United States Patent [19]

Schöyer H. F. R. et al.

[11] Patent Number:

4,938,814

[45] Date of Patent:

Jul. 3, 1990

[54]	[54] HIGH-PERFORMANCE PROPELLANT COMBINATIONS FOR A ROCKET ENGINE								
[75]		Schöyer H. F. R., Zoetermeer; P. A. O. G. Korting, Uwintsheul; J. M. Mul, Delft, all of Netherlands							
[73]	_	European Space Agency, Paris, France							
[21]	Appl. No.: 3	376,844							
[22]	Filed:	Jul. 7, 1989							
[30] Foreign Application Priority Data									
Jul. 8, 1988 [NL] Netherlands 8801739									
[51]	Int. Cl.5	C06B 45/10							
	149/36; 149/88								
[58]	Field of Sear	. 8, 1988 [NL] Netherlands							
[56] References Cited									
U.S. PATENT DOCUMENTS									
	3,345,821 10/19	67 Magee 60/214							
3,704,184 11/1972 Kuehl, et al 149									
	3,730,783 5/19								
	3,862,864 4/19 3,995,559 12/19								
	-,,								

OTHER PUBLICATIONS

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

Greleci, et al., A.R.S. Journal, 32(8), 1189-95 (1962) (especially) 1190-92).

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

Urbanski, Chemistry and Technology of Explosives, vol. 4, pp. 568-573 Pergamon Press, (1985).

Primary Examiner—Stephen J. Lechert, Jr. Attorney, Agent, or Firm—Michael N. Meller

[57] ABSTRACT

Hybrid, high-performance propellant combinations for a rocket engine are described, characterized by being constituted by a combination of polyglycidyl axide (GAP) ($[C_3H_5N_3O]_n$), poly-3,3-bis(azidomethyl)oxetane (BAMO) ($[C_4H_6N_6O]_n$) or hydroxy-terminated polybutadiene (HTPB) with hydrazinium nitroformate ($N_2H_5C(NO_2)_3$) as a solid oxidizer and pentaborane (B_5H_9) or diborane (B_2H_6) as a fuel, together with other conventional additives.

2 Claims, No Drawings

HIGH-PERFORMANCE PROPELLANT COMBINATIONS FOR A ROCKET ENGINE

This invention relates to propellant combinations for 5 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

There is a great need for high-performance propel- 10 lants 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 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 (N2O4) and monomethylhydrazide (N₂H₃CH₃) is approximately 3000 m/sec, whereas cryogenic mixtures of liquid oxygen and hydrogen offer a specific impulse of more than 25 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 30 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 appreciably, this 35 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 45 search was directed in particular to hybrid propellant combinations.

The combustion pressure and expansion ratio between the throat and the mouth of the nozzle (A_i^{Ae}) for present; (pressure-fed) rocket engines are (approxi- 50 mately) as follows:

	Combustion pressure		
Propellant	MPa	Expansion ratio	_ 4
liquid	1	125	_
solid	10	100	
hybrid	1	125	

For new rocket engines to be developed, a (pump- 60 fed) 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:

$$Isp = \sqrt{2\gamma \cdot (\gamma - 1)^{-1} \cdot R_o \cdot T_c \cdot M^{-1} \left[1 - \left(\frac{Pe}{Pc} \right) \frac{\gamma - 1}{\gamma} \right]}$$

 γ is the specific heat ratio, C_{ν}^{Cp} ,

Ro 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.

a spacecraft which is in space, but also for launching a

15 rectly 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_{ν}^{Cp} ratio also effects the specific

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:

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

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

the most important parameters affecting the performance of the propellant are M, C_p and ΔH .

One of the specific objects of the present invention is to provide a hybrid 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 inacceptable risks for men and the enviornment.

The hybrid propellant combination according to the invention is constituted by a combination of polyglycidyl azide ([C₃H₅N₃O]n), or poly-3,3-bis(azidomethyl-)oxetane ([C₄H₆N₆O]n) or hydroxy-terminated polybutadiene, with hydrazinium nitroformate (N₂H₅C(NO₂)₃) and with pentaborane (B₅H₉) as a fuel.

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

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 hybrid propellant combinations according to the invention, good results are obtained with a quantity of no more than

3

10%, calculated on the total mixture, of the (energetic) binder (HTPB, GAP or BAMO). The above amounts of binder can provide adequate mechanical strengths.

Preferred hybrid propellant combinations according to the invention are the following:

 $N_2H_5C(NO_2)_3$ (61%)+ B_5H_9 (29%)+HTPB (10%)

N2H5C(NO2)3 (55%)+B5H9 (35%)+GAP or BAMO (10%).

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 proper-

The propellant combinations according to the invention are stored prior to use, using known per se techniques, with the individual components, oxydizer and fuel component generally being in separate tanks or combustion chamber.

The propellant combinations according to the invention are distinct from known combinations by their high performance, as evidenced by the following table.

By means of a computer calculation (cf. S. Gordon and B.J. McBride, Computer Program for Calculation 30 M. B. Frankel and E. R. Wilson, Tris (2 -axidoehtyl) 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 thermody-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 perfor- 40 mances 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.

ature 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. Dadieu, 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, U.S. Pat. No. 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 an Future, Jahrestagung 1982, 245-256.
- 25 M. B. Frankel and J. E. Flanagan, Energetic Hydroxyterminated 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.
- amine and method of preparation thereof, U.S. Pat. No. 4,449,723, 1985.

What we claim is:

- 1. A hybrid propellant combination for a rocket ennamic data of the reactants and reaction products (cf. 35 gine, comprising a combination of polyglycidyl azide (GAP) ($[C_3H_5N_3O]n$), poly-3,3-bis(azidomethyl)oxetane (BAMO) ([C₄H₆N₆O]n) or hydroxyterminated polybutadiene (HTPB) with hydrazinium nitroformate (N₂H₅C(NO₂)₃) as a solid oxidizer and pentaborane (B_5H_9) or diborane (B_2H_6) as a fuel.
 - 2. A hybrid propellant combination as claimed in claim 1, selected from the group consisting of:

 $N_2H_5C(NO_2)_3$ (61%)+ B_5H_9 (29%)+HTPB (10%),

TABLE 1

Theoretical maximum specific impulses and specific impulses at equal tank volumes (oxidizer/fuel) for some liquid and hybrid combination according to the invention. The specific impulse shown is 92% of the known value. Percentages are by

			P_c	A _e /A _t	Tank vol. ratio oxidizer/	max. I _{sp} (m/s)		equal I _{sp} tank vol. (m/s)		max. gain ² in I _{sp} (m/s)		gain in I _{sp} at eg. tank vol. (m/s) ²	
Туре	Oxidizer	Fuel	(MPa)	(-)	fuel	ef	ff	cf	ff	ef	ff	ef	ff
Liquid	71% N ₂ O ₄	29% MMH ¹	1	125	1.49	3203.4	2849.7	3097.5	2947.5	0	0	0	0
Liquid	71% N ₂ O ₄	29% MMH ¹	15	750	1.49	3376.7	3069.7	3225.2	3110.8	ō	ō	ō	Ö
Hybrid	61% HNF	29% B5H9										•	•
		10% HTPB	1	125	_	3302.6	3022.4		_	99.2	172.7	_	
Hybrid 55%	55% HNF	35% B5H9											
		10% GAP	Į	125	_	3336.2	3079.6		_	132.8	229.9	_	_

Liquid reference propellant.

Compared with reference propellant.

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 liter- 65

 $N_2H_5C(NO_2)_3(55\%) + B_2H_9(35\%) + GAP$ or BAMO (10%).