United States Patent

Mueller

[15] **3,700,393**

[45] **Oct. 24, 1972**

[54] **LIQUID BIPROPELLANT SYSTEM USING AQUEOUS HYDROXYLAMMONIUM PERCHLORATE OXIDIZER**

[72] Inventor: **Kurt F. Mueller,** Washington, D.C.

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

[22] Filed: **Nov. 28, 1969**

[21] Appl. No.: **880,458**

[52] **U.S. Cl.** **60/214,** 23/85, 60/210, 60/215, 60/216, 149/75

[51] **Int. Cl.** **C06d 5/08**

[58] **Field of Search** ...149/75; 23/85, 190 A; 60/215, 60/216, 210, 214

[56] **References Cited**

UNITED STATES PATENTS

3,420,621	1/1969	Watters et al.	23/85
2,698,512	1/1955	Schirmer et al.	149/88 X
2,698,513	1/1955	Britton et al.	149/88 X
3,026,672	3/1962	Sammons	149/88 X
3,088,272	5/1963	Stengel et al.	149/36

Primary Examiner—Leland A. Sebastian

Attorney—R. S. Sciascia, J. A. Cooke and R. J. Erickson

[57] **ABSTRACT**

A bipropellant system based on a liquid oxidizer of a concentrated aqueous hydroxylammonium perchlorate solution and a liquid fuel.

23 Claims, No Drawings

LIQUID BIPROPELLANT SYSTEM USING AQUEOUS HYDROXYLAMMONIUM PERCHLORATE OXIDIZER

BACKGROUND OF THE INVENTION

This invention relates generally to a liquid bipropellant system and more particularly to a liquid bipropellant system especially useful for underwater propulsion applications.

Among the advantages of liquid bipropellants over monopropellants is the capability to utilize the maximum energy output of a particular bipropellant system. This characteristic of bipropellants is largely due to the storage separation in different tanks of the oxidizer and fuel components of the system and concomitant relative lack of concern for the sensitivity of the system. Whereas in the case of monopropellant compositions there is an obvious high concern for sensitivity, so much infact, that in order to maintain the sensitivity at safe storage and handling levels, the maximum energy outputs of these propellant compositions must be sacrificed for considerably lower energies, and consequently well below those of most bipropellants.

In the past, the mainstay of bipropellant systems have employed a high strength aqueous hydrogen peroxide as its oxidizing component. The primary limitation of this oxidizer is that it cannot be prepackaged because it decomposes at a slow rate, generating gaseous products. Another disadvantage of aqueous hydrogen peroxide is that contamination with organic material forms explosive mixtures. The low thermal stability of aqueous hydrogen peroxide is an additional weak point which makes storage temperatures above 50°C inadvisable. Moreover, inorganic contaminants such as rust, heavy metal ions or sand decrease the thermal stability even further by catalyzing the decomposition of the oxidizer. In addition, the aqueous hydrogen peroxide is an extreme eye and skin hazard.

Another bipropellant system which has been used in the past employs fuming nitric acid as the oxidizer component. It is quite obvious that this material suffers even more greatly from the limitations of the hydrogen peroxide system, especially in the areas of handling and storage. Furthermore, in view of the substantial increase in the performance of modern ships, submarines and missiles, bipropellants having performance energetics greater than those presently available are manifestly desirable.

SUMMARY OF THE INVENTION

It is therefore one object of this invention to provide an improved bipropellant system.

It is also an object of this invention to provide a bipropellant system utilizing an oxidant component which is less hazardous than those previously available.

Another object of this invention is to provide a bipropellant system utilizing an oxidant component which is more stable as well as more thermally stable than those previously available.

A further object of this invention is to provide a bipropellant system having superior storage and handling characteristics.

A still further object of this invention is to provide a bipropellant system having greater performance energetics than those previously available.

These and other objects are achieved by providing a bipropellant system which employs a liquid oxidant comprised of an aqueous solution of hydroxylammonium perchlorate (HAP) and a compatible fuel.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The bipropellant systems of the present invention are based on a liquid oxidizer comprised of a concentrated aqueous solution of hydroxylammonium perchlorate (HAP) and a compatible liquid fuel. For ultimate high energy performance, the liquid oxidizer of this invention should be as concentrated as possible (i.e., about 90 percent by weight of HAP). For effective results the HAP concentration should not go below about 50 percent. However, for a substantially insensitive solution the concentration of the present oxidizer is within the range of from about 80 to about 85 percent by weight of HAP, preferably about 82.5 percent. Alternatively, part of the HAP in the oxidizer solution of this invention may be replaced by one or more other water-soluble oxidizers. Some of these substitute water-soluble oxidizers are for example, ammonium perchlorate, perchlorates of organic amines, such as methylammonium perchlorate, ethylenediammonium diperchlorate, quaternary ammonium perchlorates, such as tetramethylammonium perchlorate, perchlorates of substituted hydroxylamines such as methyl and ethyl hydroxylamine perchlorate, metal perchlorates such as lithium perchlorate, sodium perchlorate, magnesium perchlorate and aluminum perchlorate and perchloric acid. No more than about 50 percent by weight of the HAP should be replaced, however.

For the purposes of this invention, a large number of fuels are operable herein. For instance, operable fuels include the liquid polyhydric alcohols such as glycerin, ethylene glycol, diethylene glycol, triethylene glycol, tetramethylene glycol, ethylene glycol monoethyl ether, propylene glycol, dipropylene glycol, dimethoxytetraethylene glycol and diethylene glycol monomethyl ether; liquid monohydric alcohols such as methanol, ethanol, propanol, butanol and benzyl alcohol; ethers such as dimethyl and diethyl ether, and dioxane; liquid ketones such as acetone and methyl butyl ketone; liquid nitriles such as acetonitrile; liquid sulfoxides such as dimethylsulfoxide; liquid sulfanes such as dimethyl and diethyl sulfone and the liquid cylic sulfones such as tetrahydrothiophene-1,1-dioxide; liquid amines such as ethyl amine, diethyl, ethanol amine, hydroxylamine, substituted hydroxylamines such as methyl and ethyl hydroxylamine; and mixtures thereof. Other operable and even more preferred liquid fuels which may be used include diesel fuel, hydrocarbon fuels like benzene, jet fuels such as JP1-6 fuels, hydrazine and hydrazine derivative mixed fuels, liquid dinitrate esters such as dinitroxyethane, dinitroxypropane (Otto Fuel II), dinitroxybutane, dinitroxypentane and mixtures thereof, gelled fuels such as NOTS-Gel and commercial tall oils.

The oxidizer to fuel ratio, which is ultimately fed into the combustion chamber, for the bipropellant system of this invention may very within a wide operable range, e.g. from about 50 percent by weight oxidizer to about 50 percent by weight fuel to about 95 percent by

weight oxidizer to about 5 percent by weight fuel, depending upon particular needs and requirements. Obviously for maximum energy performance a higher percentage of oxidizer to fuel is employed.

Many additives may be added to the bipropellant system of this invention to modify its properties without departing from the present invention. For example, various stabilizers may be included within the oxidant component such as ethylenediaminetetraacetic acid, the salts thereof and similar complexing agents.

The oxidant of the present bipropellant system is also characterized by the additional desirable properties of low toxicity, the non-effect of any contamination on thermal stability and is comprised of relatively inexpensive materials.

Having generally described the invention the following examples and data are given for purposes of illustration and better understanding of the invention.

TABLE I.

Oxidizer	(Sec	% by Weight Oxidizer to Fuel	Isp (Sec)	Isp × density Sec × g/cm³)
80.8% weight aqueous HAP	Diesel	91.08 to 8.92	240.1	366.9
82.5% weight aqueous HAP	Diesel	90.91 to 9.09	242.6	374.5
82.5% weight aqueous HAP	Otto Fuel II[1]	72.47 to 27.53	239.5	370.6
82.5% weight aqueous HAP	NOTS-Gel[2]	52.00 to 48.00	271.3	441.4
90% weight H_2O_2		89.11 to 10.89	266.6	339.5
70% weight H_2O_2	Ethyl Alcohol	86.35 to 13.65	232.4	273.1

[1]propylene glycol dinitrate + dibutyl sebacate + 2,4 dinitrophenylamine

[2]powdered aluminum (60%) + [methylhydrazine (86%)+hydrazine (14%)] (36.2%) +Cab-O-Sil (colloidal silicon dioxide) (3.0%) + hydroxyethylcellulose (0.8%)

A thermal stability test was performed on an 80 percent by weight aqueous hydroxylammonium perchlorate (HAP) solution at 80°C for 30 days. The results indicated no pressure build up and the change in concentration of any of the components was negligible. A differential thermal analysis showed that exothermic decomposition of this oxidizer occurs above 210°C.

The sensitivity characteristics of 82.5 weight percent HAP solutions were investigated by several methods and the results are summarized in Table II below.

TABLE II

Sensitivity Characteristics of 82.5% Aqueous HAP Solution

Test	Result
Cavity Drop	100 Kg × cm
Card Gap at 25°C	Zero cards, 5 tests
Card Gap at 50°C	Zero cards, 5 tests
Card Gap at 75°C	Zero cards, 5 tests
Blasting Cap	Negative, 13 tests Positive, 1 test
Unconfined Burning	No detonation, 5 tests
Bullet Impact	Negative, 16 tests Pressure burst, 1 test

These results of Table II indicate the very low level of sensitivity of the oxidants of this invention.

The freezing point data of various HAP-water systems is summarized in Table III below.

TABLE III

Freezing Points of Aqueous HAP Solutions

HAP (% weight)	H_2O (% weight)	Freezing Point (°C)
10	90	−1
20	80	−5
39	61	−15
49	51	−26
59	41	−37
64	36	−51
79	21	−26
85	15	−11
90	10	+4

The densities of 80 to 85 weight percent aqueous HAP solutions were determined and the results are listed in Table IV below.

TABLE IV

Density of Aqueous HAP Solutions

HAP (% weight)	Density g/m³
80.0	1.655
82.5	1.715
85.0	1.754

The simple handling characteristics of the oxidant of this invention, i.e. concentrated aqueous HAP is one of its major advantages. A comparison is given in Table V below.

TABLE V

Handling Characteristics of Various Liquid Oxidizers

	H_2O_2 (70% or higher)	82.5% Aqueous HAP	HNO_3 (fuming)
Explosion hazard	Severe when heated initiated by blasting cap, contaminated with metal salts, organic matter, dirt	very low, no explosion hazard when contaminated or initiated with blasting cap	moderate when mixed with organic matter or reducing agents
Fire	High	None, can be used to extinguish fires	High
Skin	High irritant	Slight temporary irritant	High irritant
Eye	High irritant	Slight temporary irritant	High irritant
Material in vapor phase	hydrogen peroxide and water	Water	nitric acid and nitric oxides
Inhalation	High irritant	None	High irritant
Hazards with accidental spills	High because contamination can lead to detonation or fire	None	High because contamination can lead to fire

The bipropellant system in accordance with this invention is adapted to conventional combustion chamber feeding hardware, such as the pressurized and pumped systems of propellant feeding.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent of the United States is:

1. In a method of propulsion wherein a bipropellant system of a liquid fuel and a liquid oxidizer are fed into a combustion chamber, the improvement which comprises utilizing a bipropellant system comprising a concentrated aqueous hydroxylammonium perchlorate solution as the oxidizer component and a compatible liquid fuel.

2. The improved method of claim 1 wherein said oxidizer component is from about 50 to about 90 percent by weight hydroxylammonium perchlorate.

3. The improved method of claim 1 wherein said oxidizer component further includes a stabilizer.

4. The improved method of claim 1 wherein said compatible liquid fuel is diesel fuel.

5. The improved method of claim 1 wherein said compatible liquid fuel comprises a dinitrate ester selected from the group consisting of dinitroxyethane, dinitroxypropane, dinitroxybutane, dinitroxypentane and mixtures thereof.

6. The improved method of claim 2 wherein said oxidizer component is from about 80 to about 90 percent by weight hydroxylammonium perchlorate.

7. The improved method of claim 6 wherein said oxidizer component is about 82.5 percent by weight hydroxylammonium perchlorate.

8. In a method of propulsion wherein a bipropellant system of a liquid fuel and a liquid oxidizer are fed into a combustion chamber, the improvement which comprises utilizing a bipropellant system comprising: (1) a concentrated aqueous solution of a mixture of hydroxylammonium perchlorate and a water soluble compound selected from the group consisting of ammonium perchlorate, a perchlorate of an organic amine, a metal perchlorate and perchloric acid; and (2) a compatible liquid fuel.

9. The improved method of claim 8 wherein said perchlorate of an organic amine is selected from the group consisting of methylammonium perchlorate, ethylenediammonium diperchlorate, tetramethylammonium perchlorate, methyl hydroxylamine perchlorate and ethyl hydroxylamine perchlorate.

10. The improved method of claim 1 wherein the amount of said oxidizer varies from about 50 percent to about 95 percent and the amount of fuel varies from about 50 percent to about 5 percent; wherein the percent is a weight percentage based upon the total weight of fuel and oxidizer.

11. The improved method of claim 1 wherein said compatible liquid fuel is a compound selected from the group consisting of polyhydric alcohols and monohydric alcohols.

12. The improved method of claim 1 wherein said compatible fuel is a compound selected from the group consisting of glycerin, ethylene glycol, diethylene glycol, triethylene glycol, tetramethylene glycol, ethylene glycol monoethyl ether, propylene glycol, dipropylene glycol, dimethoxytetraethylene glycol, diethylene glycol monomethyl ether, methanol, ethanol, propanol, butanol, benzylalcohol, dimethyl ether, diethyl ether, dioxane, acetone, methyl butyl ketone, acetonitrile, dimethylsulfoxide, dimethylsulfone, diethylsulfone, tetrahydrothiophene-1, 1-dioxide, ethyl amine, ethanolamine, hydroxylamine, methyl hydroxylamine, ethylhydroxylamine, benzene, and hydrazine.

13. The improve method of claim 12 wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer, and the fuel is present is an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

14. The improved method of claim 2, wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer; and the fuel is present in an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

15. The improved method of claim 3, wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer, and the fuel is present in an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

16. The improved method of claim 4, wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer, and the fuel is present in an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

17. The improved method of claim 5, wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer, and the fuel is present in an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

18. The improved method of claim 11, wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer, and the fuel is present in an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

19. The improved method of claim 6, wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer, and fuel is present in an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

20. The improved method of claim 7, wherein said oxidizer is present in an amount from about 50 percent to about 95 percent by weight based on the total weight of fuel and oxidizer, and the fuel is present in an amount of from about 50 percent to about 5 percent by weight based on the total weight of fuel and oxidizer.

21. The improved method of claim 8 wherein said water soluble compound is present in an amount up to about 50 percent by weight based upon the total weight of said water soluble compound and said hydroxylammonium perchlorate.

22. The improved method of claim 3 wherein said stabilizer is selected from the group consisting of ethylenediaminetetracetic acid and salts thereof.

23. The improved method of claim 22 wherein said stabilizer is ethylenediaminetetracetic acid.

* * * * *