

EXAMPLE 3

The procedure of Example 1 was followed using the proportions indicated herein.

Hydrazine nitrate	75
Polyepoxide	4.15
Polyester polymer	16.85
4,4'-methylene dianiline	2.25
Mg stearate	0.75
Ammonium dichromate	1.0

It will be noted that the formulation of this example contains no aluminum powder. Specimens of the foregoing formulation were cured as in Example 1 and specimens were detonated in tests of the type described in Example 1. They exhibited an average penetration of 0.086, that is, substantially less than the composition of Example 1.

EXAMPLE 4

A series of formulations were prepared having the compositions indicated in Table 1 below using the procedure of Example 1. In each case the material was cured at 120° F. for 96 hours and tested for its physical properties, which are also listed in Table 1.

Table 1

	Sample A	Sample B	Sample C
Ingredient:			
Hydrazine nitrate	65	65	65
Aluminum	12	13	13
Polyepoxide	5.22		
Polyester polymer	12.64	16.5	16.42
4,4'-methylene dianiline	1.0		
Mg stearate	0.5		
Ammonium dichromate	1.0	1.0	1.0
Dimethyl aminomethyl phenol	0.5		
Polypropylene glycol	2.14		
Hexamethylene-6,6'-dicycloethyl-ene urea		4.5	4.12
MAPO			0.46
Properties:			
Tensile strength, p.s.i.	16	66	82
Strain, in./in.	0.10	0.27	0.22
Modulus, p.s.i.	202	306	490

The data of Table 1 indicate the way in which the physical properties of the compositions can be varied by formula modification.

EXAMPLE 5

The procedure of Example 1 was followed except that the proportions of ingredients were changed as indicated below.

Hydrazine nitrate	65.0
Aluminum powder (5–8 micron)	12.0
Polyester polymer	16.81
Polyepoxide	3.19
4,4'-methylene dianiline	1.5
Mg stearate	0.5
Ammonium dichromate	1.0

The burning rate of this formulation, after curing as in Example 1, was measured on a Crawford strand burner and found to be 0.106 in./sec. at 500 p.s.i.a.

EXAMPLE 6

A composition was prepared by mixing with 18.74 parts of the polyester polymer of Example 1, 13.2 parts of aluminum powder, 1.03 parts of ammonium dichromate and 1.03 parts of an alkylphenol polyglycol ether sold under the trade name Neutronyx. After thorough mixing of these ingredients, 66 parts of hydrazine nitrate were added and mixed therewith. The resulting mixture, which contains no curing agent, was molded into a 1.5 in. diameter cord 10 inches long and detonated. It was found to have good explosive characteristics.

It is of course to be understood that the foregoing examples are intended to be illustrative only and that numerous changes can be made in the ingredients, proportions and conditions specifically set forth without departing from the spirit of the invention as defined in the appended claims.

I claim:

1. An explosive composition essentially composed of 50% to 80% by weight of hydrazine nitrate and 13% to 40% by weight of a cured carboxyl-terminated linear polyester binder cured through the carboxyl terminals thereof, said linear polyester, prior to curing, having a molecular weight of 500 to 5,000 and being the condensation product of a polycarboxylic acid and a polyhydric alcohol, said acid containing at least 24% by weight oxy-

gen and said alcohol containing at least 15% by weight oxygen.

2. An explosive composition comprising 50% to 80% by weight of hydrazine nitrate, 8% to 15% of metal powder and 13% to 40% of a polymeric binder, said binder being a cured carboxyl-terminated linear polyester, said polyester having a molecular weight of 500 to 5,000 and being the condensation product of a saturated dicarboxylic acid and a saturated dihydric alcohol, said acid containing at least 24% by weight oxygen and said alcohol containing at least 15% by weight oxygen.

3. The method of making an explosive composition which comprises mixing from 50% to 80% by weight of hydrazine nitrate with 8% to 15% of metal powder, 10% to 30% of a carboxyl-terminated linear polyester having a molecular weight of 500 to 5,000 and 3% to 10% of a curing agent for said polyester, said curing agent being selected from the group consisting of polyepoxides and polyimines, casting the resulting mixture into a desired configuration and curing said mixture to cause the polyester and curing agent to react to form an elastomer.

4. A plastic explosive composition essentially composed of 50% to 80% by weight hydrazine nitrate and 10% to 30% by weight of a binder, said binder being a carboxyl-terminated linear polyester having a molecular weight of 500 to 5,000, said polyester being the condensation product of a saturated dicarboxylic acid and a saturated dihydric alcohol, said acid containing at least 24% by weight oxygen and said alcohol containing at least 15% by weight oxygen.

5. A plastic explosive composition comprising from

50% to 80% by weight of hydrazine nitrate, from 8% to 15% of aluminum powder and from 10% to 30% of a carboxyl-terminated linear polyester having a molecular weight of 500 to 5,000, said polyester being a condensation product of a saturated dicarboxylic acid and a saturated dihydric alcohol, said acid containing at least 24% by weight oxygen and said alcohol containing at least 15% by weight oxygen.

6. A castable curable explosive composition comprising 50% to 80% by weight of hydrazine nitrate, 8% to 15% of aluminum powder, 10% to 30% of a carboxyl-terminated linear polyester having a molecular weight of 500 to 5,000 and 3% to 10% of polyepoxide, said polyester being the condensation product of a dicarboxylic acid and a dihydric alcohol, said acid containing at least 24% by weight oxygen and said alcohol containing at least 15% by weight oxygen.

7. A castable curable explosive composition comprising 50% to 80% by weight of hydrazine nitrate, 8% to 15% of aluminum powder, 10% to 30% of a carboxyl-terminated linear polyester having a molecular weight of 500 to 5,000 and 3% to 10% of polyimine, said polyester being the condensation product of a dicarboxylic acid and a dihydric alcohol, said acid containing at least 24% by weight oxygen and said alcohol containing at least 15% by weight oxygen.

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