ABSTRACT OF THE DISCLOSURE

Propellant compositions are prepared containing metals, oxidizing agents, high density solid vinylidene fluoride and perfluoropropylene with polytetrafluoroethylene.

The invention described herein 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 improved fluorocarbon propellant compositions.

In the last few years considerable interest has developed in the fluorocarbon family of polymers as potential binder materials for composite solid propellants. Binders for composite solid propellants have, historically, consisted of natural or synthetic plastics, resins, or elastomeric materials composed of the elements carbon, hydrogen, oxygen, and nitrogen. Because of their high density, thermal stability, water impermeability compatibility with a wide range of propellant ingredients, and high heat of reaction with metals, the fluorinated binders exhibit many desirable properties in the propellant field. They can be divided into two classes, those which are castable and those which must be processed by extrusion or compression molding. New high density solid vinylidene propellants and their preparation utilizing a single fluorocarbon as a binder are described in copending patent application Ser. No. 99,967 filed Mar. 31, 1961. These propellants which contain a metal-hydride as the fuel and ammonium perchlorate as the oxidizer, are processed by isostatic pressing.

The present invention is for improved fluorocarbon composite propellants which have better chemical and physical properties than other known solid propellants.

It is an object of the present invention to provide a solid propellant with a high density impulse along with a relatively high specific impulse.

Still another object is to provide a propellant with exceptionally high structural integrity.

A further object of this invention is to provide a propellant which has long storage life under varying temperature and humidity conditions.

Yet another object is to provide a propellant which can be produced in large volumes at low cost.

Another object is to provide a propellant with a wide range of burning rates and physical properties without changing over-all composition or energy level.

Another object of this invention is to provide a propellant for use in seat-ejection and cockpit-capsule-ejection devices or other devices having high inert mass to propellant volume ratio.

Other objects and many attendant advantages of this invention will be readily appreciated as the same become better understood from the following disclosure.

The present propellant composition comprises from 5 to 60 percent binder which is composed of polytetrafluoroethylene (hereinafter referred to by its trade name Teflon) and a copolymer of vinylidene fluoride and perfluoro-

propylene (hereinafter referred to by its trade name Viton), in weight ratios of from 3:1 to 1:10; from 10 to 90 percent by weight oxidizer selected from the group consisting of ammonium perchlorate, lithium perchlorate, potassium perchlorate, cyclotetramethylene tetranitramine, nitramine perchlorate, hydrazine, diperchlorate, hydrazine nitroform and hydroxylamine perchlorate; from 0 to 90 percent by weight metallic fuel selected from the group consisting of aluminum, magnesium, zirconium, hafnium, tungsten, thorium, beryllium, uranium, boron, titanium, aluminum hydride, beryllium hydride, zirconium hydride alloys and mixtures thereof; from 0 to 30 percent by weight of a member selected from the group consisting of triminoquinuadine, triminoquinuadine azide, and mixtures thereof.

In preparing these formulations the Viton is first dissolved in a solvent selected from a low boiling ketone such as acetone and methyl ethyl ketone or a low boiling ester such as ethyl acetate, methyl acetate and butyl acetate, and nitroalkanes such as nitroethane. The Teflon and other ingredients (oxidizer, fuel, and additives) are then thoroughly mixed into the Viton solution to form a uniform slurry. The slurry of propellant is washed for from 5 to 10 minutes with hexane, the volume of hexane being from one to four times the volume of slurry. After the suspension has settled the supernatant hexane is decanted or siphoned off and the resulting residue is dried under ambient conditions for 8 to 24 hours. The material is now ready for extrusion in a standard propellant extrusion press.

The slurry may be washed with normal hexane or other low boiling liquid hydrocarbon two or three times, as necessary. Other wash materials depending on solubility of propellant ingredients are Freons and chlorocarbons.

The following examples are given for a better understanding of this invention and no unnecessary limitations are to be understood therefrom.

EXAMPLE I

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vilon</td>
<td>15</td>
</tr>
<tr>
<td>Teflon</td>
<td>15</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>50</td>
</tr>
<tr>
<td>Aluminum powder</td>
<td>20</td>
</tr>
</tbody>
</table>

EXAMPLE II

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vilon</td>
<td>15</td>
</tr>
<tr>
<td>Teflon</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>42.4</td>
</tr>
<tr>
<td>Zirconium (22a)</td>
<td>35.6</td>
</tr>
<tr>
<td>Aluminum powder</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The burning rate of the above composition at 1000 p.s.i. 70° F., was 0.53 in./sec.

EXAMPLE III

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vilon</td>
<td>10</td>
</tr>
<tr>
<td>Teflon</td>
<td>15</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>55</td>
</tr>
<tr>
<td>Aluminum powder</td>
<td>20</td>
</tr>
</tbody>
</table>

This propellant was static-fired in both 2-inch and 5-inch diameter evaluation motors at 65, 70, and 165° F. The specific impulse at 70° F. was 235 lbf.-sec./lbm., corrected to 1000/14.7. The performance of this propellant was also demonstrated in two flight tests of 5-inch motors, at a ratio of inert mass to propellant volume of 550 lbf./cu. ft. These motors flew 10,515 and 10,575 yards respectively, while control rounds using a state-of-the-art polyurethane propellant flew an average of 8,350 yards.
EXAMPLE IV

Ingredients: Percent by weight
Viton A ----------------------------- 15
Teflon ----------------------------- 5
Ammonium perchlorate ------------- 65
Beryllium -------------------------- 15

The above propellant composition was successfully static-fired in 5-inch diameter motors at -65, 70, and 165°F, and was evaluated in two flight tests in 5-inch hardware at a mass-to-volume ratio of 550 lb./cu. ft. These motors flew 11,350 and 11,020 yards respectively. This represents an average increase in range of 34% over that of control rounds containing the same volume of a state-of-the-art polyurethane propellant and an increase over the range attained by the higher impulse aluminum-fluoro-carbon propellant described in Example III above.

This same composition using zirconium particles of 5μ increased the burning rate by a factor of 3. By varying the weight ratios of the 22μ and 5μ particles of zirconium, a burning rate of .34 in/sec. to 1 in/sec. was achieved.

EXAMPLE VI

Ingredients: Percent by weight
Viton A ----------------------------- 20
Teflon ----------------------------- 20
Ammonium perchlorate ------------- 30
Zirconium (22μ) ------------------- 30

The above composition has high density with less than 10% solids in the exhaust products. This is an example of the use of fluorine in the binder as an oxidizer to form gaseous metal products in place of liquid or solid oxides. This formulation is suitable for spin application where some solids in the exhaust products deposit in the combustion chamber.

EXAMPLE VII

Ingredients: Percent by weight
Viton A ----------------------------- 15
Teflon ----------------------------- 15
Ammonium perchlorate ------------- 50
Zirconium (22μ) ------------------- 40

The above propellant composition is approximately optimum (at that binder level and binder composition) on the basis of burnt velocity as a mass-to-volume ratio of 1000.

EXAMPLE VIII

Ingredients: Percent by weight
Viton A ----------------------------- 15
Teflon ----------------------------- 10
Ammonium perchlorate ------------- 44.4
Zirconium (22μ) ------------------- 30.6

This composition was successfully fired in 5" RAP projectiles (Rocket Assisted Projectile) and withstood 21,000 centrifugal G's. It is an example of a propellant that can endure severe environmental conditions and remain structurally intact. This has been demonstrated in grains ranging from 1" to 3½" in diameter.

EXAMPLE IX

Ingredients: Percent by weight
Viton A ----------------------------- 12
Teflon ----------------------------- 8
Nitrium perchlorate ------------- 45
Triaminoguanidine ------------- 15
Aluminum -------------------------- 20

The above composition is an example of fluorocarbon binder compatibility with highly energetic propellant ingredients.

EXAMPLE X

Ingredients: Percent by weight
Viton A ----------------------------- 7
Teflon ----------------------------- 5
Magnesium ------------------------- 4
Ammonium perchlorate ------------- 10
Tungsten (6.5μ) ------------------- 75

The above composition was extruded into 5-inch propellant grains. It had a measured density of 5.76 g./cm³, a measured specific impulse of 72 lb.-sec./lb., and a specific impulse efficiency of 69% in a 5-inch motor because of a large percentage of nongaseous exhaust. Although this composition was formulated for use in Tailored Exhaust Velocity Rockets (TEVR), it out-distanced state-of-the-art polyurethane propellants.

EXAMPLE XI

Ingredients: Percent by weight
Viton A ----------------------------- 12
Teflon ----------------------------- 20
Nitrogen perchlorate ------------- 50
Aluminum -------------------------- 25

This is a typical example of a high specific impulse propellant using fluorocarbon binders in accordance with this invention.

EXAMPLE XII

Ingredients: Percent by weight
Viton A ----------------------------- 15
Teflon ----------------------------- 15
Potassium perchlorate ------------- 50
Aluminum -------------------------- 19
Boron ----------------------------- 1

This is an example of a thermally stable propellant.

EXAMPLE XIII

Ingredients: Percent by weight
Teflon ----------------------------- 12.8
Viton A ----------------------------- 19.2
Ammonium perchlorate ------------- 63.0
Aluminum -------------------------- 5.0

The specific impulse of the above composition at 70°F was 230 lb.-sec./lb., corrected to 1000/14.7.

EXAMPLE XIV

Ingredients: Percent by weight
Teflon ----------------------------- 15
Viton A ----------------------------- 22.5
Ammonium perchlorate ------------- 62.5

The specific impulse of the above composition at 70°F was 214 lb.-sec./lb., corrected to 1000/14.7.

EXAMPLE XV

Ingredients: Percent by weight
Teflon ----------------------------- 15
Viton A ----------------------------- 15
Aluminum -------------------------- 25
Hydrazine diperchlorate ---------- 55

In carrying out the invention a preform or article such as a solid rod or internal star-perforated grain may be formed by pressing, by rolling, or by extrusion. The Viton-Teflon binder markedly reduces the temperature and/or pressure necessary to process and extrude the propellant in a finished well consolidated form.

Both aluminum and zirconium fuels with ammonium perchlorate as oxidizer in the Teflon-Viton binder system have produced high performance propellants. The aluminum composition yields higher specific impulses than those containing zirconium, but the latter have significantly greater densities. The choice of fuel depends on the characteristics of the system in which the propellant is to be used. The use of small amounts of tungsten in the formulation increases the density impulse without greatly
sacrificing specific impulse. Incorporating beryllium in the fluorocarbon binder yields the highest specific impulse of any of the metallic fuels.

Optimization of the fuel system requires consideration not only of theoretical performance calculations by also of such practical factors as processibility, mechanical properties and efficiency of combustion.

A large number of performance calculations were made, covering not only a wide range of fuel/oxidizer/binder ratios but also a variety of binder compositions in terms of the ratio of Teflon to Viton. The effects of compositional changes on both specific impulse and burn rate were determined. Because the effects of density on performance are greatest at high mass-to-volume ratios, the value of 1000 lb./cu. ft. was chosen as being typical of the volume limited systems in which this family of propellants would be most useful. By varying the amount of binder (consisting of 50% Teflon and 50% Viton) it was found that the 15–20% binder level is near optimum for obtaining the highest specific impulse, but that 10% or less binder is desirable for obtaining the maximum burn rate. However, for a practical system, 20% binder is about the minimum amount which can be used, based on consideration of extrudability and mechanical properties.

In the zirconium system, something over 30% binder is required to achieve maximum theoretical specific impulse. Reduction in the average particle size of the metal fuel or oxidizer results in a significant increase in both strength and modulus and in a slight decrease in elongation. The effects of Teflon particle size appears to be in the opposite direction. The use of larger sized Teflon increases the modulus significantly, and the strength to a lesser extent, while decreasing the elongation slightly. The Teflon thus acts as a binder, as well as a filler, since it can undergo appreciable elongation.

Zirconium metal powder is known to be sensitive to static electricity but it was found that the 22-micron powder which was generally used in this invention could be handled safely with normal precautions. However, a finer grade (5µ particle size) presented a serious hazard, since its electrostatic sensitivity was 1000 ergs or less. Use of the finer metal results in a rapid increase in burning rate. In order to use this material, it was necessary to desensitize it.

Other fluorocarbon polymers may be used as alternatives for Viton A in the Teflon-Viton binder. A similar copolymer selling under the trade name Fluorel (hexafluoropropylene-vinylidene fluoride) or the homopolymer of chlorotrifluoroethylene, generally known as KVF elastomers, and nitrosorubber provide properties about as good as the Viton. Also the copolymer of tetrafluoroethylene and hexafluoropropylene known to the trade as Teflon 100 was used as an alternative for polytetrafluoroethylene (Teflon) in preparing the binder.

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 propellant composition comprising the following:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer of vinylidene fluoride and perfluoropropane</td>
<td>15–20</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>5–5</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>30–45</td>
</tr>
<tr>
<td>Zirconium</td>
<td>30–40</td>
</tr>
</tbody>
</table>

2. The composition of claim 1 wherein the zirconium consists of 5µ particles.

3. The composition of claim 1 wherein the zirconium consists of 22µ particles.

4. The composition of claim 1 wherein the zirconium consists of a mixture of 5µ and 22µ particles.

5. A propellant composition comprising the following:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer of vinylidene fluoride and perfluoropropane</td>
<td>12</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>8</td>
</tr>
<tr>
<td>Nitromium perchlorate</td>
<td>50</td>
</tr>
<tr>
<td>Aluminum</td>
<td>5</td>
</tr>
<tr>
<td>Aluminum hydride</td>
<td>25</td>
</tr>
</tbody>
</table>

6. A propellant composition comprising the following:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer of vinylidene fluoride and perfluoropropane</td>
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</tr>
<tr>
<td>Nitromium perchlorate</td>
<td>15</td>
</tr>
<tr>
<td>Aluminum</td>
<td>20</td>
</tr>
</tbody>
</table>

7. A propellant composition comprising the following:

<table>
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<tr>
<th>Ingredients</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer of vinylidene fluoride and perfluoropropane</td>
<td>7</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>4</td>
</tr>
<tr>
<td>Magnesium</td>
<td>10</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>75</td>
</tr>
</tbody>
</table>

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U.S. Cl. X.R.
149—20, 21, 36, 114