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3,268,376

ROCKET PROPELLANTS CONTAINING POLYETHYLENEHYDRAZINE AND BORON COMPOUNDS

Robert George Haldeman, South Norwalk, and Robert Charles Bell, Norwalk, Conn., assignors to American Cyanamid Company, New York, N.Y., a corporation of Maine

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This invention relates to rocket propellants, and more particularly, to solid compositions suitable for use as a rocket propellant and to a process for preparing a propellant grain from such compositions.

For the propulsion of rockets, the many propellant systems known may be classified broadly into two classes, viz., liquid propellants and solid propellants. The present invention relates to a new and improved solid propellant and to a method of making grains thereof.

In general, the known solid propellants comprise an intimate mixture of fuel and oxidizer, with or without additional additives for special purposes, in the form of one or more solid grains. Such solid fuel-oxidizer propellants release energy by the formation of oxides of carbon, hydrogen, and such other atoms as may be present and capable of oxidation. Typically, these materials have flame temperatures ranging from about 2800° F. to about 5000° F. and require elevated pressures in order to ignite the propellant grain and sustain propellant burning.

The composition of the present invention is a solid propellant which releases energy by the formation of boron nitride rather than by a oxidation of carbon and hydrogen. This composition provides a high performance solid propellant that burns with a relatively low flame temperature and which can be ignited and burned under a relatively low pressure as compared with the usual fuel-oxidizer solid propellant which relies on the oxidation of carbon and hydrogen for release of energy.

The relatively low flame temperature and the relatively low pressures involved in the burning of the propellant composition of this invention permit reductions in motor case and motor case lining weight; a feature the importance of which is obvious for rocket applications. Additionally, the fact that the propellant of this invention can even be ignited and burned under pressures less than atmospheric further simplifies the problem of igniting such propellant, particularly for use in the upper stages of multi-stage motors which are ignited in the near vacuum at extreme altitudes.

In accordance with this invention, the foregoing advantages, and other advantages as well appear hereinafter as the specification proceeds, are attained with the novel propellant composition which namely comprises the product of mixing polyethylene-hydrazine with a compound selected from the group consisting of dihydrazinium perhydrodecaborate mono-dihydrazinate, dihydrazinium perhydrodecaborate dihydrazinate, and triaminoguanidinium nonaborohydride-14.

In contrast to the preparation of the usual fuel-oxidizer solid propellants previously known (which process generally involves kneading or working a solid crystalline oxidizer material into a plastic mass of binder fuel with the concomitant difficulties in obtaining uniform mixing and good temperature control), the compositions of the present invention may be prepared by mixing together the ingredients, heating (either during or after mixing) sufficiently to melt the mixture, molding the thus produced molten material to the desired grain shape, and cooling the material to harden it. Should greater uniformity of composition be desired, the thus produced grain may be comminuted while in a solid state to produce particles

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which may be mixed together, remelted, remolded into a desired grain shape, and resolidified.

Because the mixture obtained in the process of manufacturing the propellant composition of this invention is a liquid at elevated temperatures appreciably below the auto-ignition temperature of such mixture, the problems of obtaining uniformity in mixing of the ingredients and good temperature control throughout the mass of the mix during the mixing process are minimized. More particularly, the propellant compositions of this invention start to flow at temperatures of about 65 to 75° C., which temperatures are appreciably below the auto-ignition temperatures of these compositions. Thus, the heating of these compositions to produce the melt for molding may be performed without danger of auto-ignition by the use of hot water under atmospheric pressure.

The melt may be molded by any conventional molding technique, such as, by casting into a hollow mold, by extruding through a suitable orifice, or by injecting under pressure into a hollow mold.

While the foregoing concise description of the invention should be sufficiently clear and exact as to enable any person skilled in the art to practice this invention, further description of specific illustrative examples will be given to illustrate preferred modes contemplated for the carrying out of this invention.

It is expressly understood that the following illustrative examples merely illustrate preferred modes of carrying out the invention and are not to be construed as limiting the invention except insofar as limitations appear in the subjoined claims.

EXAMPLE 1

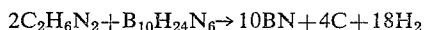
To a mixing device of the jacketed, sigma-blade type was charged 13.9 grams of solid granulated polyethylenehydrazine. Water at a temperature between 70° C. and 100° C. was circulated through the mixer jacket and the polyethylenehydrazine was masticated until it had been converted into a tough plastic mass. Then, 26.1 grams of dihydrazinium perhydrodecaborate monohydrazinate were charged in three equal proportions and mixing was continued until the mixture of polyethylenehydrazine and dihydrazinium perhydrodecaborate monohydrazinate was converted into a homogeneous viscous fluid. The temperature of the water in the jacket was kept between 70° and 100° C. during this mixing. The viscous liquid thus produced was then poured from the mixer into whatever mold was desired, such as a rocket-motor case equipped with casting fixtures to give the desired grain configuration. The propellant was allowed to cool whereupon it hardened to a somewhat tough rubbery solid.

Polyethylenehydrazine may be prepared by the method disclosed in an article by R. F. Evans and J. I. Jones entitled "Polymeric Derivatives of Hydrazine," on page 915 in the July 19, 1958, issue of Chemistry and Industry, a publication of The Society of Chemical Industry, London.

Dihydrazinium perhydrodecaborate monohydrazinate may be prepared by the method disclosed in pages 73 and 74 of the Thiokol Chemical Corporation, Reaction Motors Division report RMD 210-Q6 entitled, "High Performance Solid Rocket Propellants," September 1 to November 30, 1959.

The propellant made by the foregoing process had a flow point of 65 to 68° C. and an auto-ignition temperature of 193 to 194° C. It will thus be seen that there is a wide range of temperatures below the auto-ignition temperature which can be used for processing this material above the flow point. A grain of this propellant was found to have a 0% impact sensitivity of 28 kg.-cm. (zero positives in 10 tests) and an electrostatic discharge sensitivity of 2.53 joules at 5,000 volts.

The burning of the product of the foregoing process which mixed about 2 moles of polyethylenhydrazine with 1 mole of dihydrazinium perhydrodecaborate monohydrazinate may be illustrated by the following equation:



While the foregoing equation and process illustrates production of a rocket propellant which was balanced with respect to boron and nitrogen to produce boron nitride, proportions other than these stoichiometric portions may be used to still produce useful products.

EXAMPLE 2

The product of Example 1 was further cooled, as with solid carbon dioxide, to further harden it. This cooled grain was then comminuted to reduce it to a powder or mass of small granules which were then mechanically mixed together with each other. These mixed particles were then remelted and molded into a desired grain shape which was then cooled.

The propellant grain further treated by the process of this example had a further improvement in homogeneity over the grain of Example 1 and had a flow point of 70° C. and an auto-ignition temperature of 192° C. This grain had a 0% impact sensitivity of 40 kg.-cm. and an electrostatic discharge sensitivity of 0.028 joule at 5,000 volts. This grain, which had a bulk density of less than 1.03 gm./cc., had a vacuum stability of 15.3 ml. non-condensable gas per gram at 100° C. for a 40-hour period.

EXAMPLE 3

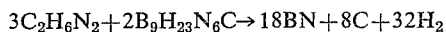
13.9 grams of solid granulated polyethylenhydrazine and 26.1 grams of dihydrazinium perhydrodecaborate monohydrazinate were mixed together as solid particles. After these ingredients were adequately mixed they were placed in a suitable leakproof container and heated to a temperature between 70° C. and 100° C. to obtain melting and fusion of the mixture. The fused mixture was then hardened by cooling while still in the leak-proof container which served as a mold. It was found that this grain had the same properties as the grain produced in Example 1 wherein the mixing of the ingredients was conducted concurrently with the heating. On burning in a strand burner, it was found that this propellant had a burning rate of 1.33 inches per second at 1,000 lbs. pressure at 70° F. and a pressure exponent (n) of 0.64.

EXAMPLE 4

By the process of Example 1, 13.1 grams of polyethylenhydrazine were mixed with 36.9 grams of triaminoguanidinium nonaborohydride-14 to produce a melt which was cast as a propellant grain. This propellant had a flow point of less than 75° C. and an auto-ignition temperature of 104 to 106° C. This grain was found to have a 0% impact sensitivity of 18 kg.-cm. and an electrostatic discharge sensitivity of 0.0072 joule at 5,000 volts.

Triaminoguanidinium nonaborohydride-14 may be prepared by the method disclosed and claimed in copending application Serial No. 219,367, filed August 22, 1962, by Benjamin, Stafiej, and Takacs and assigned to the assignee of the present invention, and more particularly as described in Example 3 thereof.

The burning of the product of the foregoing process which mixed about 3 moles of polyethylenhydrazine with 2 moles of triaminoguanidinium nonaborohydride-14 may be illustrated by the following equation:



While the foregoing equation and process illustrates production of a rocket propellant which was substantially balanced with respect to boron and nitrogen to produce boron nitride, proportions of other than these stoichiometric proportions may be used to still produce useful products.

EXAMPLE 5

By a process similar to that of Example 1, 13.0 grams of polyethylenhydrazine were admixed with 37.0 grams of bis-triaminoguanidinium perhydrodecaborate.

Bis-triaminoguanidinium perhydrodecaborate may be prepared by the method disclosed in pages 13 to 20 of the American Cyanamid Company progress report #3 entitled "Integrated Research and Development on Solid Rocket Propellants," January 1 to March 31, 1960.

The product of this mixture did not have a clear flow point but swelled at about 136° C. Thus, this product was difficult to make and could not be easily processed without operating at elevated temperatures tending to approach the auto-ignition temperature of 185–188° C. for this material. It is thus seen that there is a significant difference, between triaminoguanidinium nonaborohydride-14 and bis-triaminoguanidinium perhydrodecaborate with respect to the nature of its interaction with polyethylenhydrazine in the present process for preparing a rocket propellant grain.

EXAMPLE 6

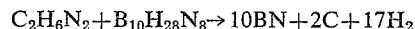
By a process similar to that of Example 1, 34.0 parts of polyethylenhydrazine, 30.5 parts of triaminoguanidine, and 35.6 parts of decaborane were mixed together. This produced a product which could not be melted since it had an auto-ignition temperature of 81–83° C. and, as such, would be too dangerous to try to prepare for use as a rocket propellant.

EXAMPLE 7

By the same process as described in Example 1, 9.4 grams of polyethylenhydrazine and 40.6 grams of dihydrazinium perhydrodecaborate dihydrazinate were mixed to produce a propellant grain having a flow point of less than 80° C. and a bulk density of less than 1.03 gm./cc.

Dihydrazinium prehydrodecaborate dihydrazinate may be prepared by the method disclosed in pages 7 to 9 of the Rohm and Haas report R-59-12 entitled, "Quarterly Progress Report on Synthetic Chemistry, Part I, Metal-Organic Chemistry," January 1 to June 30, 1959.

The burning of the product of the foregoing process which mixed about 1 mole of polyethylenhydrazine with 1 mole of dihydrazinium perhydrodecaborate dihydrazinate may be illustrated by the following equation:



While the foregoing equation and process illustrates production of a rocket propellant which was balanced with respect to boron and nitrogen to produce boron nitride, proportions other than these stoichiometric proportions may be used to still produce useful products.

EXAMPLE 8

It is also possible to utilize other additives to the mixture for the purpose of improving specific properties. For example, utilizing the process of Example 2, 33.87 parts of polyethylenhydrazine, 64.87 parts of dihydrazinium perhydrodecaborate monohydrazinate, and 1.25 parts of toluene diisocyanate were mixed to produce a propellant grain having tensile properties somewhat improved as compared with the product of Example 1. The propellant produced by this example had an auto-ignition temperature of 188° C., a 0% impact sensitivity of 18 kg.-cm. and an electrostatic discharge sensitivity of 0.028 joule at 5,000 volts. This product had a vacuum stability of 22 ml. non-condensable gas per gram at 100° C. for a 40-hour period and had a burning rate of 2.0 inches per second at 1,000 lbs. pressure at 70° F.

It is thus seen that there has been provided herein new and useful rocket propellant compositions and a novel process for preparing rocket propellant grains utilizing such compositions.

What is claimed is:

1. A rocket propellant comprising the product of mixing polyethylenhydrazine with a compound selected from the group consisting of dihydrazinium perhydrodecaborate monohydrazinate, dihydrazinium perhydrodecaborate dihydrazinate, and triaminoguanidinium nonaborohydride-14.

2. A rocket propellant comprising the product of mixing polyethylenhydrazine with dihydrazinium perhydrodecaborate monohydrazinate.

3. A rocket propellant comprising the product of mixing polyethylenhydrazine with dihydrazinium perhydrodecaborate dihydrazinate.

4. A rocket propellant comprising the product of mixing polyethylenhydrazine with triaminoguanidinium nonaborohydride-14.

5. A process for preparing a rocket propellant grain comprising mixing together polyethylenhydrazine with a compound selected from the group consisting of dihydrazinium perhydrodecaborate monohydrazinate, dihydrazinium perhydrodecaborate dihydrazinate, and triaminoguanidinium nonaborohydride-14; heating sufficiently to melt said mixture; molding the thus produced molten material to the desired grain shape; and cooling said material to harden it.

6. A process for preparing a rocket propellant grain comprising mixing together polyethylenhydrazine with dihydrazinium perhydrodecaborate monohydrazinate; heating sufficiently to melt said mixture; molding the thus produced molten material to the desired grain shape; and cooling said material to harden it.

7. A process for preparing a rocket propellant grain comprising mixing together polyethylenhydrazine with dihydrazinium perhydrodecaborate dihydrazinate; heating sufficiently to melt said mixture; molding the thus produced molten material to the desired grain shape; and cooling said material to harden it.

8. A process for preparing a rocket propellant grain comprising mixing together polyethylenhydrazine with triaminoguanidinium nonaborohydride-14; heating suffi-

ciently to melt said mixture; molding the thus produced molten material to the desired grain shape; and cooling said material to harden it.

9. A process as defined in claim 5 wherein said molding is done by casting into a hollow mold.

10. A process as defined in claim 5 wherein said molding is done by extruding through a suitable orifice.

11. A process as defined in claim 5 wherein said molding is done by injecting under pressure into a hollow mold.

12. A process as defined in claim 5 wherein said heating is to a temperature above 65° C. but below the auto-ignition temperature of the materials present.

13. A process as defined in claim 5 wherein said heating step is performed simultaneously with said mixing step.

14. A process as defined in claim 5 wherein said heating step is performed subsequent to said mixing step.

15. A process for preparing a rocket propellant grain comprising mixing together polyethylenhydrazine with a compound selected from the group consisting of dihydrazinium perhydrodecaborate monohydrazinate, dihydrazinium perhydrodecaborate dihydrazinate, and triaminoguanidinium nonaborohydride-14; heating sufficiently to melt said mixture; cooling said melt sufficiently to harden it to a solid mass; comminuting said solid mass; mixing the resultant particles together; remelting the resulting mixture; molding the thus produced molten material to the desired grain shape; and cooling said material to harden it.

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BENJAMIN R. PADGETT, *Acting Primary Examiner.*

CARL D. QUARFORTH, *Examiner.*

L. A. SEBASTIAN, *Assistant Examiner.*