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MULTIPHASE EXTRUDABLE EXPLOSIVES CONTAINING CYCLOTRIMETHYLENETRINITRAMINE OR CYCLOTETRAMETHYLENETETRANITRAMINE

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This invention was made in the course of, or under, performance of Contract No. W–7405–ENG–48 with the United States Atomic Energy Commission.

The present invention relates to high explosive compositions and more particularly to multiphase explosive compositions especially adapted for extrusion and fabrication as by polymerization in molds.

There has long existed a need for an explosive which is sufficiently fluid and pliable to allow transfer and shaping by extrusion methods at ambient temperatures. Solid explosives are obviously not extrudable at ambient temperatures. The known liquid explosives, while offering little resistance to being transferred through conduits as in molding systems, have either a lower explosive energy density than is required for many applications, or are unduly sensitive and dangerous, as for instance, nitroglycerin. On the other hand, explosives which contain a solid high explosive dispersed in an inert medium, fail to obtain the maximum energy densities obtainable since the addition of the inert non-explosive medium necessarily displaces some of the solid explosive and the diminution of high explosive per unit volume goes hand in hand with a loss of explosive energy density.

If solid shapes of explosives are required, they are conventionally formed from the more powerful explosives by machining or milling operations which are cumbersome as well as expensive and require special safety precautions.

In accordance with the invention, there is now provided a high energy density multiphase explosive composition which is especially adapted for transfer by fluid or plastic flow into molds for forming and fabrication at low, e.g., ambient temperatures and which can be cured thereafter to produce rigid dimensionally stable forms. More specifically, the composition includes selected proportions of certain solid high explosives as a solid phase dispersed in a fluidic vehicle phase, which itself possesses explosives characteristics as employed in the present formulations. Certain additives may be included to control stability and the like. Proportions are expressed in percent by weight herein unless otherwise specified.

A primary object of the present invention is to provide an explosive composition which may be fabricated by processes involving fluidic or plastic flow.

Another object of the present invention is to provide a multiphase explosive composition having a high explosive energy content.

A further object of the present invention is to provide a multiphase explosive composition which is relatively insensitive to shock.

Still another object of the present invention is to provide a multiphase explosive composition which is extrudable and chemically stable over a wide range of temperatures.

Yet another object of the present invention is to provide a multiphase high explosive composition which can be injected into a mold and polymerized at low pressures.

A still further object of the present invention is to provide an explosive composition which has a long shelf life.

Other objects and advantages will become apparent upon consideration of the following description.

The solid phase of the explosive formulation of the present invention of the class generally characterized as a cyclicnitramine, specifically including the solid explosive cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitramine, hereinafter referred to as HMX, and cyclo-1,3,5-trimethylene-2,4,6-trinitramine, hereinafter referred to as RDX. The fluid in which the solid phase is dispersed is a liquid vehicle comprising one or a combination of the liquid explosives of the gem-dinitro aliphatic class, such as methyl-4,4-dinitropentanoate, ethyl 4,4-dinitropentanoate, dinitropentano nitrile, 2,2-dinitropropyl acrylate, 1,2-bis (2,2-difluoro-2-nitroacetoxyethane) and bis (2,2-dinitro-2-fluoroethyl) formal, hereinafter referred to as MDNP, EDNP, DNPN, DNPA, BEAF, and FEFO, respectively.

Compositions which are readily extrudable with low pressures include up to 75% by weight of HMX or RDX and have a particle size of no less than about 2 microns with a preferred particle size of about 15–25 microns and a maximum particle size of about 30 microns. The practical range of HMX content lies between about 50 and 75% by weight. The composition may also include a stabilizer such as colloidal silica or poly-DNPA, added to increase the stability of the composition. An explosive composition of the above description is distinctly superior to known explosives with respect to a combination of properties including extrudability, energy density, and insensitivity to shock.

General preferred formulations of the multiphase explosive composition have an HMX content of about 65–75% by weight, and have an HMX particle size of about 20 microns. Variations in the HMX content and the particle size of the HMX greatly influence three important properties of the composition: extrudability, energy density, and stability, or shelf-like. Regulation of the HMX content and particle size adapts the composition to varying requirements. The energy density of the explosive formulation is directly proportional to the HMX content and is largely independent of the particle size. At HMX contents between 65 and 75% by weight, the energy density of the explosive is intermediate between that of the high explosives trinitrotoluene (TNT), and octol (75% HMX, 25% TNT).

Concerning the relation between the HMX content, particle size, and viscosity, it has been found that the fluid or plastic flow properties as related to the ease of extruding of the present explosives, decreases with increasing HMX content and also with decreasing particle size. With the HMX content increased beyond 75%, the HMX being present as particles of an average diameter of about 20 microns, the viscosity rapidly rises to excessive magnitudes as represented by a flow rate of about 1 cc. per sec. through a tube 1/16 in. in diameter and 3 inches long at a driving pressure of about 1000 p.s.i. Ordinarily, it is preferred that driving pressures of up to a few hundred p.s.i. maximum are required to produce transfer of the material to fill the mold in a few seconds at the most. The stability of the solid particle phase or the tendency of the solid phase to settle out from the multiphase explosive depends on the particle size and is inversely related to the average particle diameter. At one extreme, no phase separation or settling has been observed with HMX particles of an average diameter of about 2 microns. A dispersement of such small particles, however, severely restricts the flow rate due to the high surface area of the solid constituent. To alleviate this difficulty a coarser grade HMX is used together with a stabilizer such as colloidal silica or poly-dinitropropyl

acrylate. A particle size of 20 microns for the solid HMX along with 1 or 2% of colloidal silica renders an explosive composition of satisfactory phase stability and plastic flow rate. With an intermediate particle size, correlatively lesser amounts of the stabilizer are required to provide stable multiphase explosive formulations.

Whereas all of the fluid phase components mentioned above confer fluidic or plastic flow properties to obtaining the desired extrudability of the explosive composition, optimum properties including the energy content, sensitivity, and the additional property of injection moldability, i.e., introduction into a mold by a procedure involving fluid or plastic flow, depend on the particular choice of the components for the liquid phase.

Preferred major constituents of the fluid or liquid phase are EDNP, DNPN, and MDNP, used singularly or in combination with each other or with DNPA as liquid phase vehicles for the HMX, they provide explosive formulations which are characterized by safety from the point of view of insensitivity to mechanical shock and temperature variations. For example, drop heights for 50% explosion probability exceeded 177 cm. for such compositions if their HMX content is less than 75% by weight, with the remainder being such a liquid phase and up to about 2% per weight of a stabilizer.

The use of FEFO as the fluid for liquid phase offers a distinct advantage in that FEFO is more energetic than the other liquid explosives and hence provides an especially high contribution to the energy density of the explosive. On the other hand, formulations based on FEFO are somewhat more sensitive to shock. However, if FEFO is intermixed with one or more of the liquids, MDNP, EDNP, and DNPA, the sensitivity of the final formulation is appreciably diminished. BEAF is another higher energy density, but also more sensitive, liquid phase constituent. It is to be understood that in all of the above descriptions, RDX can be substituted for HMX without substantial modification.

The explosive compositions are prepared by premixing the ingredients thoroughly. Subsequently, they are milled and deaerated by conventional operations as practiced in the art.

In general, the multiphase or paste explosives of the above description find use in applications where it is desired to transfer the explosive rapidly from one place of long time storage and confinement to another, e.g., immediately prior to the time of detonation to be detonated while still in a fluidic or paste form. In other applications, it is desirable to provide the explosive in the form of a solid body as described more fully hereinafter. An especially advantageous feature of formulations having a liquid vehicle phase on the energetic monomer DNPA is that these compositions are especially adapted for injection into a mold and subsequent polymerization. The polymerized explosive is dense and uniform and explosive bodies made of the material are characterized by high mechanical strength in addition to their high explosive energy density, stability, and safety. Moreover, the advantageous flow properties of these explosive formulations allow their use in the formation of explosive bodies having complicated shapes of precise dimensions by a process of zone curing under pressure. To carry out this process, the mixture is first deaerated and then injected from a transfer cylinder, piston or extruder into a mold under pressure. The explosive is cured by heating to a tempearture corresponding to the conventional curing temperatures for acrylic resins and contact laminating resins, i.e., ambient temperatures up to about 70° C. To compensate for the shrinkage of the material during the solidification produced by curing, the mixture is cured zonewise beginning the curing process in those sections of the explosive body which are furtherest removed from the injection nozzle. The mixture is kept under continuous pressure until the curing is completed. In this manner, uncured material is continuously introduced into the volume vacated by the receding body of the curing or setting material and hence offsets the shrinkage effects, since no voids are allowed to develop.

Specifically, multiphase explosive compositions which are injection moldable and polymerizable under low pressure comprise the solid explosive HMX in proportions of about 65% by weight to 75% by weight and a liquid phase vehicle comprising one or more of the liquid explosives MDNP, EDNP, DNPN, BEAF and FEFO, and/or at least about 15% of DNPA. They may also include a dispersion agent, such as colloidal silica up to about 2% by weight and small amounts of cross linking agents, typically fractions of a percent, such as di- and triacrylates, i.e., acrylate esters containing two, three, or more unsaturated double bond linkages. Inasmuch as the cross linking agents are present in small quantities only, any equivalent nonenergetic or reagent producing this result may be substituted without impairing the energy density of the formulation appreciably. Finally, the composition may include small amounts of catalysts, generally of the free radical initiator type, e.g., organic peroxides such as benzoyl peroxide, methyl ethyl ketone peroxide, etc.

While such injection moldable, low pressure polymerizable formulations are generally subject to the same principles elaborated above with respect to extrudability, sensitivity and explosive energy density, phase stability demands are much less stringent. The settling rate of the solid explosive particles has to be only sufficiently slow to prevent separation during the comparatively short time between the mixing of the explosive and completion of the molding and polymerization process. Consequently, it is possible to increase the particle size of the HMX and hence also the HMX content to yield a maximum viscosity limit imposed by retention of adequate extrudability for carrying out the injection process.

If some of the DNPA is added in prepolymerized form rather than as the monomer, the shrinkage of the explosive body during the curing can be reduced. In this manner, it is possible to control the overall tolerances attainable and the ease with which the process can be carried out.

EXAMPLES

The procedure for mixing the ingredients of the following examples was in each case a preliminary mixing of the ingredients in a vertical planetary motion propeller type mixer. The premixed dispersion was then passed three times through a 3 roll paint mill. In each case the air was removed from the mixture by passing it through a ram-orifice deaerator after which the explosive was ready for use.

EXAMPLE I

Composition:

HMX, average particle size about 20 microns	percent	73
EDNP [1]	do	22.1
MDNP	do	3.9
Colloidal SiO_2	do	1

[1] Ethyl 4,4-dinitropentanoate-2-methyl-4,4-dinitropentonoate.

Properties:

Density	g./cc.	1.673
Detonation velocity	mm./m. sec.	7.84

EXAMPLE II

Composition:

HMX	percent	71.45
DNPN [1]	do	27.06
Colloidal SiO_2	do	1.49

[1] Dinitropentano nitrile.

Properties:

Density	g./cc.	1.70
Detonation velocity	mm./m. sec.	7.98

EXAMPLE III

Composition:

HMX	percent	67.67
BEAF [1]	do	30.92
Colloidal SiO_2	do	1.41

[1] 1,2-bis(2,2-difluoro-2-nitroacetoxyethane).

Properties:

Density	g./cc.	1.79
Detonation velocity	mm./m. sec.	8.15

EXAMPLE IV

Composition:

HMX	percent	67.54
FEFO [1]	do	31.05
Colloidal SiO_2	do	1.41

[1] Bis (2,2-dinitro-2-fluoro ethyl) formal.

Properties:

Density	g./cc.	1.79
Detonation velocity	mm./m. sec.	8.44

EXAMPLE V

Composition:

HMX	percent	70
DNPA [1]	do	20
EDNP [2]	do	7
Dimethacrylate	do	1
Benzoyl peroxide	do	1/10

[1] 2,2-dinitropropyl acrylate.
[2] Ethyl 4,4-dinitropentanoate.

After mixing, milling, and deaerating this composition as elaborated in the preamble of the examples, the mixture is injected under a pressure of 50–200 p.s.i. through an inch orifice into the mold of the desired shape of the final explosive body, e.g., a 1 m. long rod of diameter. While under continuous pressure, the mold is heated to 40–60° C. for about 40 minutes per zone, of a zone several cm. in length moved progressively along the mold beginning at the zone furthest removed from the injection nozzle. The entire process is completed in about 2 hours.

We claim:

1. A multiphase explosive composition of matter comprising a solid phase of powdered explosive material selected from the group consisting of cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitramine and cyclo-1,3,5-trimethylene-2,4,6-trinitramine and a liquid phase comprising at least one material selected from the group consisting of methyl-4,4-dinitropentanoate, 2,2-dinitropropyl acrylate, dinitropentano nitrile, ethyl-4,4-dinitropentanoate, and bis (2,2-dinitro-2-fluoroethyl) formal; said cyclo-1,3,5,7-tetramethylene - 2,4,6,8 - tetranitramine being dispersed throughout said liquid.

2. The composition of claim **1** wherein said powdered explosive has an average particle diameter of at least 2 microns.

3. The composition of claim **1** wherein said powdered explosive has an average particle diameter of about 20 microns.

4. The composition of claim **1** wherein there is included a stabilizing agent.

5 The composition of claim **4** wherein said stabilizing agent is selected from the group consisting of colloidal silica and poly-dinitropropyl acrylate.

6. A multiphase explosive composition comprising a solid phase selected from the group consisting of cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitramine and cyclo-1,3,5-trimethylene-2,4,6-trinitramine and a liquid phase comprising at least about 40% by weight bis(2,2-dinitro-2-fluoroethyl)formal and at least one liquid selected from the group consisting of methyl-4,4-dinitropentanoate, dinitropentanonitrile, and ethyl-4,4-dinitropentanoate.

7. A polymerizable multiphase explosive composition comprising a solid phase selected from the group consisting of cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitramine and cyclo - 1,3,5 - trimethylene - 2,4,6 - trinitramine and a liquid phase comprising 2,2-dinitropropyl acrylate.

8. The explosive composition of claim **7** further defined by including at least one explosive selected from the group comprising methyl-4,4-dinitropentanoate; dinitro pentanonitrile; ethyl-4,4-dinitropentanoate; bis(2,2-dinitro-2-fluoroethyl) formal, and 1,2-bis(2,2-difluoro-2-nitroacetoxy) ethane.

9. The composition according to claim **7** wherein the composition includes a dispersing agent.

10. The composition according to claim **7** wherein the composition includes prepolymerized 2,2-dinitropropyl acrylate.

11. The composition of claim **7** wherein the composition includes a crosslinking agent.

12. The composition of claim **10** wherein the crosslinking agents are selected from the group consisting of di- and tri-acrylates.

13. The composition of claim **7** wherein said solid phase is between 50 and 75% by weight.

14. The composition of claim **7** wherein said 2,2-dinitropropyl acrylate is at least 15% by weight.

No references cited

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