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EXPLOSIVE COMPOSITION CONTAINING LITHIUM PERCHLORATE AND A NITRATED AMINE

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ABSTRACT OF THE DISCLOSURE

An explosive composition comprising a dispersion of a solid explosive such as RDX or HMX in a substantially homogeneous mixture of a polymerizable acrylate, a plasticizer and lithium perchlorate.

The invention described herein was made in the course of, or under, a contract with the United States Atomic Energy Commission.

BACKGROUND OF THE INVENTION

This invention pertains to explosive compositions having solid particles dispersed in an organic resin matrix containing an alkali metal oxygen-halogen salt. More particularly it pertains to dispersions of hexahydro-1,3,5-trinitro-s-triazine (RDX) or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in plasticized polyacrylates containing lithium perchlorate.

Compositions of bonded explosives are well known in the art. Thus, stearic acid or other waxy material has been used with Tetryl; waxy compositions of pentaerythritol tetranitrate (PETN) or Cyclonite (RDX) have been press-loaded in shells; moldable compositions of PETN or RDX have been used to some extent for demolition purposes, but, generally, plastic explosives have been "far-from-perfect." (Kirk and Othmer, Encyclopedia of Chemical Technology, Interscience, N.Y., vol. 6, "Explosives," pp. 58–60.) Compositions of RDX or HMX in various organic bonding resins are known, e.g., in polyisobutylene (U.S. Pat. 3,117,044) or a butadiene-acrylonitrile copolymer (U.S. Pat. 3,269,880).

Propellant compositions of various perchlorates and organic bonding resins useful as propellants for rockets are known: perchlorates in polyacrylonitrile (U.S. Pat. 3,214,308); lithium perchlorate in polylactam (U.S. Pat. 3,107,185); lithium perchlorate in polyurethane (U.S. Pat. 3,117,898); and others. Such compositions are characterized by a controlled burning rate and stability to detonation rather than the property of high detonation velocity and almost instananeous energy release desired in a high explosive.

The compositions of the present invention are distinguishable from propellants in that the present compositions are useful as high explosives, i.e., for blasting, demolition, excavation, of military purposes.

SUMMARY OF THE INVENTION

An object of this invention is to provide a high energy moldable explosive composition having high cohesive and compressive strength. Another object is the provision of an explosive composition that is insensitive to normal handling shock. Still another object is the provision of a low viscosity explosive composition that is easily milled and molded, and can thereafter be converted to a plastic form that is flexible over a wide temperature range.

These and other objects hereinafter defined are met by the invention wherein there is provided (1) a composition comprising a dispersion of solid explosive particles in a substantially homogeneous mixture of (a) a polymerizable monomer selected from the group consisting of β-hydroxyethyl acrylate, β-cyanoethyl acrylate and glycidyl acrylate: (b) a plasticizer selected from the group consisting of ethylene glycol, diethylene glycol dimethyl ether, dimethylformamide, methyl-2-pyrrolidinone, and butyrolactone; and (e) lithium perchlorate; and (2) said composition cured. Curing is defined herein as exposing to such conditions of temperature and pressure, with or without a catalyst, for such a period of time, as are sufficient to bring about polymerization of the polymerizable monomer.

The present invention employs a substantially homogeneous mixture of lithium perchlorate, polymerizable monomer or the resin derived therefrom by curing, and a plasticizer, as a bonding agent for a high explosive. We have found that such a composition provides several advantages over prior art materials. First, the lithium perchlorate is present as an oxidant for the monomer or resin, and the plasticizer. In its preferred form, the lithium perchlorate is present in at least the stoichiometric amount calculated for the oxidation of the monomer, the plasticizer and combustibles other than the explosive to carbon monoxide and steam. This results in more efficient utilization of the explosive which is itself balanced as to oxygen content for oxidizable elements. In older plastic-bonded explosives of RDX containing no perchlorates there was a deficiency of oxidant and hence an inferior explosive action. It is well-known in the art (e.g., Cook, "The Science of High Explosives," Reinhold, N.Y., 1958, page 9) that "balanced dope" combinations of dynamite containing combustible fillers together with equivalent sodium nitrate to give oxygen-balanced mixtures are highly efficient. Prior to our invention, compositions of RDX or HMX in polyisobutylene or butadiene-acrylonitrile copolymers were relatively inefficient explosives because of their oxygen imbalance. We have overcome this problem by our use of lithium perchlorate in the resin systems disclosed herein.

These lithium perchlorate-plasticizer-resin systems exhibit energy coefficients generally equivalent to trinitrotoluene (TNT) as determined by a hydrodynamic test developed to measure relative metal-accelerating ability of explosives. The method has been published by J. W. Kury et al., "Metal Acceleration by Chemical Explosives," Proceedings of Fourth Symposium on Detonation, U.S. Naval Ordnance Laboratory, Oct. 12–15, 1965, Office of Naval Research, ACR–126 (Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., $5.00). By this test the energy coefficient for TNT is −0.5%. The energy coefficient is defined as the decrease in relative energy for 1 volume percent replacement of HMX by binder. Furthermore the detonation properties of the present lithium perchlorate-containing systems are generally within the expected calculated values using the method of M. J. Kamlet et al., "Chemistry of Detonations—(I) A Simple Method for Calculating Detonation Properties of C—H—N—O Explosives," The Journal of Chemical Physics, vol. 48, pages 23–35, 1968.

Second, the polymerizable monomer or combination of monomers is selected from a group of monomers which are excellent solvents for lithium perchlorate. In combination with the plasticizer, the monomer dissolves the lithium perchlorate, and the resin resulting therefrom on curing can hold it in solution without crystallization occurring even at low temperatures. It is well known that crystallized explosives are sensitive to shock presumably because of the effect of friction or pressure on the crystals. This undesired sensitivity of compositions containing crystalline perchlorates is herein avoided by using the homogeneous compositions containing the monomers we have disclosed.

Third, the problems previously encountered in making cohesive plastic explosives, such as the problem of milling a thick rubbery mass, are avoided by using a low-viscosity composition, easily compounded, yet moldable and curable to a flexible coherent mass, as we have disclosed. Another advantage of these compositions is that they are workable in the pre-cured condition with relatively high concentrations of explosive present, e.g., 75% by weight of the composition. The cured products have excellent tensile strength and retain their flexibility at temperatures as low as —40° C. Their high elongation is an indication that they are not brittle and do not crack easily. The products are smooth and flexible, free of voids, and capable of maintaining close dimensions on casting or molding.

Another advantage of the present compositions is that they employ monomers and plasticizers having low volatility and they may therefore be evacuated so as to degas while casting without loss of any components.

For certain applications in which plastic-bonded explosives of moderate or lesser efficiency are useful, the amount of lithium perchlorate used in the mixture may be reduced below the stoichiometric amount. Although lithium perchlorate is the preferred oxidant because of its solubility, other perchlorates and mixtures thereof may be employed, e.g., cesium, barium, calcium, magnesium, or strontium perchlorate, to the extent that they are soluble in the monomer or resin.

For the purposes of this invention we have found that the polymerizable monomer is preferably either β-hydroxyethyl acrylate, β-cyanoethyl acrylate or glycidyl acrylate or mixtures thereof; other acrylates of comparable volatility may be substituted in part, provided that the solubility of the oxidant is not reduced thereby and that the properties of the cured composition are not adversely affected. Various polymerizable acrylates may be used with the monomers specified above, e.g., ethylene glycol diacrylate, to cause crosslinking in the polymerized composition and thereby increase the modulus and the tensile strength of the composition.

The plasticizer is preferably either ethylene glycol, diethylene glycol dimethyl ether, dimethylformamide, methyl-2-pyrrolidinone or butyrolactone, used either separately or in mixtures; others which may be substituted in part include ethanolamine, triethanolamine, and diethylene glycol.

The proportion of monomer to plasticizer may be varied from 30:70 to 80:20 by weight to give a range of properties in the uncured and cured compositions. Generally the higher proportions of plasticizer give lower viscosity mixes. Too much plasticizer has an adverse effect upon tensile strength.

A catalyst is normally employed for curing the monomer, preferably benzoyl peroxide in an amount of from about 0.01 to about 1.0% by weight of the composition.

The composition may be cured at any temperature below the decomposition temperature of the mixture, usually below about 250° C. A preferred range is from about 60° C. to about 120° C. The time for curing is easily determined experimentally: for 0.05% benzoyl peroxide it is about 16 hours at 60° C. and about 1–2 hours at 120° C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention is further illustrated by, but not limited to, the following examples.

Example 1

This example illustrates the preparation of explosive compositions containing β-hydroxyethyl acrylate as the monomer.

A solution of lithium perchlorate in the monomer and plasticizer was first prepared in each instance by adding the prescribed amount of lithium perchlorate as shown in the table below to a mixture of β hydroxyethyl acrylate (the monomer) and ethylene glycol (the plasticizer), and mixing at room temperature until dissolved. The solution was then filtered to remove traces of solids by filtering through a 70–100μ porosity fritted-glass filter. One part by weight of this solution was used for every 3 parts by weight of HMX (octahydro-tetranitro tetrazocine or "octogen") and the mixture was well mixed, together with benzoyl peroxide in an amount corresponding to 0.05% by weight of the formulation, then cast and cured at 60° C. for 16 hours.

EXPLOSIVE COMPOSITIONS

	Components (parts by weight)			
	g-Hydroxyethyl acrylate	Ethylene glycol	Lithium perchlorate	HMX
Material:				
1-A	60	40	133	609
1-B	60	40	162	786
1-C	80	20	137	711
1-D	30	70	200	900

The products were smooth, well-bonded compositions, e.g., Material 1–A had a tensile strength of 48 lbs. per sq. in. and elongation at break of 50%.

When a formulation similar to 1–B but containing no HMX was prepared and cured, the resulting material showed no tendency to become opaque within 8 days at —20° C., showing that no crystallization of lithium perchlorate occurred.

Formulation 1–C was difficult to mix because of its high viscosity, but nevertheless could be mixed.

Example 2

This example illustrates the preparation of an explosive composition containing glycidyl acrylate.

To a mixture of 50 parts by weight of glycidyl acrylate and 50 parts by weight of ethylene glycol was added 150 parts by weight of lithium perchlorate, with mixing until practically all dissolved. Traces of solids were removed by filtering.

The solution is mixed with HMX in the proportions of one part by weight per three parts by weight of HMX. Benzoyl peroxide is added in an amount corresponding to 0.05% by weight of the formulation. The composition, when molded and cured at 60° C. for 16 hours, yields a well-bonded explosive product.

Example 3

This example illustrates the preparation of an explosive composition containing β-cyanoethyl acrylate.

To a mixture of 60 parts by weight of β-cyanoethyl acrylate and 40 parts by weight of ethylene glycol was added 150 parts by weight of lithium perchlorate.

After thorough mixing and filtering to remove traces of undissolved solids, the solution is mixed with HMX in the proportions of one part by weight per three parts by weight of HMX, together with 0.05% by weight of benzoyl peroxide. The mixture when molded and cured at 70° C. for 10 hours, yields a product of excellent properties.

What we claim is:

1. A composition comprising a dispersion of solid explosive particles selected from the group consisting of hexahydro - 1,3,5 - trinitro-s-triazine and octahydro-1,3,5,7 - tetranitro - 1,3,5,7 - tetrazocine in a substantially homogeneous mixture of

(a) a polymerizable monomer selected from the group consisting of β-hydroxyethyl acrylate, β-cyanoethyl acrylate and glycidyl acrylate;

(b) a plasticizer selected from the group consisting of ethylene glycol, diethylene glycol dimethyl ether, dimethylformamide, methyl-2-pyrrolidinone, and butyrolactone; and

(c) lithium perchlorate.

2. A cured composition of claim 1.

3. The composition of claim 1 wherein the lithium perchlorate is present in at least the stoichiometric amount calculated for the oxidation of the monomer and the plasticizer to carbon monoxide.

4. The composition of claim 1 wherein the plasticizer is ethylene glycol.

5. The composition of claim 1 wherein the monomer is β-hydroxyethyl acrylate and the plasticizer is ethylene glycol.

6. The composition of claim 1 wherein the monomer is β-cyanoethyl acrylate and the plasticizer is ethylene glycol.

7. The composition of claim 1 wherein the monomer is glycidyl acrylate and the plasticizer is ethylene glycol.

References Cited

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