

# United States Patent [19]

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## [54] HIGH-PERFORMANCE PROPELLANT COMBINATIONS FOR A ROCKET ENGINE

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### [30] Foreign Application Priority Data

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[58] Field of Search ..... **149/22, 76, 36, 88, 149/42**

### [56] References Cited

#### U.S. PATENT DOCUMENTS

3,345,821 10/1967 Magee ..... 60/214  
3,704,184 11/1972 Kuehl et al. .... 149/1  
3,730,783 5/1973 Pilipovich et al. .... 148/285  
4,405,762 9/1983 Earl et al. .... 149/109.4

## OTHER PUBLICATIONS

Dadiou et al., *Raketentreibstoffe*, pp. 109-112, 638, 675-676, Springer-Verlag, (1968).

Greleci et al., *A.R.S. Journal*, 32(8), 1189-1195, (1962), (especially 1190-1192).

Haberman, *Chemical Engineering Progress*, 68(7), 72-76, (1964).

Urbanski, *Chemistry and Technology of Explosives*, vol. 4, pp. 568-573.

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### [57] ABSTRACT

A solid high-performance propellant for a rocket engine is described. The propellant is constituted by a combination of polyglycidylazide (GAP)  $[(C_3H_5N_3O)_n]$  or poly-3,3-bis(azidomethyl)oxetane (BAMO)  $[(C_4H_6N_6O)_n]$  with boron, aluminum, or aluminum hydride ( $AlH_3$ ) and a compound selected from the group consisting of hydrazinium nitroformate ( $N_2H_5C(NO_2)_3$ ), nitronium perchlorate ( $NO_2ClO_4$ ), or ammonium perchlorate ( $NH_4ClO_4$ ), together with other conventional additives.

**2 Claims, No Drawings**

## HIGH-PERFORMANCE PROPELLANT COMBINATIONS FOR A ROCKET ENGINE

This invention relates to propellant combinations for a rocket engine. More specifically, the invention relates to a propellant combination having a high performance and which, prior to use, can be stored for a considerable time.

There is a great need for high-performance propellants which, whether or not in combination, can be stored for a considerable time, for example, in a spacecraft, and can be used not only to change the position of a spacecraft which is in space, but also for launching a spacecraft into space.

Storable combinations of propellants of the prior art, generally consisting of an oxidizer component and a fuel component, have performances inferior to those of conventional, cryogenic combinations.

Thus the specific impulse (Isp) of a rocket engine fed with a combination of dinitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) and monomethylhydrazide (N<sub>2</sub>H<sub>3</sub>CH<sub>3</sub>) is approximately 3000 m/sec, whereas cryogenic mixtures of liquid oxygen and hydrogen offer a specific impulse of more than 4000 m/sec.

The effect of specific impulse on spacecraft payload capabilities is dramatic. If, for example, a velocity of 2000 m/sec is required for bringing a spacecraft into orbit, or for changing a given orbit, then with a specific impulse of 2943 m/sec, half of the spacecraft launch mass would consist of propellant. Raising the specific impulse to 4415 m/sec would reduce the propellant mass to 37.5%. As the mass of the propulsion system itself would not have to be changed materially, this freely available mass of 12.5% could be used completely for orbiting means of telecommunication etc. For a spacecraft of 2000 kg, this means an increase in payload by 250 kg.

The invention is based on the proposition of developing a propellant combination that can be stored for a prolonged period of time prior to use and is capable of providing a specific impulse which is at least equal to, or exceeds that obtainable by known combinations. The search was directed in particular to solid propellant combinations.

The combustion pressure and ex ratio between the throat and the mouth of the nozzle

$$\left( \frac{A_e}{A_t} \right)$$

for present, (pressure-fed) rocket engines are (approximately) as follows:

| Propellant | Combustion pressure<br>MPa | Expansion ratio |
|------------|----------------------------|-----------------|
| liquid     | 1                          | 125             |
| solid      | 10                         | 100             |
| hybrid     | 1                          | 125             |

For new rocket engines to be developed, a (pumped) combustion chamber pressure of 15 MPa and an expansion ratio of 750 are foreseen.

The search for the novel combinations was carried out with particular regard to the above operating conditions.

As is well known, the theoretical performance of a propellant or propellant combination can generally be expressed by the following formula:

$$I_{sp} = \sqrt{2\gamma \cdot (\gamma - 1)^{-1} \cdot R_o \cdot T_c \cdot M^{-1} \left[ 1 - \left( \frac{P_e}{P_c} \right)^{\frac{\gamma - 1}{\gamma}} \right]}$$

where

$\gamma$  is the specific heat ratio,  $C_p/C_v$ ,

$R_o$  is the universal gas constant,

$T_c$  is the flame temperature,

$M$  is the mean molar mass of combustion products,

$P_c$  is the combustion chamber pressure, and

$P_e$  is the nozzle exit pressure.

This equation shows that the specific impulse is directly proportional to the square root of the chamber temperature and inversely proportional to the square root of the mean molecular mass of the combustion products, while the  $C_p/C_v$  ratio also affects the specific impulse.

The combustion chamber temperature is primarily determined by the energy released during the combustion of the propellant components and the specific heat of the combustion products:

$$T_c = \frac{\Delta H}{C_p}$$

Because

$$\frac{C_p}{C_v} = \frac{C_v = \frac{R_o}{M}}{C_v} = \frac{C_p}{C_p - \frac{R_o}{M}}$$

the most important parameters affecting the performance of the propellant are  $M$ ,  $C_p$  and  $\Delta H$ . One of the specific objects of the present invention is to provide a solid propellant combination, the use of which leads to the combination of these parameters having an optimum value while neither the starting materials, nor the reaction products involve unacceptable risks for men and the environment. The solid propellant combination according to this invention is constituted by a combination of polyglycidyl azide ( $[(C_3H_5N_3O)]_n$ ) or poly-3,3-bis-(azidomethyl)oxetane ( $[(C_4H_6N_6O)]_n$ ) with boron, aluminium, or aluminium hydride and a compound selected from the group consisting of hydrazinium nitroformate ( $N_2H_5C(NO_2)_3$ ), nitronium perchlorate ( $NO_2 \cdot ClO_4$ ) or ammonium perchlorate ( $NH_4ClO_4$ ).

The compounds referred to will also be designated by the following acronyms hereinafter:

Dinitrogen tetroxide : NTO

55 Tetranitromethane : TNM

Polyglycidyl azide : GAP

Poly 3,3-bis-(azidomethyl)oxetane : BAMO

Hydrazinium nitroformate : HNF

Nitronium perchlorate : NP

60 Ammonium perchlorate : AP

Hydroxy-terminated polybutadiene : HTPB

Monomethylhydrazine : MMH

The proportions of the components, i.e. oxydizer and fuel component, in the propellant combinations according to this invention are not critical. Generally speaking, the components are mixed with each other prior to the reaction in such proportions that the mixing ratios are around the stoichiometric ratio. In the solid propel-

lant combinations according to the invention, generally speaking an amount of no more than 20%, calculated on the total mixture, of the energetic binder (BAMO or GAP) is included.

Preferred propellant combinations according to the invention are the following:

( $\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$  (70–80%)+B (10%)+GAP or BAMO (10–20%)

$\text{NO}_2\text{ClO}_4$  (66–76%)+B (14%)+GAP or BAMO (10–20%)

$\text{NH}_4\text{ClO}_4$  (68–78%)+B (12%)+GAP or BAMO (10–20%)

$\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$  (59–69%)+Al (21%)+GAP or BAMO (10–20%)

$\text{NO}_2\text{ClO}_4$  (61–71%)+Al (19%)+GAP or BAMO (10–20%)

$\text{NH}_4\text{ClO}_4$  (57–67%)+Al (23%)+GAP or BAMO (10–20%)

$\text{NO}_2\text{ClO}_4 + \text{AlH}_3 + \text{GAP}$  or BAMO

$\text{NO}_4\text{ClO}_4 + \text{AlH}_3 + \text{GAP}$  or BAMO

Generally speaking, minor proportions, specifically up to no more than a few percent by weight, of substances such as nitrogen monoxide, phthalates, stearates, copper or lead salts, carbon black etc., are added to the propellant combinations according to the invention. These additives are known to those skilled in the art and serve to increase stability, keeping characteristics and combustion characteristics, etc. of the propellant as well as to promote their anti-corrosion properties.

The propellant combinations according to the invention are stored prior to use, using known per se techniques, with the components generally being in admixture.

The propellant combinations according to the invention are distinct from known combinations by their high performance.

Propellant combinations based on hydrazinium nitroformate (HNF), aluminium and an energetic binder such as GAP or BAMO, exhibit an improvement of the specific impulse relative to conventional ammonium perchlorate propellants of 214 m/sec. In addition, the combustion gases are much cleaner, because HNF does not contain chlorine and the environment is not burdened with hydrogen chloride gas.

By means of a computer calculation (cf. S. Gordon and B.J. McBride, Computer Program for Calculation of Complex Chemical Equilibrium Compositions,

Rocket performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations, NASA SP-273, Interim Revision, March 1976) and using the thermodynamic data of the reactants and reaction products (cf. D.R. Stull and H. Prophet, JANAF Thermochemical Tables, Second Edition, NSRDS-NBS 37, 1971 and JANAF supplements; I. Barin, O. Knacke and O. Kubaschewski, Thermochemical properties of inorganic substances, Springer-Verlag, 1977) the performances of the propellant combinations were verified. Calculations were made for both chemical equilibrium (ef) and for a "frozen flow" condition in space after the combustion chamber (ff). The values obtained are summarized in the following Table 1.

TABLE 1

| Theoretical maximum performance of a number of solid propellant combinations according to this invention. The specific impulse shown is 92% of the known value. Percentages are by weight. |          |                |                  |                |        |                           |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|----------------|------------------|----------------|--------|---------------------------|----|
| Oxidizer                                                                                                                                                                                   | Fuel     | $P_c$<br>(MPa) | $A_e/A_t$<br>(—) | max. Isp (m/s) |        | max. gain<br>in Isp (m/s) |    |
|                                                                                                                                                                                            |          |                |                  | ef             | ff     | ef                        | ff |
| 76% $\text{NH}_4\text{ClO}_4$                                                                                                                                                              | 13% Al   | 10             | 100              | 2946.5         | —      | 95.8                      | —  |
|                                                                                                                                                                                            | 11% HTPB |                |                  |                |        |                           |    |
| 70% HNF                                                                                                                                                                                    | 10% B    | 10             | 100              | 3042.3         | 2772.5 | 120.5                     | —  |
|                                                                                                                                                                                            | 20% GAP  |                |                  |                |        |                           |    |
| 66% $\text{NO}_2\text{ClO}_4$                                                                                                                                                              | 14% B    | 10             | 100              | 3067.0         | 2798.2 | —35.5                     | —  |
|                                                                                                                                                                                            | 20% GAP  |                |                  |                |        |                           |    |
| 68% $\text{NH}_4\text{ClO}_4$                                                                                                                                                              | 12% B    | 10             | 100              | 2911.0         | 2672.5 | 214.4                     | —  |
|                                                                                                                                                                                            | 20% GAP  |                |                  |                |        |                           |    |
| 59% HNF                                                                                                                                                                                    | 21% Al   | 10             | 100              | 3160.9         | —      | 16.1                      | —  |
|                                                                                                                                                                                            | 20% GAP  |                |                  |                |        |                           |    |
| 61% $\text{NO}_2\text{ClO}_4$                                                                                                                                                              | 19% Al   | 10             | 100              | 2962.6         | —      | 80.9                      | —  |
|                                                                                                                                                                                            | 20% GAP  |                |                  |                |        |                           |    |
| 57% $\text{NH}_4\text{ClO}_4$                                                                                                                                                              | 23% Al   | 10             | 100              | 3027.4         | —      |                           |    |
|                                                                                                                                                                                            | 20% GAP  |                |                  |                |        |                           |    |

It is noted that the substances constituting the components of the propellant combinations according to the invention, and some of which are known per se as a propellant component, have been described in the literature as regards both their preparation and their chemical and physical properties.

In this connection particular reference is made to the following publications:

B. Siegel and L. Schieler, *Energetics of Propellant Chemistry*, J. Wiley & Sons Inc., 1964.

S.F. Sarner, *Propellant Chemistry*, Reinhold Publishing Corporation, 1966.

R.C. Weast, *Handbook of Chemistry and Physics*, 59th Edition, CRC press, 1979.

A. Dadiou, R. Damm and E.W. Schmidt, *Raketentreibstoffe*, Springer-Verlag, 1968.

G.M. Faeth, Status of Boron Combustion Research, U.S. Air Force Office of Scientific Research, Washington D.C. (1984).

R.W. James, *Propellants and Explosives*, Noyes DATA Corp., 1974.

G.M. Low and V.E. Haury, Hydrazinium nitroformate propellant with saturated polymeric hydrocarbon binder, United States Patent, 3,708,359, 1973.

K. Klager, Hydrazine perchlorate as oxidizer for solid propellants, *Jahrestagung* 1978, 359–380.

L.R. Rothstein, *Plastic Bonded Explosives Past, Present and Future*, *Jahrestagung* 1982, 245–256.

M.B. Frankel and J.E. Flanagan, Energetic Hydroxy-terminated Azido Polymer, U.S. Pat. No. 4,268,450, 1981.

G.E. Manser, *Energetic Copolymers and method of making some*, U.S. Pat. No. 4,483,978, 1984.

M.B. Frankel and E.R. Wilson, Tris (2 - axidoethyl) amine and method of preparation thereof, U.S. Pat. No. 4,449,723, 1985.

What we claim is:

1. A solid propellant combination for a rocket engine, comprising a combination of polyglycidylazide (GAP)  $[(C_3H_5N_3O)_n]$  or poly-3,3-bis(azidomethyl)oxetane (BAMO)  $[(C_4H_6N_6O)_n]$  with boron, aluminium, or aluminium hydride ( $AlH_3$ ) and a compound selected from the group consisting of hydrazinium nitroformate ( $N_2H_5C(NO_2)_3$ ), nitronium perchlorate ( $NO_2ClO_4$ ), and ammonium perchlorate ( $NH_4ClO_4$ ),.

2. A solid propellant combination as claimed in claim 1, selected from the group consisting of

$N_2H_5C(NO_2)_3$  (70-80%) + (10%) + GAP or BAMO (10-20%),

5  $NO_2ClO_4$  (66-76%) + B (14%) + GAP or BAMO (10-20%),

$NH_4ClO_4$  (68-78%) + B (12%) + GAP or BAMO (10-20%),  $N_2H_5C(NO_2)_3$  (59-69%) + Al + (21%)

10 + GAP or BAMO (10-20%),  $NO_2ClO_4$  (61-71%) + Al (19%) + GAP or BAMO (10-20%),

$NH_4ClO_4$  (57-67%) + Al (23%) + GAP or BAMO (10-20%),  $NO_2ClO_4$   $AlH_3$  + GAP or BAMO, and

$NO_4ClO_4$  +  $AlH_3$  + GAP or BAMO.

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