# United States Patent

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[73] Assignee **The United States of America as represented by the Secretary of the Navy**


## [54] CASTABLE FLUOROCARBON COMPOSITE PROPELLANTS

**8 Claims, No Drawings**


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[50] Field of Search ..... 149/88, 17–19, 20



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**CLAIM:** 1. A propellant composition comprising

a fluorocarbon binder;

a metal fuel; and

an inorganic oxidizer;

said binder comprising a fluorocarbon monomer selected from the group consisting of 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacylate, 1H, 1H, 7H-Dodecafluoro-1-heptanoacrylate, 1H, 1H, 5H-Octafluoro-1-pentanoacrylate, and mixtures thereof; a plasticizer selected from the group consisting of triethylene glycol dinitrate, pentaerythritol trinitrate, trimethylol ethane trinitrate, diethylene glycol dinitrate, butanediol dinitrate, a copolymer of vinylidene fluoride and perfluoropropylene, bis(2-fluoro-2,2-dinitroethyl)formal and mixtures thereof; a cross-linking agent selected from the group consisting of triallylcyanurate and divinyl benzene; and a free radical catalyst selected from the group consisting of azo-bisisobutyro-nitrile, benzoyl peroxide, dichlorobenzoyl peroxide, and methylethylketone peroxide;

said fuel being a member selected from the group consisting of aluminum, beryllium, and zirconium; and

said oxidizer selected from a group consisting of ammonium perchlorate, sodium perchlorate, potassium perchlorate, sodium nitrate, potassium nitrate and barium nitrate.

# CASTABLE FLUOROCARBON COMPOSITE PROPELLANTS

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.

This invention relates to a novel castable high-density composite propellant composition and to the preparation thereof.

Those concerned with the development of solid propellants have long recognized the need for a propellant with a high-delivered density impulse, high-temperature stability and good safety characteristics along with ease of preparation. A propellant of this type finds its greatest use in those rocket and missile systems where the propellant burnout mass is very large compared to the propellant volume. Work on metallized extruded fluorocarbon propellants has demonstrated that propellants with high-density and moderate to high-specific-impulse can be obtained. An aluminum, ammonium perchlorate extruded fluorocarbon propellant gave a delivered specific impulse of 239 sec. with a density of 2.01 g./cm.$^3$. The theoretical performance calculations for this particular propellant indicated a specific impulse of 254 sec. with a density of 2.03 g./cm.$^3$. Thus these extruded fluorocarbon propellants have done much to increase the range of rocket and missile systems. Production of extruded large diameter propellant grains is very expensive. Processing and safety problems are encountered due to the high temperature and pressures required for extrusion.

The present invention for castable fluorocarbon propellant compositions attains a specific impulse ranging from 220 sec. with density of 2.64 g./cm.$^3$ to 271 sec. with a density of 1.90 g./cm.$^3$. These new compositions also have high-temperature stability.

Therefore, an object of this invention is to produce a castable dense composite propellant which will have a higher boost velocity than existing solid propellants.

Another object is to produce a high-density castable composition which shows stability at high temperatures as the primary physical requirement.

A further object of this invention is to provide a propellant composition amenable to large scale production which has commendable safety characteristics.

Still another object is to provide a product which has the economic advantage of being faster to process and less expensive than extruded material.

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

The composite propellant compositions of the present invention comprise a fluorocarbon binder (described in copending patent application, Ser. No. 394,379, filed 28 Aug. 1964), a metal fuel, such as aluminum, beryllium and zirconium, and an oxidizer selected from the group consisting of ammonium perchlorate, rodium and potassium perchlorate, sodium, potassium and barium nitrates, and the like.

The binder comprises a fluorocarbon monomer selected from the group consisting of 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate, 1H, 1H, 7H-Dodecafluoro-1-heptanoacrylate, 1H, 1H, 5H-Octafluoro-1-pentanoacrylate and mixtures thereof; a plasticizer selected from the group consisting of triethylene glycol dinitrate, pentaerythritol trinitrate, trimethylol ethane trinitrate, diethylene glycol dinitrate, butanediol dinitrate, a copolymer of vinylidene fluoride and perfluoropropylene (Viton), bis(2-fluoro-2,2-dinitraethyl)formal, a fluorinated polyester and mixtures thereof; a cross linking agent selected from the group consisting of triallylcyanurate and divinyl benzene; and a free radical catalyst selected from the group consisting of azo-bisisobutyronitrile, benzoyl peroxide, dichlorobenzoyl peroxide, and methylethylketone peroxide.

Vinyl monomers selected from the group consisting of acrylic acid, acrylonitrile, vinylacetate, dinitropropylacrylate and styrene may also be admixed with the fluorocarbon monomers, above set out.



The following examples are believed to better illustrate the present invention, but should not be considered as limiting it.

## EXAMPLE I

| Ingredients | Percent by weight |
|---|---|
| Binder | 20 |
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 65% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 19.95% |
| Copolymer of vinylidene fluoride and perfluoropropylene (Viton) | 10% |
| Styrene | 5% |
| Benzoyl peroxide | 0.05% |
| Aluminum | 20 |
| Ammonium perchlorate | 60 |

The delivered specific impulse of the above composition was 230 sec. (chamber pressure 1,000 to 14.7 p.s.i.), and the theoretical impulse 252 sec. The firing was conducted with an experimental motor known to be a heat sink.

Benzoyl peroxide is a free radical catalyst which was used because of its availability. Others include azo-bisisobutyronitrile, dichlorobenzoyl peroxide and methylethylketone peroxide.

## EXAMPLE II

| Ingredients | Percent by weight |
|---|---|
| Binder | 23 |
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 66% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 21.85% |
| Copolymer of vinylidene fluoride and perfluoropropylene (Viton) | 12% |
| Benzoyl peroxide | 0.15% |
| Aluminum | 18 |
| Ammonium perchlorate | 59 |

The delivered specific impulse of the above composition was 221 sec. with a chamber pressure of 1,000 to 14.7 p.s.i. and the theoretical impulse was 251 sec. The firing was conducted in the same motor as in example I above.

## EXAMPLE III

| Ingredients | Percent by weight |
|---|---|
| Binder | 22 |
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 65% |
| Copolymer and perfluoropropylene (Viton) | 10% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 19.95% |
| Styrene | 5% |
| Benzoyl peroxide | 0.05% |
| Beryllium | 16 |
| Ammonium perchlorate | 62 |

## EXAMPLE IV

| Ingredients | Percent by weight |
|---|---|
| Binder | 23 |
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 64% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 20.85% |
| Copolymer of vinylidene fluoride and perfluoropropylene (Viton) | 15% |
| Benzoyl peroxide | 0.15% |
| Aluminum | 18 |
| Ammonium perchlorate | 59 |

## EXAMPLE V

| Ingredients | Percent by weight |
|---|---|
| Binder | 20 |
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 65% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 29.5% |
| Triallylcyanurate | 0.30% |
| Perfluorooctanoic acid | 0.10% |
| Acrylonitrile | 5.0% |
| Benzoyl peroxide | 0.10% |
| Aluminum | 20 |
| Ammonium perchlorate | 60 |

## EXAMPLE VI

| Ingredients | Percent by weight |
|---|---|
| Binder | 21 |
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 66% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 21.85% |
| Copolymer of vinylidene fluoride and perfluoropropylene | 12% |
| Benzoyl peroxide | 0.15% |
| Zirconium | 45 |
| Ammonium perchlorate | 34 |

## EXAMPLE VII

| Ingredients | Percent by weight |
|---|---|
| Binder | 22 |
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 53.25% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 17.50% |
| Copolymer of vinylidene fluoride and perfluoropropylene | 12% |
| Trimethylol ethane trinitrate | 15% |
| Triallylcyanurate | 2% |
| Benzoyl peroxide | 0.25% |
| Aluminum | 20 |
| Ammonium perchlorate | 58 |

Various modifications of the formulation set out in examples I–VI were made. When specific impulse tends to be more important than density, cyclotrimethylenetrinitramine and cyclotetramethyletrinitramine can be added to increase the energy of the system. When density becomes more important than specific impulse, metal fuels such as tungsten and uranium can be added or used alone with an oxidizer.

The formulations described herein were mixed in accordance with standard procedure and general propellant casting techniques were employed. Before any rocket motors were cast numerous experimental castings were prepared in the laboratory. Immediately after the casting was completed the exposed portions of the propellant were coated with a material that is impervious to oxygen in order to insure complete polymerization. Ordinary paraffin wax worked very well. The motors were then cured for about 48 hours at 125° F.

A 13-inch diameter rocket motor was cast using the aluminized fluorocarbon composition (example I) and after curing operation was X-rayed. There was no evidence of cracks or of case-bonding failure.

The following theoretical performance calculations are representative of the cast fluorocarbon propellants prepared in accordance with this invention.

TABLE I

| Sample No. | Composition (wt. percent) Binder | Fuel | Oxidizer $NH_4ClO_4$ | Specific impulse (sec.) | Density (g./cm.$^3$) |
|---|---|---|---|---|---|
| 1 | 10 | 35 Al | 55 | 246 | 2.14 |
| 2 | 22 | 19 Al | 59 | 252 | 2.02 |
| 3 | 30 | 15 Al | 55 | 248 | 1.98 |
| 4 | 19 | 16 Be | 65 | 271 | 1.91 |
| 5 | 21 | 16 Be | 63 | 271 | 1.91 |
| 6 | 25 | 14 Be | 61 | 269 | 1.90 |
| 7 | 19 | 40 Zr | 41 | 222 | 2.65 |
| 8 | 23 | 50 Zr | 27 | 203 | 2.92 |

Binder —consisting essentially of 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate, 1H, 1H, 5H-Octafluoro-1-pentanoacrylate, the copolymer of vinylidene fluoride and perfluoropropylene, a vinyl monomer, a free radical catalyst, and a cross-linking agent.

$NH_4ClO_4$—ammonium perchlorate

Al—aluminum

Be—beryllium

Zr—zirconium

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

a fluorocarbon binder;

a metal fuel; and

an inorganic oxidizer;

said binder comprising a fluorocarbon monomer selected from the group consisting of 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate, 1H, 1H, 7H-Dodecafluoro-1-heptanoacrylate, 1H, 1H, 5H-Octafluoro-1-pentanoacrylate, and mixtures thereof; a plasticizer selected from the group consisting of triethylene glycol dinitrate, pentaerythritol trinitrate, trimethylol ethane trinitrate, diethylene glycol dinitrate, butanediol dinitrate, a copolymer of vinylidene fluoride and perfluoropropylene, bis(2-fluoro-2,2-dinitroethyl)formal and mixtures thereof; a cross-linking agent selected from the group consisting of triallylcyanurate and divinyl benzene; and a free radical catalyst selected from the group consisting of azo-bisisobutyronitrile, benzoyl peroxide, dichlorobenzoyl peroxide, and methylethylketone peroxide;

said fuel being a member selected from the group consisting of aluminum, beryllium, and zirconium; and

said oxidizer selected from a group consisting of ammonium perchlorate, sodium perchlorate, potassium perchlorate, sodium nitrate, potassium nitrate and barium nitrate.

2. A propellant composition comprising the following ingredients:

| Ingredients | Percent by weight |
|---|---|
| Binder | 23 |
| Aluminum | 18 |
| Ammonium perchlorate | 59; |

said binder consisting essentially of the following:

| | |
|---|---|
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 66% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 21.85% |
| Copolymer of vinylidene fluoride and perfluoropropylene and | 12% |
| Benzoyl peroxide | 0.15%. |

3. A propellant composition consisting essentially of the following:

| Ingredients | Percent by weight |
|---|---|
| Binder | 22 |
| Aluminum | 20 |
| Ammonium perchlorate | 58; |

said binder consisting essentially of the following:

| | |
|---|---|
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 53.25% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 17.50% |
| Copolymer of vinylidene fluoride and perfluoropropylene | 12% |
| Trimethylol ethane trinitrate | 15% |
| Triallylcyanurate | 2% |
| Benzoyl peroxide | 0.25%. |

4. A propellant composition comprising the following ingredients:

| Ingredients | Percent by weight |
|---|---|
| Binder | 20–22 |
| Metal fuel | 16–20 |
| Oxidizer | 60–62 |

said binder comprising a fluorocarbon monomer selected from the group consisting of 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate, 1H, 1H, 7H-Dodecafluoro-1-heptanoacrylate, 1H, 1H, 5H-Octafluoro-1-pentanoacrylate, and mixtures thereof; a vinyl monomer selected from the group consisting of acrylic acid, acrylonitrile, vinylacetate, dinitropropylacrylate and styrene; a plasticizer selected from the group consisting of triethylene glycol dinitrate, pentaerythritol trinitrate, trimethylol ethane trinitrate, diethylene glycol dinitrate, butanediol dinitrate, a copolymer of vinylidene fluoride and perfluoropropylene, bis(2-fluoro-2,2-dinitroethyl)formal and mixtures thereof; a free radical catalyst selected from the group consisting of azo-bisisobutyronitrile, benzoyl peroxide, dichlorobenzoyl peroxide, and methylethylketone peroxide.

5. A propellant composition comprising the following:

| Ingredients | Percent by weight |
|---|---|
| Binder | 20 |
| Aluminum | 20 |
| Ammonium perchlorate | 60; |

said binder consisting essentially of

| | |
|---|---|
| 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate | 65% |
| 1H, 1H, 5H-Octafluoro-1-pentanoacrylate | 19.95% |
| Copolymer of vinylidene fluoride and perfluoropropylene | 10% |
| Styrene | 5% |
| Benzoyl peroxide | 0.05%. |

6. A propellant composition comprising the following:

| Ingredients | Percent by weight |
|---|---|
| Binder | 22 |
| Beryllium | 16 |
| Ammonium perchlorate | 62; |

said binder consisting essentially of
65 percent 1H, 1H, 9H-Hexadecafluoro-1-nonanomethaerylate,
19.95 percent 1H, 1H, 5H-Octafluoro-1-pentanoacrylate,
10 percent Copolymer of vinylidene fluoride and perfluoropropylene,
5 percent Styrene and
0.05 percent Benzoyl peroxide.

7. A propellant composition comprising the following:

| Ingredients | Percent by weight |
|---|---|
| Binder | 20 |
| Aluminum | 20 |
| Ammonium perchlorate | 60 |

said binder consisting essentially of
65 percent 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate,
29.5 percent 1H, 1H, 5H-Octafluoro-1-pentanoacrylate,
0.30 percent Triallylcyanurate,
0.10 percent Perfluoroactanoic acid,
5.0 percent Acrylonitrile, and
0.11 percent Benzoyl peroxide.

8. A propellant composition comprising the following ingredients:

| Ingredients | Percent by weight |
|---|---|
| Binder | 21 |
| Zirconium | 45 |
| Ammonium perchlorate | 34 |

said binder consisting essentially of
66 percent 1H, 1H, 9H-Hexadecafluoro-1-nonanomethacrylate,
21.85 percent 1H, 1H, 5H-Octafluoro-1-pentanoacrylate,
12 percent Copolymer of vinylidene fluoride and perfluoropropylene, and
0.15 percent Benzoyl peroxide.

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