PLASTIC-BONDED EXPLOSIVE COMPOSITIONS AND THE PREPARATION THEREOF

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8 Claims

The invention herein described may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to new and improved plastic-bonded explosive compositions and the preparation thereof. In one of its more specific aspects it relates to a novel binder system for plastic-bonded explosives.

In the field of compressible explosives it has been found that most of the high temperature binders, including fluorinated binders, with such conventional curing agents as benzoyl peroxide and organic amines require high curing temperatures in order to achieve desired physical properties. Pressed densities were often low initially, were further lowered by curing conditions, or costly modifications were required to permit curing under pressure.

The general purpose of this invention is to provide a suitable binder for an insensitive, heat resistant, plastic-bonded, compressible explosive, which embraces all the advantages of similarly employed binder systems and possesses none of the aforesaid disadvantages.

An object of the present invention is the provision of a compressible explosive composition to be used in applications involving aerodynamic heating.

Another object is to provide a plastic bonded explosive which has the economic advantages of savings in time and equipment in preparation.

A further object of the invention is the provision of a binder system for explosives which reduces possible safety hazards at high temperatures.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same become better understood by reference to the following detailed description.

Broadly, this invention contemplates incorporating a new binder for plastic-bonded explosives comprising a fluorocarbon-silicone system which would, among other things, eliminate lengthy, high-temperature postcuring cycles previously considered necessary to obtain desired physical properties. The optimum "parent" explosive composition comprises about 95% diaminothiobenzene (hereinafter referred to as DTAB), about 4% of a copolymer of vinylidene fluoride and perfluoropropene (hereinafter referred to as Vilon) and 1% of a synthetic organic silicone resin (hereinafter referred to as Chemlok). This ratio of fluorocarbon to silicone gives the best physical properties consistent with good processability. Cyclotetramethylenehexanitramine (HMX) was substituted in place of diaminothiobenzene (DATB) with good all-around results.

In the following examples of plastic bonded explosive compositions made in accordance with the present invention, it will be understood that they are exemplary and are not to be construed as limited the invention.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1:</td>
<td></td>
</tr>
<tr>
<td>DATB</td>
<td>56</td>
</tr>
<tr>
<td>Vilon</td>
<td>4%</td>
</tr>
<tr>
<td>Chemlok</td>
<td>1%</td>
</tr>
</tbody>
</table>

The binder ingredients of the above examples may vary from about 2.5 to 4.5% by weight Vilon and from about 0.1 to 2.5% by weight Chemlok.

All the DTAB-Vilon-Chemlok formulations above set out were initially made in a Baker-Perkins mixer. The Chemlok, which is supplied in methanol solution, was first applied as a precoat to the DATB and the solvent was partially removed by evaporation. The Vilon, dissolved in either acetone or ethyl acetate, was then incorporated. After thoroughly mixing, the material was dried under vacuum at ambient temperature.

For greater safety in processing, particularly where large batches were to be made, it was considered desirable to devise a slurry procedure. Two were studied and both gave essentially the same type pressed product with the same characteristics as those resulting from the Baker-Perkins approach.

The processing methods used in preparing the plastic-bonded explosive compositions of this invention will now be described.

**EXAMPLE A**

Aqueous slurry method for preparing a DATB-Vilon-Chemlok composition

**Components:**

<table>
<thead>
<tr>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>DATB</td>
</tr>
<tr>
<td>Vilon</td>
</tr>
<tr>
<td>Chemlok</td>
</tr>
</tbody>
</table>

A plastic bonded explosive having the above composition (Example 1 above) was prepared using the following procedure:

91 grams of Vilon were dissolved in 1600 ml. of acetone forming a Vilon lacquer. 2157 grams of DATB were placed in a mixing kettle and the Vilon lacquer, prepared beforehand, along with 460 ml. of Chemlok in methanol solution (containing 23 grams Chemlok solids) were added initially and during mixing to maintain the consistency of a somewhat heavy paste. Mixing was continued for about 45 minutes at approximately 175 r.p.m.
3,728,170

until a smooth consistency resulted. 25 pounds of tap water were added under continued agitation, the mixing rate being reduced slightly and agitation continued for from 1 to 2 minutes. The water was then decanted and the resulting coagulant filtered, aspirated and oven dried at 80° C. Approximately 2267 grams of the DATB-Viton-Chemlok explosive resulted having the composition as hereinabove set forth.

It should be noted that the particle size of the final product may be affected by the rate of water addition.
The optimum rate must be determined for each piece of equipment and for each size batch.

EXAMPLE B

Aqueous slurry method for preparing HMX-DATB-Viton-Chemlok composition

Components:             Percent by weight
HMX........................................ 70
DATB................................. 25
Viton..................................... 4
Chemlok................................. 1

200 grams of the above composition (Example 5) were prepared by the same procedure as described in Example A. 140 grams of HMX and 50 grams of DATB were placed in a mixing kettle to which 8 grams of Viton dissolved in 70 ml. of ethyl acetate and 40 ml. of Chemlok (containing 2 grams of solids) were added, and thoroughly mixed until a pastelike consistency resulted. 1000 ml. of water were used to coagulate the product. The water was then decanted and the resulting coagulant was filtered, aspirated and oven dried at about 80° C.

EXAMPLE C

Aqueous slurry method for preparing HMX-Al-Viton-Chemlok composition

Components:             Percent by weight
HMX........................................ 75
Al........................................... 20
Viton..................................... 4
Chemlok................................. 1

100 grams of the above composition (Example 8) were prepared as follows: 4 grams of Viton were dissolved in 80 ml. of ethyl acetate forming a Viton lacquer. 75 grams of HMX were placed in a mixing kettle to which the Viton lacquer, prepared beforehand, was added and hand-mixed. 20 grams of aluminum and 20 ml. of Chemlok (containing 1 gram of solids) were added and processed under the same conditions as described in Example A.

EXAMPLE D

Non-aqueous slurry method for preparing DATB-Viton-Chemlok composition

Components:             Percent by weight
DATB................................. 95
Viton..................................... 4.2
Chemlok................................. 0.8

20 grams of a plastic-bonded explosive having the above composition were prepared as follows: 0.84 gram of Viton was dissolved in 15 ml of ethyl acetate. 19 grams of DATB were placed in the mixing kettle to which 80 ml of ethyl acetate were added and then hand-mixed. 15 ml of the Viton-ethyl acetate solution and 3.20 ml. of Chemlok was added in methanol (containing about .16 gram of solids) were now added and mixed until all lumps were broken down and the material appeared homogeneous. 150 ml of Stoddard Solvent were added during continued agitation. (Hexane may be used in lieu of Stoddard Solvent.) The mixture was stirred very slowly for 2-3 minutes, then the liquid decanted and the product or coagulant filtered, aspirated, and oven dried at 80° C.

EXAMPLE E

Baker-Perkins method for preparing DATB-Viton-Chemlok compositions

Components:             Percent by weight
DATB................................. 95
Viton..................................... 4
Chemlok................................. 1

200 grams of a plastic-bonded explosive having the above composition (Example 1) were prepared by the following procedure:

8 grams of Viton were dissolved in 160 ml of acetone by refluxing and stirring. 190 grams of DATB were weighed out and placed in a Baker-Perkins mixer. 40 ml of Chemlok (containing 2 grams of solids) and the Viton-acetone solution were added along with additional acetone as may be required to maintain a fluid paste. The ingredients were mixed well at 36-40 r.p.m. When all lumps were broken down and the mixture appeared smooth and homogenous, vacuum was applied with continued mixing to remove acetone. When most, but not all the solvent was removed, the damp material was transferred to trays and dried in an oven at 80° C.

In the studies which led to the present invention a number of different binder mixtures comprising Viton and Chemlok were evaluated, with respective ratios of Chemlok and Viton ranging from 50-50 down to 5-95. The higher Chemlok concentrations produced a strong but brittle pressed composition, which showed a tendency to crack upon exposure to thermal shock. Also under certain pressing conditions high pressed densities were more difficult to achieve when the Chemlok content exceeded 20% of the total binder. The optimum percentage of Chemlok in the binder appears to be about 0.8 to 1.0% of the total composition. This concentration was found to be most consistent with good compressibility, high initial strength, and retention of strength after exposure to heat. The Chemlok percentages are based on the commonly supplied methanol solution which runs about 5 percent solids by evaporation. This material tends to be basic in nature.

Table I below shows some properties of a typical optimum composition containing nominally 95 parts DATB, 4 parts Viton and 1 part Chemlok. One-half-inch diameter cylinders were pressed at 135° C., 20,000 p.s.i. and 5 minutes dwell, with die cooling before ejection. Ten samples were tested for compressive strength and modulus. Detonation velocity was determined in triplicate.

TABLE I

Properties of DATB-Viton-Chemlok compositions

Impact sensitivity: No fires at 300 cm.1
Autoignition point, ° C. 275-285, DATB melts.
Vacuum thermal stability, ml./g./.48 hr.: at 120° C. 0.2.
at 200° C. 3.0.
Detonation velocity, m./sec. 7295 at 98.3% TMD.
Plate dent, inches 0.09.
Compressive strength, p.s.i. 14,300.

2.2 lb. wt., type 12 tool, 35 mg., 1/8 in. D Pellets, Composition B std. 60% pt.m.30-30 cm.
19° C./min. temperature rise. Samples inserted in steel block. Recorded temperature is that of block at time transition occurs.
3. Measured for 3/4 in. D x 1/4 in. high pellets pressed at 185° C., 5 min. dwell, 20,000 p.s.i., and ejected at ambient temperature.

Table II following presents physical strength data at various temperatures for compositions containing varying amounts of synthetic organic silicone (Chemlok 607) in the binder. Ten samples were pressed, each at 135° C., 20,000 p.s.i., and 5 minute dwell with cold ejection. All samples were held at the test temperature for a minimum of two hours prior to testing.
Substitution of HMX for some of the DATB in DATB-fluorocarbon-silicone compositions appears to be a feasible means of increasing energy potential without necessitating too great a sacrifice in sensitivity.

Autoignition values for various DATB-HMX-Viton-Chemlok compositions are presented in Table III below.

Values for the pure explosive, i.e., without binders, and for a few binary compositions are also shown for comparison. The variation in reproducibility of these temperatures may range as high as ±5° C.; however, it is usually within 2–3° C.

Examination of the autoignition results shows the immediate effect of HMX substitution to be a lowering of the ignition point to a value slightly but significantly below that of HMX by itself. This effect is observable even when comparatively small percentages of HMX are present (10%). The reduction below 255° C., the autoignition point of HMX alone, is probably due to some interaction between the HMX and Chemlok and possibly to a lesser extent between DATB and HMX, since compositions in which these combinations occur seem to ignite consistently at a temperature lower than that for HMX alone. Another noteworthy observation is the rapidity with which the ignition of the HMX-DATB-Viton-Chemlok compositions occurs once the final exotherm is initiated. This phenomenon does not appear to be characteristic of the binary mixtures containing either one or the other explosive constituent plus Chemlok or Viton.

The physical properties of DATB-HMX-Viton-Chemlok compositions are illustrated in Table IV following:

It is noted that as the HMX content increases, mechanical strength falls off markedly. This observation has been confirmed in similar investigations on analogous aluminozinc systems. HMX-Viton compositions in general do not seem to yield as high compressive strength values as DATB-Viton or HMX-nylon. The inclusion of additional Chemlok in the binder as set out in this invention do doubt improves the properties of formulations high in HMX.

The DATB-Viton-Chemlok compositions, herein disclosed, after pressing are very resistant to attack by solvents such as ethyl acetate. This possibly indicates some kind of crosslinking action since DATB-Viton alone has no solvent resistance. When HMX is included in the DATB-Viton-Chemlok formulation, solvent resistance dropped somewhat. It was still superior, however, to the DATB-Viton without Chemlok.

The effect of 300° F. exposure on pellets pressed from the various compositions is shown in Table V below. Each entry represents an average of two determinations except the zero time results which were taken from Table IV. Again, the overall decrease in compressive strength with increase in HMX content may be noted. Furthermore, the samples which contained HMX appear to deteriorate to a somewhat greater extent in respect to compressive strength. Temperature effects on dimensions and density did not appear to vary much as HMX increased.

### Table II

<table>
<thead>
<tr>
<th>Percent Chemlok total composition</th>
<th>Test temp.</th>
<th>Compr. SD</th>
<th>density range</th>
<th>Compr. modulus</th>
<th>Ejection at ambient temp.</th>
<th>TMD</th>
<th>Density</th>
<th>Approx. Compressibility</th>
<th>Approx. Compressive strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>83</td>
<td>10,000</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.5</td>
<td>89</td>
<td>11,200</td>
<td>0.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>85</td>
<td>11,500</td>
<td>0.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>89</td>
<td>12,200</td>
<td>0.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note—All samples 3/4 in. D x 3/4 in. high, pressed at 100°–140° C., 20,000 p.s.i.猛然 dwell, ignition at ambient temperature. Density range 96.4–99.0% TMD. Molding powder prepared by Baker-Pekinus technique.

### Table III

<table>
<thead>
<tr>
<th>Composition</th>
<th>DATB-HMX-Viton-Chemlok</th>
<th>Density</th>
<th>TMD</th>
<th>Approx. Compressibility</th>
<th>Approx. Compressive strength</th>
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</thead>
<tbody>
<tr>
<td>0.3</td>
<td>209</td>
<td>10,000</td>
<td>0.77</td>
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<tr>
<td>0.5</td>
<td>211</td>
<td>11,500</td>
<td>0.74</td>
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</tr>
<tr>
<td>1.0</td>
<td>215</td>
<td>12,200</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>220</td>
<td>13,500</td>
<td>0.65</td>
<td></td>
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</tbody>
</table>

### Table IV

<table>
<thead>
<tr>
<th>HMX-DATB</th>
<th>Density</th>
<th>TMD</th>
<th>Approx. Compressibility</th>
<th>Approx. Compressive strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>79</td>
<td>10,000</td>
<td>97.0</td>
<td>10.0</td>
</tr>
<tr>
<td>0.5</td>
<td>82</td>
<td>11,500</td>
<td>98.5</td>
<td>12.0</td>
</tr>
<tr>
<td>1.0</td>
<td>90</td>
<td>12,500</td>
<td>99.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

### Table V

<table>
<thead>
<tr>
<th>HMX-DATB</th>
<th>Density</th>
<th>TMD</th>
<th>Approx. Compressibility</th>
<th>Approx. Compressive strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>79</td>
<td>10,000</td>
<td>97.0</td>
<td>10.0</td>
</tr>
<tr>
<td>0.5</td>
<td>82</td>
<td>11,500</td>
<td>98.5</td>
<td>12.0</td>
</tr>
<tr>
<td>1.0</td>
<td>90</td>
<td>12,500</td>
<td>99.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

### Table VI

<table>
<thead>
<tr>
<th>HMX-DATB</th>
<th>Density</th>
<th>TMD</th>
<th>Approx. Compressibility</th>
<th>Approx. Compressive strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>79</td>
<td>10,000</td>
<td>97.0</td>
<td>10.0</td>
</tr>
<tr>
<td>0.5</td>
<td>82</td>
<td>11,500</td>
<td>98.5</td>
<td>12.0</td>
</tr>
<tr>
<td>1.0</td>
<td>90</td>
<td>12,500</td>
<td>99.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>
nature at which DATB alone or with inert binders starts to melt and ignite under comparable test conditions.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A plastic-bonded explosive composition comprising a high explosive selected from the group consisting essentially of dianimotrinitrobenzene, cyclotetramethylene- nitramine, and mixtures thereof, the copolymer of vinylidene fluoride and perfluoropropene and a synthetic organic silicone resin.

2. A plastic-bonded explosive composition comprising dianimotrinitrobenzene, a copolymer of vinylidene fluoride and perfluoropropene and an organic silicone resin.

3. A plastic-bonded explosive composition comprising a mixture of cyclotetramethyleneetetranitramine and dianimotrinitrobenzene, a copolymer of vinylidene fluoride and perfluoropropene and an organic silicone resin.

4. A plastic-bonded explosive composition comprising cyclotetramethyleneetetranitramine, a copolymer of vinylidene fluoride and perfluoropropene and an organic silicone resin.

5. A plastic-bonded explosive composition comprising about 95% dianimotrinitrobenzene, about 4% copolymer of vinylidene fluoride and perfluoropropene and about 1% organic silicone resin.

6. A plastic-bonded explosive composition consisting essentially of about 95% by weight dianimotrinitrobenzene, from 2.5 to 4.5% by weight of the copolymer of vinylidene fluoride and perfluoropropene and from about 0.5 to 2.5% by weight organic silicone resin.

7. A process for the preparation of an improved plastic-bonded explosive comprising adding an acetone solution of a copolymer of vinylidene fluoride and perfluoropropene to a weighed amount of dianimotrinitrobenzene and mixing for about 30 minutes until a homogeneous mixture results then adding a methanol solution of synthetic organic silicone and mixing again until the mixture has the consistency of paste, continuing mixing while adding a volume of water equal to about 6 times the volume of mixture, decanting excess liquid and drying the resulting residue overnight at 80° C.

8. A process for the preparation of an improved plastic-bonded explosive comprising adding an ethyl acetate solution of the copolymer of vinylidene fluoride and perfluoropropene and a methanol solution of the synthetic organic silicone resin to a weighed amount of dianimotrinitrobenzene and hand-mixing until a homogeneous mixture results, then adding hexane during continued agitation, until a coagulant forms, decanting the hexane, filtering the coagulant and drying at 80° C.

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BENJAMIN R. PADGETT, Primary Examiner

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