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HIGH DENSITY SOLID PROPELLANTS AND METHOD OF PREPARATION USING FLUORO-POLYMERS

Filed April 17, 1964 2 Sheets-Sheet 1

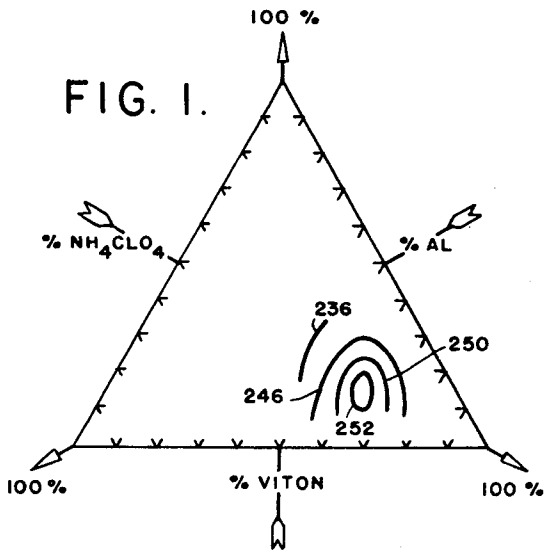


FIG. 1.

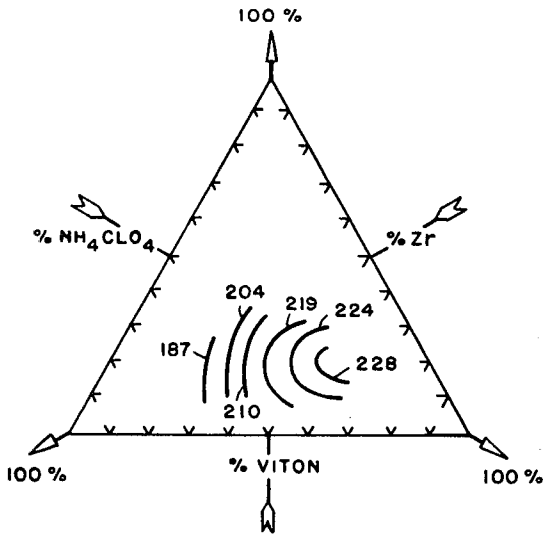


FIG. 2.

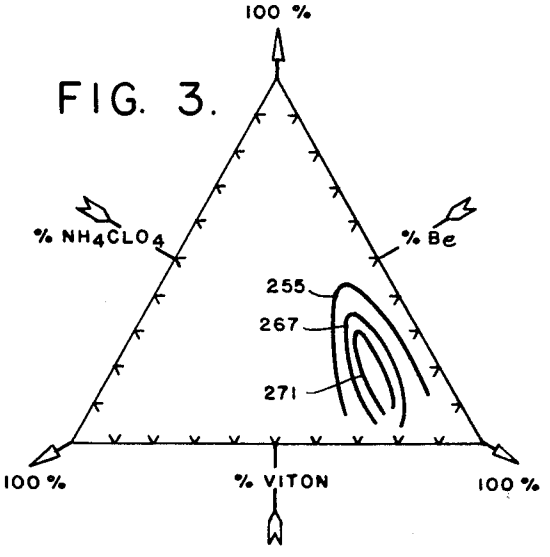


FIG. 3.

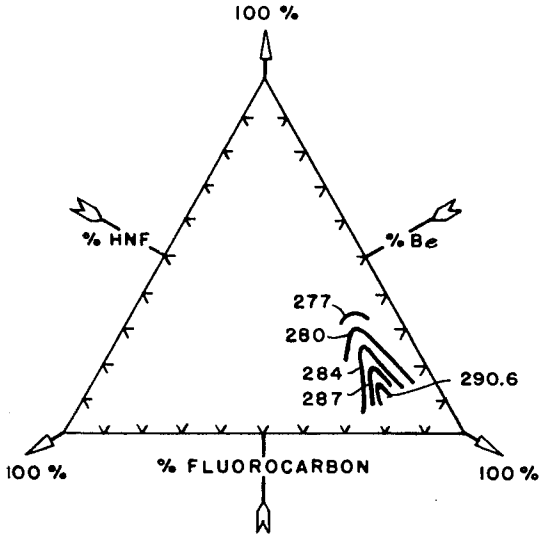


FIG. 4.

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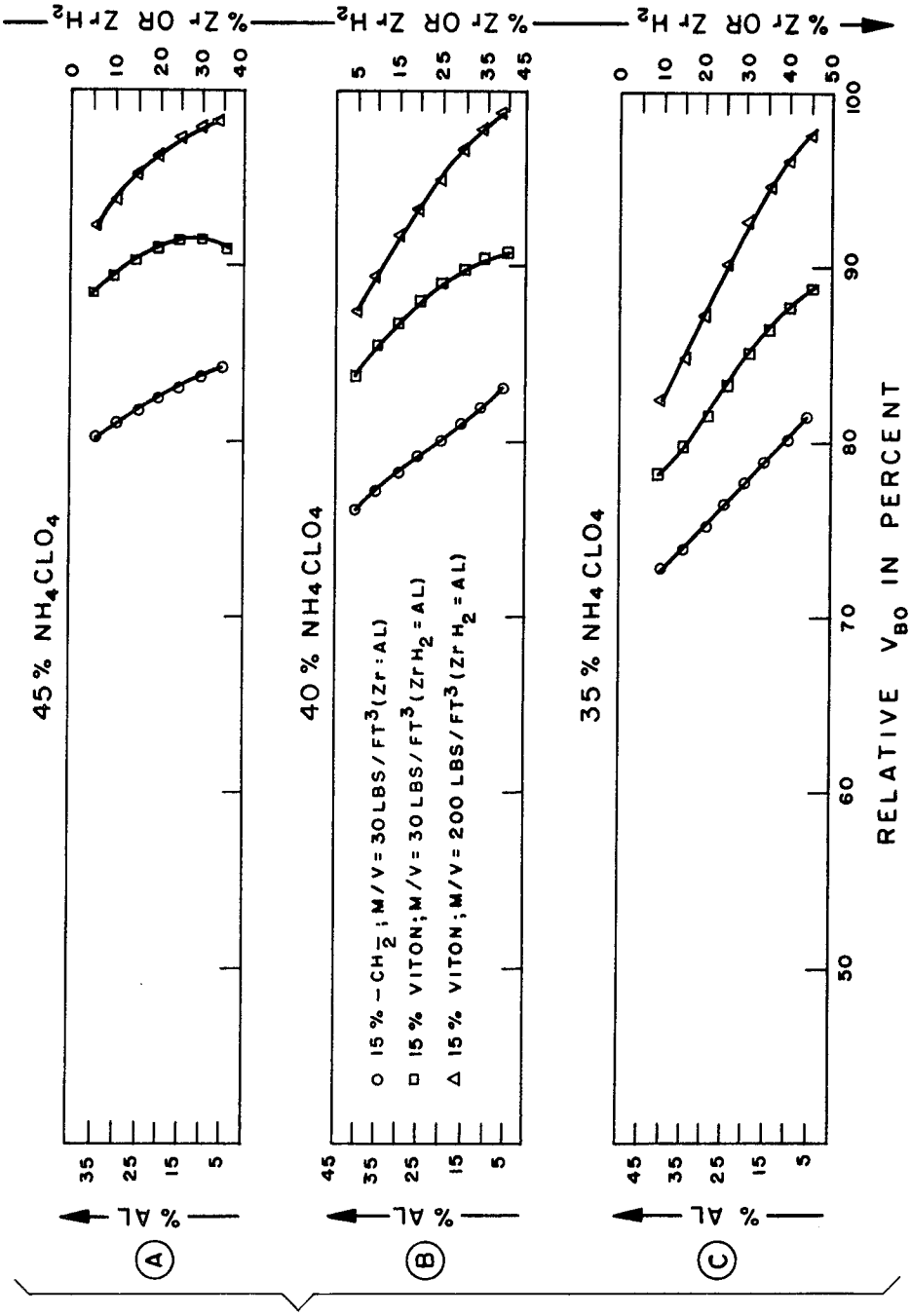


FIG. 5.

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3,734,788

HIGH DENSITY SOLID PROPELLANTS AND METHOD OF PREPARATION USING FLUOROPOLYMERS

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Int. Cl. C06d 5/06
U.S. Cl. 149—19 2 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 an improved high density solid propellant and to the method of preparation thereof.

Those concerned with the development of solid propellants have long known and recognized the need for a propellant with a high delivered density impulse, high temperature stability and good safety characteristics. A propellant of this kind finds greatest use in the system where the propellant burnout mass is very large compared to the propellant volume. As variations in the properties are required for a specific application, variations in the formulation are needed. Propellants presently available have density specific impulse values on the order of 430–470 g.-sec./cc.

The present invention attains a very high theoretical density impulse of a value between 490 and 622 g.-sec./cc. which is a considerable increase over prior propellant compositions. Physical properties are changed; for instance, tensile strength is increased. Burning rate modifiers can be added to a basic composition in order to improve ballistic properties of the composition. The general purpose of this invention, therefore, is to produce a basic family of dense propellants with suitable impulses that increased range results from their use in volume limited boost type application.

It is an object of this invention to produce a high density solid propellant material which will have greater boost velocity than existing propellants.

Another object is to provide a product which is relatively safe to handle.

Still another object of the present invention is to provide a process amenable to large scale production of propellant, pyrotechnics and explosives materials.

Other objects and many attendant advantages of this invention will be readily appreciated as the same become better understood by reference to the following detailed description when considered in connection with the accompanying graphs, wherein

FIG. 1 is a graph showing the theoretical impulse as a function of the basic composition;

FIG. 2 is a graph showing the theoretical impulse as a function of a zirconium modified basic composition;

FIG. 3 is another graph showing the theoretical impulse as a function of a beryllium modified composition;

FIG. 4 is yet another graph showing the theoretical impulse as a function of another modified basic composition; and

FIG. 5 is a graphic comparison of the boost velocities of fluorocarbon bound propellants with propellants containing conventinoal binders.

In the present invention many compositions were studied, pressed and fired. This invention is illustrated, but not liimted, by the following basic composition consisting essentially of a fluorocarbon binder, such as a copolymer of vinylidene fluoride and perfluoropropene (Viton) and a copolymer of vinylidene fluoride and trifluorochloroethylene (Kel-F elastomer), in the range of

from 10 to 35; elemental fuels and their hydrides or mixtures thereof, such as aluminum, boron, zirconium, beryllium, titanium, magnesium, and their hydrides, in the range of from about 5 to 70%; and an oxidizer, generally an inorganic oxidizer such as ammonium or alkali metal perchlorate in the range of from about 25 to 75%.

In the use of very dense metals, less binder is required on a weight basis as the fuel volumes get smaller. For example, the density of boron is 2.34 g./cc., but the density of lead is 11.4 g./cc., and that of tungsten is 19.32 g./cc.

Oxidizers such as ammonium or alkali perchlorates and nitrates are interchangeable as far as processing is concerned. Calculations indicate that oxidizers such as hydrazine nitroformate will theoretically provide even better performance.

The following basic composition was modified as hereinafter described.

BASIC COMPOSITION

Constituents:	Percent by weight
Ammonium perchlorate	59
Aluminum	21
Viton A	20

The addition of various fuel mixtures to above basic composition provided changes in burning rates which are shown in the following table. For example, the addition of copper, iron, boron, chromium, zirconium, or their derivatives at the 5% level in Viton showed significant burning rate changes:

TABLE I.—BURNING RATE

[in./sec.]

	1,000 p.s.i.	4,000 p.s.i.
Basic formulation	0.47	1.07
Basic formulation modified by addition of—		
Fenocene	0.70	1.5
Copper	0.54	1.1
Boron	0.72	1.65
Chromium	0.5	1.1
Copper chromite	0.64	1.5
Copper stearate	0.56	1.2
Copper oxide	0.56	1.2
Lead salicylate	0.52	1.0
Lead resorcylate		1.10
Titanium dioxide	0.58	1.37
Zirconium boride	0.53	1.35
Lead carbonate	0.52	1.35

Mixtures of aluminum and zirconium also produced significant changes in the burning rate of the basic composition as shown in the following table:

TABLE II

Composition (percent by weight)							Burning rate (in./sec.)	
Viton	AP	AN	Al	KP	Zr	Tef	1,000 p.s.i.	4,000 p.s.i.
15	45		20		15	5	0.60	1.35
15	45		20		20		0.77	1.95
30			20	50			0.47	1.22
20	80						0.40	0.82
25	75						0.40	0.84
15	85						0.06	0.15
15	75	10					0.45	0.92
16	50		20		10	4	0.63	1.35
18.5	45		16.5		16.5	3.5	0.53	1.25

NOTE.—AP=ammonium perchlorate; AN=ammonium nitrate; Al=aluminum; KP=potassium perchlorate; Zr=zirconium; Tef=Teflon.

Other modifications of the basic composition which showed significant changes in the burning are as follows:

MODIFIED COMPOSITION A

Constituents:	Percent by weight
Viton	18.5
Sodium azide	9.1
Ammonium perchlorate	54.6
Aluminum	18.15

The sodium azide acts as a catalyst. Burn rate results were as follows:

0.37 in./sec. at 1000 p.s.i.
0.78 in./sec. at 4000 p.s.i.

MODIFIED COMPOSITION B

Constituents:	Percent by weight
Viton	25
Magnesium	20
Ammonium perchlorate	55

Burn rate results were as follows:

0.54 in./sec. at 1000 p.s.i.
1.07 in./sec. at 4000 p.s.i.

The process by which the present invention is made uses a resin kettle with a fast propeller stirrer and a stiff rubber baffling device to prevent vortex formation. A stainless steel drum may be used to make larger batches. The required quantity of binder is placed in a container and dissolved in acetone or other suitable solvents such as methylethyl ketone and ethyl acetate. Approximately 25 cc. of acetone per gram of Viton or Kel-F elastomer is used. Into this solution at room temperature are stirred the dry solid ingredients, the metal powder and oxidizer. After about 5 minutes of stirring a quantity of a precipitant for the fluorocarbon, about two and one-half times by volume that of solvent is added with stirring. Hexane was used in this instance. Other hydrocarbons such as petroleum ether may be used. After an additional 5 minutes of stirring, the solid is permitted to settle and the liquid is decanted off. Care must be taken at this point to prevent complete decantation, especially prior to the first washing. Residual solvent will permit easy agglomeration of the powder at this stage if most of the hydrocarbon evaporates off. The latter is detrimental to the preparation of a free-flowing molding powder. The remaining wet solid receives a second hexane wash after which it is decanted off, filtered and air dried or oven dried at 90° C. In this manner agglomeration is avoided. If a finer powder is desired, the second hexane wash may be decanted off and the wet solid screened.

Referring now to the drawings, FIG. 1 is a graphic view of the theoretical specific impulse as a function of the basic formulation, as above set out, consisting essentially of Viton, aluminum, and ammonium perchlorate. FIG. 2 illustrates the theoretical specific impulse as a function of the composition wherein the basic formulation was modified by using zirconium as the elemental fuel in place of aluminum. In FIG. 3 the theoretical specific impulse as a function of the composition is shown in which beryllium was the elemental fuel used. FIG. 4 illustrates the theoretical impulse as a function of the composition wherein hydrazine nitroformate is the oxidizer with a fluorocarbon binder and the fuel, beryllium. FIG. 5 compares the boost velocities of fluorocarbon bound propellants with propellants bound with conventional binders such as polyurethanes and polyhydrocarbons. These conventional binders are designated by the symbol —CH_2—.

The performance of an ideal rocket, i.e., no pressure thrust, drag or gravitation or what may be termed "a gravitationless vacuum" is given by

$$V_{BO}=C\ln_{av}\frac{m_t}{m_t-m_p};\ C_{av}-I_{sp}g$$

The logarithmic relation makes V_{BO} very dependent on a mass ratio. If the rocket were all propellant the V_{BO} would theoretically be infinite. Now if

$$m_{BO}\ (\text{mass of rocket at burnout})=m_t-m_p$$

and since,

m_p=density of propellant, $\rho_p\times$volume of propellant, V_p

$$\frac{mt}{m_t-m_p}=\frac{m_{BO}+m_p}{m_{BO}};\ 1+\frac{m_p}{m_{BO}}=1+\frac{\rho_p}{m_{BO}/V_p}$$

so that

$$V_{BO}=I_{sp}g\ln\left(1+\frac{\rho_p}{m_{BO}/V_p}\right)$$

wherein

V_{BO}=Velocity of rocket at propellant burnout
C_{av}=Time average exhaust velocity (cm./sec.)=I_{sp}
m_t=Total rocket mass at time zero
m_p=Total propellant mass at time zero
t=Time
I_{sp}=Specific impulse
g=Gravity.

Since the mass of a rocket without propellant, and the volume to be occupied by the propellant generally are both fixed by design, the ratio m_{BO}/V_p (very often called the mass to volume ratio) is independent of propellant characteristics and actually characterizes the rocket or missile.

In FIG. 5 it is shown that the boost velocity (V_{BO}) of fluorocarbon bound propellant is considerably better than the conventional binders.

The following table shows test results of several batches of propellants mixed in accordance with the present invention.

TABLE III

Composition (percent by weight)				Composition, by analysis, V/AP/Al/Zr	Measured density	Percent theoretical, maximum density	Measured I_{sp}
Viton	AP	Al	Zr				
20	65	15		22.08/63.39/14.53	1.987	99.35	283
20	59	21			1.984	99.20	228
20	62	18		21.98/60.48/17.54	2.027	99.36	239
20	25		55	19.19/25.04/55.06	2.994	96.89	149
20	30		50	20.68/29.55/49.77	2.824	96.71	162
20	35		45	19.64/35.04/45.32	2.754	99.01	175
20	40		40	19.90/39.63/40.11	2.621	97.80	194
20	45		35	19.85/44.88/35.37	2.510	99.21	196
20	50		30	20.05/49.89/30.09	2.397	99.05	200
25	35		40	24.37/34.86/40.77	2.607	98.75	185

NOTE.—AP=Ammonium perchlorate (100μ); V=Viton; Al=Aluminum; Zr=Zirconium.

Obviously many modifications and variations of the present invention are possible in 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. The process for preparing a high density impulse solid propellant comprising the steps of

(1) dissolving a copolymer of vinylidene fluoride and perfluoropropylene in methylethylketone forming a solution;

(2) adding while stirring weighed quantities of dry ammonium perchlorate and zirconium of about 20μ particle size to said solution until a consistent mixture results;

(3) adding while stirring a volume of hexane about three times the volume of methylethylketone;

(4) permitting a stand without stirring until all the solids settle;

(5) decanting off sufficient liquid to leave about a one-half inch level above the solid residue thereby preventing agglomeration;

(6) washing the residue a second time with hexane of about three times the volume of methylethylketone;

(7) filtering out said residue; and

(8) air drying.

2. A high density solid propellant composition consisting essentially of the following:

Constituent:	Percent by weight
Copolymer of vinylidene fluoride and perfluoropropylene	20–25
Zirconium	30–55
Ammonium perchlorate	25–50

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U.S. Cl. X.R.

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