FLEXIBLE EXPLOSIVE COMPRISING RDX, HMX OR PETN AND MIXED PLASTICIZER

John D. Hopper, Succasunna, and Franklin B. Wells, Wharton, N.J., assignors to the United States of America as represented by the Secretary of the Army
No Drawing. Filed Apr. 19, 1966, Ser. No. 545,790
14 Claims. (Cl. 149—18)

ABSTRACT OF THE DISCLOSURE

A flexible explosive of high power made essentially from a high explosive; a plasticizer which includes a liquid organic nitric acid ester, trimethylol methane triurate; and a high-octane nitrocellulose, and methods for making said flexible explosive.

The invention described herein may be manufactured and used by or for the Government for governmental purposes without payment to us of any royalty thereon.

This invention relates to an explosive composition and more particularly concerns a flexible, self-supporting, water-resistant explosive and methods of making therefor.

Our composition comprises a particulate explosive employing a plasticized binder wherein the plasticizer for the binder contains a liquid organic nitric acid ester; the composition being useful in explosive metal-forming processes and admirably suited for demolition purposes. The composition is characterized further by safety in handling and may readily be formed into any desired shape as by rolling, extrusion, compression-molding, etc. into strips, blocks, sheets, and the like.

It is therefore an object of this invention to provide an explosive having the aforementioned characteristics.

Another object of this invention is to provide a flexible explosive of high power (up to at least 25% greater than that of TNT) and high brisance (rate of detonation up to at least 75,000 m./sec.) based on a finely divided explosive such as PETN, or preferably cyclotrimethylene trinitramine (RDX) and/or cyclohexamethylene tetranitramine (HMX).

Still another object of this invention is to provide an explosive which, in the form of sheets one-quarter inch or more thick, possesses sufficient flexibility so that it may be made to conform to the contour of uneven surfaces with a minimum of manipulation, thus aiding in the complete destruction of the device to be demolished.

A further object of this invention is to provide a flexible explosive having high resistance to impact and friction while retaining good cap-sensitivity characteristics.

A still further object of this invention is to provide a flexible explosive which is more heat-stable than similar materials currently available.

Yet another object of this invention is to provide a flexible explosive which is not adversely affected by water.

A first object of this invention is to provide an explosive of sufficient resilience so that when made in block or other massive form it will resist breaking up upon impact with a hard surface when striking such a surface with a velocity of at least 150 feet/second.

Our further objects of this invention will become apparent as the invention is further described hereinafter.

We have found that the foregoing objects may be attained through provisions of an explosive composition comprising about 43-68% (preferably about 63%) of a particulate explosive such as PETN, RDX, HMX, or mixtures thereof, and having an average particle size of up to about 25 microns, preferably not over 13 microns. One hundred percent of the aforementioned particulate explosive must pass through a #200 U.S. Standard sieve, and at least 90% and preferably not less than 97.5% should pass through a #32S U.S. Standard sieve.

Our composition will also contain about 22.2-52.2%, preferably about 28.2%, of a plasticizer, one portion thereof being selected from the group consisting of tributyl acrylate (preferred), diocetyl sebacate, triethylene glycol di(2ethylbutyrate), or other similar materials, preferably those having pour points of —40° C. or below, and being present to the extent of 4.2-26.2% of the total flexible explosive composition, and the other portion thereof being the liquid nitric acid ester trimethylene triurate (TMETN) to the extent of 2-40% of the total explosive composition, about 4-10%, preferably about 5-8% of a high-octane nitrocellulose binder containing about 12.1-12.5% nitrogen, of such a degree of polymerization as to have a viscosity, using a 4% solution of nitrocellulose and a 5/16 inch diameter steel ball, of at least 90 seconds and preferably greater than 140 seconds, as described hereinbelow, and about 0.3-1.0%, preferably about 0.3-0.8%, of a pigment to impart any desired color to the finished product.

In the determination of the nitrocellulose viscosity aforementioned, the steel ball shall weigh about 2.025 to 2.045 grams, the viscosimeter shall consist of a glass tube 14 inches in length and an internal diameter of 1 inch, immersed to the level of its liquid contents in a constant temperature bath maintained at 25°±0.2° C., and the time of passage of the ball between markings shall be noted.

The aforementioned viscosity test is run in accordance with Specification MIL—N—244A, paragraphs 4.4.5 et seq., dated Feb. 13, 1962, with the exception that the quantities of materials used are: 8 grams nitrocellulose, 21.3 grams of ethyl alcohol, and 170.7 grams of acetone. The 21.3 gram/170.7 gram alcohol/acetone ratio is used to maintain the 5% ratio required in the specification.

For purposes of camouflage, an olive-drab coloration of the explosive is most desirable. Less than 0.2% pigment is insufficient to give a satisfactory coloration to the product where a color other than white is desired and the presence of more than 1% pigment is not necessary for effective coloring. The preferred pigment which imparts an olive-drab coloration to our explosive comprises one part lampblack and 8 parts lead chromate (chrome yellow, medium).

Liquid organic nitric acid esters other than TMETN which have been tried for possible use as plasticizers for nitrocellulose are glyc erine trinitrate, glycol dinitrate, ethylene glycol dinitrate, 1,2,4-butanetriol trinitrate, triethylene glycol dinitrate, 1,2,6-hexanetriol trinitrate, and the like. Each of these esters presents a major drawback for its intended use, such as poor thermal stability, excessively high sensitivity, low explosive power, weak brisance, or tendency to cause the well known nitroglycerine "headaches," and the like.

TMETN, upon contact with ordinary nitrocellulose, softens the outer layers thereof, but is incapable of colloidizing the nitrocellulose normally used in the manufacture of single and double-base propellants. The high-molecular-weight nitrocellulose required for use in the present invention is even less affected by TMETN. We have discovered methods of colloidizing the high-octane nitrocellulose in the presence of a high proportion of TMETN.

A series of tests has shown that the particulate explosive content of our explosive composition may be varied somewhat without appreciably altering the properties of the resultant composition, except the rate of detonation, provided that the nitrocellulose total plasticizer ratio remains substantially within a 1:2.9—6 range and the inert ester (such as tributyl acrylate) nitric
acid ester ratio remains substantially within the coincident range of 4.2:24 to 4.6:2. However, while a composition containing 43% RDX, 8% nitrocellulose, 8.2% tributyl acetylclitate, 40% TMETN, and 0.8% pigment had characteristics substantially identical with those of a composition containing 63% RDX, 8% nitrocellulose, 8.2% tributyl acetylclitate, 20% TMETN, and 0.5% pigment, attempts to increase the RDX content above about 68% resulted in products which were somewhat stiff or which became rather hard after standing overnight.

In another series of tests it was found that the presence of about 0.4% added diphenylamine (DPA), a crystalline solid, improved the thermal stability of the explosive composition.

The products and processes of our invention are further described and illustrated by the examples hereunder set forth.

EXAMPLE I

The following materials were thoroughly blended about 5 minutes in a sigma-blade mixer at 135°±5° F.:  

**Grams**  

| Dry Type B, Class E RDX | 315  
| Tributyl acetylclitate | 41  

1. Specification MIL-R-5083C dated Aug. 22, 1942. The RDX used in this and subsequent examples contained 7.8% RDX unless otherwise noted.

Fourty grams of nitrocellulose (96-second viscosity in 4% solution) was thoroughly wet with 40% ml. ethanol containing 2 grams DPA in solution. This alcohol-wet DPA-treated nitrocellulose and 4 grams of the aforedescribed lampblack-chrome yellow pigment were added to the RDX-tributyl acetylclitate mixture, the mixer closed, and the contents mixed about 30 minutes while maintaining the temperature in the mixer at 135°±5° F. During mixing, about 50 ml. alcohol was added to obtain a heavy dough-like consistency. After mixing, the mix was placed in a covered container and let age overnight. In the preparation of other identical mixes, it was found that the addition of about 50 ml. of a nitrocellulose solvent, such as ethyl acetate, to the mixture which is to be aged, prior to TMETN addition, shortens the aging period and aids in the subsequent incorporation of the TMETN into the mix. The aged mix was then returned to the mixer, which was held at 135°±5° F., 100 grams TMETN added, and the whole blended 30 minutes with the mixer open. The mix was then rolled on polished steel rolls held at 135°±5° F., first with a roll gap of 0.010 inch to assure evaporation of volatile, and then at a setting of about 0.230-0.240 inch to consolidate the material into a substantially 1/4 inch thick sheet which was smooth and uniform in appearance. During the preparation of additional identical mixes, it was found that the first rolling at a setting of 0.010 inch may be advantageously carried out at a temperature of 150°±5° F., that below 130° F. volatiles evaporation is undesirably slow, and that consolidation into sheets about 1/4 inch thick is most advantageously carried out at about 125°-130° F., although both higher and lower temperatures may be used. It was found, also, that the flexible explosive this prepared was well-suited for formation of desired shapes by extrusion. Perfect filaments as small as 1/8 inch in diameter were prepared by extrusion at about 135° F. Test values obtained with this material were:

- **Rate of detonation**  
  7186 m./sec.  

**EXAMPLE II**

The composition of this example varied from that of Example I only in that 6.2% of tributyl acetylclitate and 22% of TMETN, rather than 8.2% and 20% respectively, were used. Also, 140-second viscosity (in 4% solution) nitrocellulose was used, and 50 ml. ethyl acetate was added to the mix before aging prior to TMETN addition. This mix produced a sheet which was smooth and uniform in appearance. Test values obtained with this material were:

- **Rate of detonation**  
  7515 m./sec.  

**EXAMPLE III**

The composition of this example varied from that of Example I in that no DPA was present and 4.2% of tributyl acetylclitate and 24% of TMETN were used. This mix produced a sheet which was smooth and uniform in appearance but was somewhat stiffer than the sheets obtained from the mixes of the preceding examples.

Compositions containing 63% RDX but with decreasing amounts of substitution of TMETN for tributyl acetylclitate gave smooth uniform sheets which, as the TMETN content dropped toward 0%, showed a substantially uniform density decrease to a value of about 1.470, a rate of detonation decrease to about 7000 m./sec, and a decrease in ballistic mortar test value to about 1.0. Compositions containing small amounts of TMETN could be worked up into smooth uniform sheets without aging or addition of ethyl acetate or other nitrocellulose solvent.

**EXAMPLE IV**

The composition of this example varied from that of Example I only in that 20.2% of tributyl acetylclitate and 6.0% TMETN were used. This mix produced a sheet having a smooth uniform appearance.

**EXAMPLE V**

The composition of this example varied from that of Example I only in that 26.2% tributyl acetylclitate and
3,400,025

2% TMETN were used. This mix produced a sheet having a smooth uniform appearance.

\[ d_{20} \quad \text{Rate of detonation (m/sec)} \quad 1.47 \quad 7008 \]

**EXAMPLE VI**

This composition was prepared by the procedure outlined in Example I, but the RDX content was reduced from 63% to 43%, and the TMETN content was increased from 20% to 40%. The product obtained was substantially identical with that obtained in Example I except that its rate of detonation was lowered slightly, as expected, due to the partial substitution of an explosive (TMETN) having a rate of detonation of about 7000 m./sec. for another (RDX) having a rate of detonation of about 8200 m./sec. The density of this composition was 1.5114 g./cc.

**EXAMPLE VII**

The explosive of this example was identical in composition to Example I. This material was extruded in one-quarter-inch thick strips having an average density of 1.6140 g./cc. It was also extruded in 2-inch x 4-inch bars whose average density was 1.6081 g./cc. Another identical mix was extruded in one-quarter-inch thick strips which had an average density of 1.6197 g./cc; one-quarter-inch thick sheets obtained by rolling had an average density of 1.5450 g./cc.

**EXAMPLE VIII**

The composition of this example varied from that of Example VII only in that 112-second viscosity (in 4% solution) nitrocellulose was used in HMX and substituted for RDX. This material was rolled to give a smooth, uniform, one-quarter-inch thick sheet. Test values obtained with this material were:

\[ d_{20} \quad \text{Vacuum stability (5 g./40 hrs./100° C.) . mL gas} \quad 1.6036 \quad 126 \]

Picatinny Arsenal Impact Sensitivity

Test 11

Picatinny Arsenal Explosion Temperature

Test, smoke 262

Rate of detonation m./sec 7549

Cap sensitivity cap No. 3 M6

In accordance with Specification MIL-C-45548A (MU) dated May 15, 1964.

**EXAMPLE IX**

The composition of this example varied from that of Example VIII only in that the particulate high explosive used consisted of a mixture containing equal proportions of RDX and HMX so that there was 31.5% of each in the finished flexible explosive, which was rolled into a smooth uniform one-quarter-inch thick sheet. Test results obtained with this material were:

\[ d_{20} \quad \text{Vacuum stability (5 g./40 hrs./100° C.) . mL gas} \quad 1.5697 \quad 123 \]

Picatinny Arsenal Impact Sensitivity

Test 13

Picatinny Arsenal Explosion Temperature

Test, smoke 246

Rate of detonation m./sec 7407

Cap sensitivity cap No. 8

**EXAMPLE X**

The composition of this example varied from that of Example VII only in that the particulate high explosive used consisted entirely of fine PETN. This composition was rolled into a smooth, uniform, one-quarter-inch thick sheet. Test values obtained with this material were:

\[ d_{20} \quad \text{Vacuum stability (5 g./40 hrs./100° C.) . mL gas} \quad 1.4863 \quad 1.55 \]

Picatinny Arsenal Impact Sensitivity

Test 9

Picatinny Arsenal Explosion Temperature

Test, flame inches 235

Rate of detonation m./sec 7274

Cap sensitivity cap No. 5

While the present invention has been described in detail, it will be apparent to those skilled in the art that there are many variations possible without departing from the scope of this invention, which is limited only by the appended claims.

We claim:

1. A self-supporting, resilient, high-powered, brisant, flexible explosive composition of good cap-sensitivity, low impact-sensitivity, good heat stability and water resistance including a particulate explosive selected from the group consisting of cyclotrimethylenetrinitramine (RDX), cyclohexylmethylene-trinitramine (HMX), and pentaerythritol tetranitrate (PETN), said flexible explosive composition comprising; about 43–68 weight percent of at least one member selected from the group consisting of RDX, HMX, and PETN, about 23.2–48.2 weight percent of a mixed plasticizer including a first portion and a second portion, said second portion being a liquid organic nitric acid ester trimethylolethane trinitrate, said second portion of said plasticizer comprising about 2–40 percent weight percent of total flexible explosive composition, and about 4–10 weight percent of a high viscosity nitrocellulose.

2. The composition of claim 1 further characterized by said particulate explosive having an average particle size of up to about 25 microns.

3. The composition of claim 1 wherein said first portion of the mixed plasticizer is selected from the group consisting of tributyl acetylcitrinate, dioctyl sebacate, and triethylene glycol di (2-ethylbutyrate), said first portion of the plasticizer having a pour point not exceeding about 40° C. and comprising about 4.2–26.2% of the total flexible explosive composition.

4. The composition of claim 1 wherein 100.4 parts thereof contain 9.4 part of a diphenylamine stabilizer.

5. The composition of claim 1 including about 0.2 to 1.0 weight percent of a pigment consisting essentially of one part lampblack and 8 parts chrome yellow medium.

6. The composition of claim 1 wherein said high viscosity nitrocellulose contains preferably about 12.1 to 12.5 weight percent nitrogen.

7. A method for the preparation of a flexible, high-powered explosive composition of good cap-sensitivity, low impact-sensitivity, good heat stability and water resistance comprising the steps of blending about 63 parts by weight of a particulate high explosive selected from the group consisting of RDX, HMX, PETN, and mixtures thereof and about 8.2 parts by weight of tributyl acetyl-citrinate in a mixer at elevated temperatures to form a first mixture, wetting about 8 parts by weight of a high viscosity nitrocellulose with about 8 parts by volume of ethanol containing 0.4 part by weight of diphenylamine stabilizer in solution to form a second mixture, thoroughly mixing said first mixture and said second mixture at elevated temperatures while adding therein to about 10 parts by volume of ethanol to form a resultant mixture, removing said resultant mixture from said mixer, aging said resultant mixture, blending said resultant mixture with 20 parts by weight of trimethylolethane trinitrate at elevated tempera-
7. Mixture to form a final mixture and forming said final mixture into a desired shape.
8. A method according to claim 7 wherein said forming step comprises extruding.
9. The method of claim 7 further characterized by mixing about 0.8 part by weight of pigment comprising about one part lampblack and about 8 parts lead chromate to said second mixture.
10. The method of claim 7 further characterized by said first mixture containing about 4.2–26.2 parts by weight of tributyl acetylceitanate and said resultant mixture is blended with about 2–40 parts by weight of trimethylolmethane trinitrate such that the total amount of tributyl acetylctitate and trimethylolmethane trinitrate totals about 23–48.2 parts by weight.
11. The method of claim 10 further characterized by mixing about 0.8 part by weight of pigment comprising about one part lampblack and about 8 parts lead chromate to said first and said second mixture.
12. A method according to claim 7 wherein said explosive comprises RDX, about 10 parts by volume ethyl acetate is incorporated into said resultant mixture, and said forming step comprises rolling.

13. The method of claim 11 further characterized by said first mixture containing about 4.2–26.2 parts by weight of tributyl acetylctitate and said resultant mixture is blended with about 2–24 parts by weight of trimethylolmethane trinitrate such that the total amount of tributyl acetylctitate and trimethylolmethane trinitrate totals about 28.2 parts by weight.
14. A method according to claim 7 wherein said elevated temperature is about 135° F. and said high viscosity nitrocellulose contains about 12.1 to 12.5 weight percent nitrogen.

References Cited

UNITED STATES PATENTS

2,768,072 10/1956 Stark ------------ 149—92 X
2,852,359 9/1958 Achilles ------------ 149—93 X
2,916,996 12/1959 Coffee ------------ 149—93 X

LELAND A. SEBASTIAN, Primary Examiner.
CARL D. QUARFORTH, Examiner.