United States Patent

Sarten et al.

[15] 3,663,322

[45] May 16, 1972

[54] **HYPERGOLIC SOLID FUELS OF HIGH STORAGE STABILITY FOR HYBRID ROCKET ENGINES AND PROCESS FOR MAKING THE SAME**

[72] Inventors: **Paula Sarten**, Munich; **Winfried Mair**, Riemerling, both of Germany

[73] Assignee: **Messerschmitt-Bolkow, Gesellschaft mit beschrankter Haftung**, Ottobrunn near Munich Germany

[22] Filed: **Jan. 16, 1969**

[21] Appl. No.: **791,803**

[30] **Foreign Application Priority Data**

Jan. 20, 1968 Germany ....P 16 46 310.8

[52] **U.S. Cl.** ....**149/19,** 149/36, 149/87, 149/20, 260/308 R, 60/219

[51] **Int. Cl.** **C06d 5/10**

[58] **Field of Search** ....149/36, 87, 19, 20; 260/308 R; 60/219

[56] **References Cited**

UNITED STATES PATENTS

3,338,762	8/1967	Oja	149/19
3,398,215	8/1968	Spenadel et al.	264/3
3,403,062	9/1968	Ponnell et al.	149/36
3,499,289	3/1970	Olsen	60/218

Primary Examiner—Carl D. Quarforth
Assistant Examiner—E. A. Miller
Attorney—McGlew and Toren

[57] **ABSTRACT**

A hypergolic solid fuel of high storage stability for hybrid rocket engines, comprising incorporated in a small amount of a binder a combination of compounds extremely rich in hydrogen and rich in nitrogen as compared to the contents in carbon, said nitrogen being in the form of cyano- or hydrazine groups and capable of releasing high energy upon contact with an oxidizer. The invention also relates to a process for making the fuels.

11 Claims, No Drawings

HYPERGOLIC SOLID FUELS OF HIGH STORAGE STABILITY FOR HYBRID ROCKET ENGINES AND PROCESS FOR MAKING THE SAME

SUMMARY OF THE INVENTION

The present invention relates to hypergolic solid fuels of high storage stability for hybrid rocket engines and to a process of producing the fuels.

"Hypergolic" denotes the capacity of self-ignition upon contact with another chemical.

The known, presently used solid fuels for hybrid engines consist of polyethylene, polyester, polyurethanes, polyamides and others, which are rendered hypergolic by the addition of metals, hydrides, ferrocene and the like, when contacted with gaseous or liquid oxidizers. Upon reaction with the second component, the gaseous or liquid oxidizer, the combustion process leads to an undesirable deposition of carbon in the form of soot and/or solid oxidation products and causes surface incrustations, thus leading to a poor performance of the fuel. Moreover, a desired re-ignition is thus made more difficult, if not impossible, since due to carbonization or incrustation of the binder, a surface layer will result which prevents re-ignition or will at least make re-ignition unreliable. Moreover, due to the incomplete combustion, part of the combustible substance is entrained unburned by the effluent and deposited together with the soot, whereby the specific efficiency is decreased.

Attempts have been made to overcome these difficulties by addition of moderate amounts of oxidizers or by incorporation to nitro groups into the fuel, thereby enhancing combustion and, sometimes, facilitating reignition. However, by these additions and by the introduction of nitro groups, the stability of such solid fuels during storage is considerably impaired; furthermore, by incorporation of high energy substances, the chemical stability of the fuel may be endangered.

It is the object of the present invention to overcome the existing shortcomings of known solid rocket fuels for hybrid rocket engines.

It is another object of the invention to provide solid rocket fuels for hybrid engines which will ensure re-ignition of the fuels after each combustion and which, moreover, are of higher energy that will be utilized to the highest degree.

It is yet another object to provide solid rocket fuels which will be very stable during storage and handling.

It is also an object to provide a process for producing the solid rocket fuels above mentioned.

Other objects and advantages of the invention will become apparent from the detailed description hereinbelow.

The solid fuels according to the invention comprise a combination of components which upon reaction with oxygen is capable of releasing an extremely high percentage of hydrogen and a high percentage of high energy nitrogen, both calculated on the carbon present, the nitrogen being present in the form of hydrazine of cyano groups.

Solid fuels according to the invention may have the following compositions:

All parts are by weight.

1. 20–90 parts of 4-aminodihydrazino-1,2,4-triazole, as well as the acid, neutral and basic carbonate of 4-aminodihydrazino-1,2,4-triazole, also the neutral and basic thiocyanate of 4-aminodihydrazino-1,2,4-triazole, primarily the neutral and basic cyanide of 4-amino-dihydrazino-1,2,4-triazole;

moreover:

2. 5 – 20 parts of binder, mostly free of oxygen, basically consisting of hydrocarbon polymers, if de-sired combined with terpene resins and, in some cases, up to

3. 50 parts of additives of the type of powdered metals, e.g. Be, Mg, Al, B, Zr, etc. or hydrides of Li, Na, Be, K, etc. or alanates and boranates of Li, Na, K, Be, etc. or alkyls of Li, Na, K, Be, Al, Mg, Zn, etc. or colloids of Li, Na, K, etc. or a cyano derivative or substances of the type of ferrocenes, nickelo- or cobaltocenes, etc.,

and

4. 0.1 – 10 parts of other additives of the type of plasticizers, catalysts and/or surfactants. Another embodiment of the invention comprises solid fuels of the following compositions:

1. 10 – 90 parts of triaminoguanidine, as well as the acid, neutral and basic carbonate of triaminoguanidine, also the neutral and basic thiocyanate of triaminoguanidine, primarily the neutral and basic cyanide of triaminoguanidine,

furthermore:

2. 5 – 20 parts of binder, based on polybutadiene or epoxy resins modified with, natural resins based on terpenes,

if desired also up to

3. 50 parts of additives of the type of powdered metals, e.g. Be, Mg, Al, B, Zr, etc. or hydrides of Li, Na, Be, K, etc. or alanates and boranates of Li, Na, K, Be,etc. or alkyls of Li, Na, K, Be, Al, Mg, Zn, etc. or colloids of Li, Na, K, etc. or ferrocenes, nickelo- or cobaltocenes or a cyano derivative of the type of dihydrazinodicyanodiimine;

finally, if desired,

4. 0.1 – 10 parts of other additives of the type of a plasticizer, catalyst and/or surfactant.

It should be noted that the binder is present in comparatively small amounts.

In the preparation of the solid fuels according to the invention, we may proceed in different ways.

Either the oxygen-free binder of the type indicated above is mixed at normal temperature with the triaminoguanidine and/or a derivative thereof, or the 4-aminodihydrazino-1,2,4-triazole and/or a derivative thereof, and the additives are admixed last; or,

triaminoguanidine and its derivatives or 4-aminodihydrazino-1,2,4-triazole and its derivatives are first mixed with the additives and the binder is added last; or,

the binder may first be mixed with the additives, and the triaminoguanidine or its salts, or the 4-aminodihydrazino-1,2,4-triazole or its salts are added last.

Other additives of the type of copper chromite, plasticizer and surfactant are finally added.

In the following, the invention will be more fully described by a number of examples which are given by way of illustration, but not of limitation. Parts are by weight.

EXAMPLE 1

About 25 parts of 4-aminodihydrazino-1,2,4-triazole
about 40 parts of triaminoguanidine or triaminoguanidine thiocyanate
About 25 parts of $NaAlH_4$
About 8 parts of binder
About 1–2 parts of various additives (in the nature of plasticizers, catalysts, hardeners).

EXAMPLE 2

About 67.5 parts of triaminoguanidine cyanide
About 20 parts of Mg powder
About 7.5 parts of binder
About 1-2 parts of various additives (in the nature of plasticizers, catalysts, hardeners).

EXAMPLE 3

About 10 parts of 4-aminodihydrazino-1,2,4-triazole
About 50 parts of triaminoguanidine cyanide
About 20 parts of dihydrazinodicyanodiimine
About 10 parts of binder
About 1–2 parts of various additives (in the nature of plasticizers, catalysts, hardeners).

EXAMPLE 4

About 70 parts of 4-aminodihydrazino-1,2,4-triazole
About 20 parts of Na colloid
About 10 parts of binder
About 1–2 parts of various additives (in the nature of plasticizers, catalysts, hardeners).

EXAMPLE

About 70 parts of 4-aminodihydrazino-1,2,4-triazole thiocyanate
About 25 parts of $NaAlH_4$
About 8 parts of binder
About 1–2 parts of various additives (in the nature of plasticizers, catalysts, hardeners).

EXAMPLE 6

About 30 parts of 4-aminodihydrazino-1,2,4-triazole cyanide
About 30 parts of triaminoguanidine cyanide
About 20 parts of dihydrazinodicyanidediimine
About 20 parts of $NaAlH_4$
About 8 parts of binder
About 1–2 parts of various additives (in the nature of plasticizers, catalysts, hardeners).

EXAMPLE 7

About 40 parts of 4-aminodihydrazino-1,2,4-triazole
About 50 parts of triaminoguanidine cyanide
About 20 parts of dihydrazinodicyanodiimine
About 20 parts of $NaAlH_4$
About 15 parts of binder
About 1–2 parts of various additives (in the nature of plasticizers, catalysts, hardeners).

As oxidizers we may use gaseous or liquid substances of the type of fluorine derivatives, such as ClF_3, ClF_5 and others, liquid oxygen, etc., H_2O_2, N_2O_4, preferably however HNO_3, WFNA (white fuming nitric acid), RFNA (red fuming nitric acid plus 1 percent HF) or perchloric acid which will react hypergolically with the mentioned fuels and make re-ignition possible.

The solid fuels according to the invention burn with a flame which becomes extinguished when the engine is cut off, without causing incrustations or soot deposition and without the risk of explosion. Thus, upon restarting the engine, i.e. upon renewed addition of the oxidizer, dependable re-ignition is guaranteed.

As compared to known rocket fuels, the fuels according to the invention are distinguished by an extremely high amount of hydrogen and a high amount of nitrogen in the form of hydrazine- or cyano groups, calculated on carbon. The mentioned substances generate a high combustion temperature and due to their high energy cause a considerably increased rate of reaction and therewith increased rate of propulsion.

What is claimed is:

1. A hypergolic solid propellant charge of high storage stability for hybrid rocket engines, comprising about 8–15 percent of substantially oxygen free binder comprising polyhydrocarbons and a major amount of a compound selected from the group consisting of
4-aminodihydrazine-1,2,4-triazole
4-aminodihydrazino-1,2,4-triazole acid carbonate
4-aminodihydrazino-1,2,4triazole carbonate
4-aminodihydrazino 1,2,4-tiazole thiocyanate
4-aminodihydrazino-1,2,4-tiazole cyanide
triaminoguanidine
triaminoguanidine acid carbonate
triaminoguanidine carbonate
triaminoguanidine thiocyanate
triaminoguanidine cyanide.

2. The propellant charge according to claim **1** further comprising dihydrazinodicyanodiimine.

3. The propellant charge according to claim **1**, wherein the binder is admixed with natural resins based on terpenes.

4. Solid fuel according to claim **1**, comprising
About 25 parts by weight of 4-aminodihydrazino-1,2,4-triazole
about 40 parts by weight of triaminoguanidine thiocyanate
about 25 parts by weight of $NaAlH_4$ and
about 8 parts by weight of said binder.

5. Solid fuel according to claim **1**, comprising
about 67.5 parts by weight of triaminoguanidine cyanide
about 20 parts by weight of Mg powder and
about 7.5 parts by weight of said binder.

6. Solid fuel according to claim **1**, comprising
about 10 parts by weight of 4-aminodihydrazino-1,2,4-triazole
about 50 parts by weight of triaminoguanidine cyanide
about 20 parts by weight of dihydrazinodicyanodiimine and
about 10 parts by weight of said binder.

7. Solid fuel according to claim **1**, comprising about 70 parts by weight of 4-aminodihydrazino-1,2,4-triazole thiocyanate
about 20 parts by weight of Na colloid and
about 10 parts by weight of said binder.

8. Solid fuel according to claim **1**, comprising
about 70 parts by weight of 4-aminodihydrazino-1,2,4-triazole cyanide
about 25 parts by weight of $NaAlH_4$ and
about 8 parts by weight of said binder.

9. Solid fuel according to claim **1**, comprising
about 30 parts by weight of 4-aminodihydrazino-1,2,4-triazole
about 30 parts by weight of triaminoguanidine cyanide
about 20 parts by weight of dihydrazinodicyanodiimine
about 20 parts by weight of $NaAlH_4$ and
about 8 parts by weight of said binder.

10 Solid fuel according to claim **1**, comprising
about 40 parts by weight of 4-aminodihydrazino-1,2,4-triazole
about 50 parts by weight of triaminoguanidine cyanide
about 20 parts by weight of dihydrazinodicyanodiimine
about 20 parts by weight of $NaAlH_4$ and
about 15 parts by weight of said binder.

11. A process for producing a hypergolic propellant charge for hybrid rocket engines, which comprises the steps of incorporating at normal temperature into a viscous prepolymer of a substantially oxygenfree binder comprising polyhydrocarbon a compound selected from the group consisting of
4-aminodihydrazine-1,2,4-triazole
4-aminodihydrazino-1,2,4-triazole acid carbonate
4-aminodihydrazino-1,2,4-triazole carbonate
4-aminodihydrazino-1,2,4-triazole thiocyanate
4-aminodihydrazini-1,2,4-triazole cyanide
triaminoguanidine
triaminoguanidine acid carbonate
triaminoguanidine acid carbonate
triaminoguanidine thiocyanate
triaminoguanidine cyanide mixing the said binder and said compound, while excluding oxygen, adding further high energy releasing compounds, and further admixing additives of the nature of a catalyst and a plasticizer, completely mixing the entire mixture, and finally causing hardening of the so prepared propellant.

* * * * *