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METHOD OF ROCKET PROPULSION

2,857,737

Filed July 28, 1953

2 Sheets-Sheet 1

MELTING POINTS
TRIETHYL- and TRIMETHYL TRITHIOPHOSPHITE
BLENDS

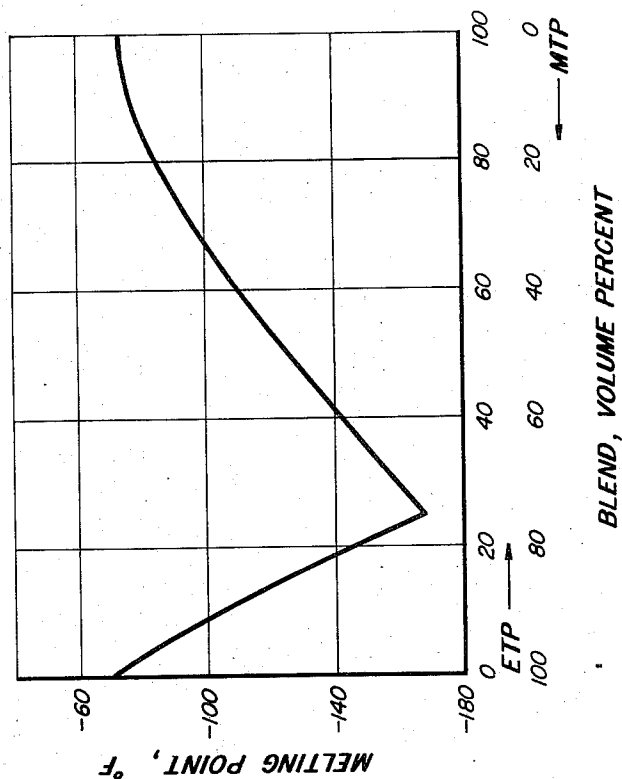


Fig. 1

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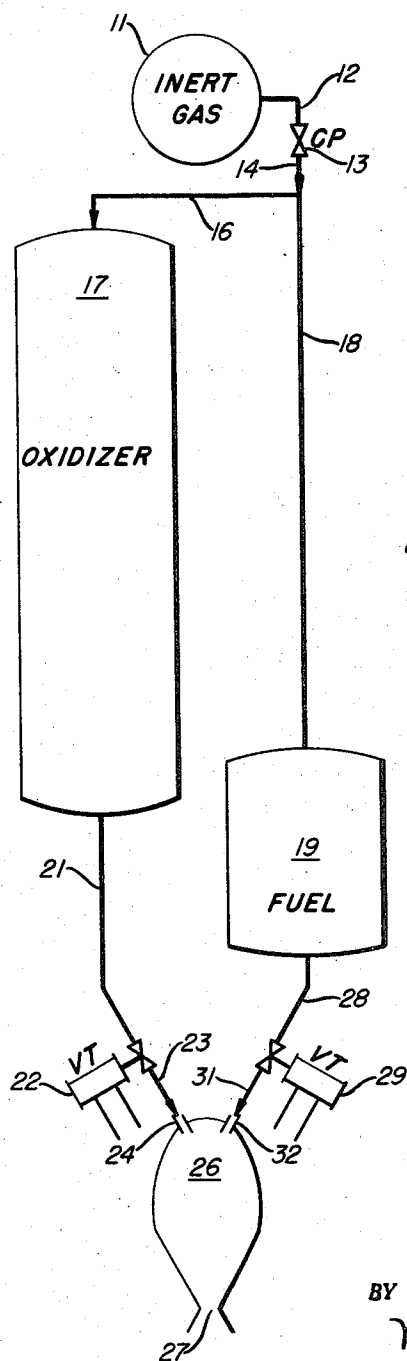
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METHOD OF ROCKET PROPULSION

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4 Claims. (Cl. 60—35.4)

This invention relates to gas generation and rocket propulsion. More particularly the invention relates to a liquid rocket fuel which has a melting point below about -100° F.

Bipropellant rockets have assumed a larger and larger place in the military and commercial fields both in missiles and in the assisted take-off of aircraft. In the bipropellant rocket a liquid fuel and a liquid oxidizer are injected separately and substantially simultaneously into the combustion chamber of the rocket motor; the fuel and oxidizer ignite hypergolically or are ignited by an external system such as a spark plug and burn to form a large volume of gases at high temperature; these gases are passed from the combustion chamber by way of an exit orifice.

A hypergolic fuel-oxidizer system is preferred because an auxiliary igniting system is thereby eliminated. In general the hypergolic activity of liquid fuels and nitric acid oxidizers decreases markedly with lowering of the temperature of the fuel and oxidizer. An air-to-air missile usually is exposed to the extreme cold of high altitudes for a period long enough to substantially attain atmospheric temperature. At the altitudes now commonly utilized by military aircraft, temperatures on the order of about -100° F. are not uncommon.

It is an object of this invention to produce a rocket fuel which has a melting point below about -100° F. Another object is a liquid rocket fuel which is characterized by a melting point of below about -100° F. and is hypergolic with nitric acid oxidizers at this temperature. Still another object is a method of gas generation by the hypergolic reaction of a nitric acid oxidizer and a liquid rocket fuel at temperatures below about -100° F.

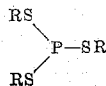
Figure 1 shows the melting points of blends of triethyl trithiophosphite and trimethyl trithiophosphite.

Figure 2 shows the schematic layout of a bipropellant rocket.

It has been found that a composition consisting essentially of between about 10 and about 65 volume percent of triethyl trithiophosphite and the remainder trimethyl trithiophosphite is characterized by a melting point below about -100° F.

The above-defined composition has a satisfactory hypergolic activity with nitric acid oxidizers, e. g., red fuming nitric acid, when the fuel and the oxidizer at the moment of contact in the gas generation chamber are at a temperature below about -100° F.

The trithiophosphites of this invention are believed to have the empirical formula R_3S_3P . Infrared analysis of very high purity trithiophosphites indicate that an equilibrium mixture may be present. This equilibrium mixture apparently consists of:



and

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70

Analyses indicate that the pentavalent phosphorus compound exists in very slight amounts, if at all. Herein the term "trithiophosphite" is intended to include not only an essentially pure trivalent phosphorus compound, but also the equilibrium mixture of the trivalent and pentavalent phosphorus compounds.

The trithiophosphites are oxidized quite readily by atmospheric oxygen. Slight amounts of oxidation products have little adverse effect on the hypergolic activity of the composition of this invention. However, small amounts of oxidation products have an extremely deleterious effect on the viscosity of the composition and therefore suitable precaution should be taken to avoid prolonged exposure to the atmosphere. However, it is intended that the term "trithiophosphite" shall also include slight amounts of these oxidation products.

The trithiophosphites may be made by the reaction of a mercaptan and phosphorus trichloride, in which case slight amounts of these materials may be present in the trithiophosphite product. When the trithiophosphite is made by the reaction of a disulfide and phosphorus, slight amounts of these materials may be present in the trithiophosphite product. The term "trithiophosphite" is intended to include the presence of slight amounts of material such as mercaptans, disulfides, etc. In general it is preferred that trithiophosphites of high purity be used in the composition of this invention.

The composition of this invention consists essentially of a mixture of triethyl trithiophosphite and trimethyl trithiophosphite. The relative proportions of these trithiophosphites are such that the composition is characterized by a melting point below about -100° F. A composition consisting essentially of between about 10 and about 65 volume percent of triethyl trithiophosphite and between about 90 and about 35 volume percent, i. e., the remainder, of trimethyl trithiophosphite is characterized by a melting point below about -100° F.

A composition consisting essentially of between about 15 and about 50 volume percent of triethyl trithiophosphite and the remainder trimethyl trithiophosphite is characterized by a melting point below -100° F., e. g., -120° F. and even lower.

Trimethyl trithiophosphite and triethyl trithiophosphite and mixtures thereof react spontaneously, i. e., are hypergolic, with nitric acid oxidizers. At about $+75^{\circ}$ F. these trithiophosphites react hypergolically with 70% nitric acid. These fuels are hypergolic at about -100° F. with 90% fuming nitric acid and with white fuming nitric acid containing 4% of potassium nitrate and 4% of water as freezing point depressors. These fuels are hypergolic at temperatures below -100° F. with red fuming nitric acid, e. g., 16% and 22% RFNA. Satisfactory hypergolic activity is obtainable at these very low atmospheric temperatures when using WFNA containing a sufficient amount of nitromethane, nitroethane and/or nitropropane to depress the melting point of the blend to about -100° F. or lower. Suitable nitric acid oxidizers are blends of nitric acid and oleum or nitric acid and alkanesulfonic acid, e. g., methanesulfonic acid. The preferred nitric acid oxidizers at these very low atmospheric temperatures are red fuming nitric acid containing at least about 16% of N_2O_4 , WFNA-oleum mixtures and WFNA-methanesulfonic acid mixtures.

Example I

The low melting points obtainable with blends of triethyl trithiophosphite (ETP) and trimethyl trithiophosphite (MTP) are illustrated below. The trithiophosphites of this example were prepared by the reaction of the corresponding disulfide and yellow phosphorus according to the method of U. S. Patent 2,542,370. These materials were carefully distilled. Infrared analysis indicated the presence of trace amounts of a pentavalent phosphorus compound. The melting points were determined by first freezing the sample by means of liquid nitrogen—seeding was necessary in some cases—and then noting the temperature range over which the solid melted. The compositions have a great tendency to supercool and freeze in the form of a glass rather than crystals; therefore, it is extremely difficult to obtain precise melting points. The data presented below represent an average of several individual determinations:

Composition, Vol. Percent		Melting Point, ° F.
ETP	MTP	
None	100	-74 to -64
25	75	-164 (Viscous)
50	50	-132 (Viscous)
75	25	-104 to -73
100	None	-77 to -72

The above data have been set out in graphical form in Figure 1. It is believed that considering the extreme difficulty of operation at these extremely low temperatures and the peculiar characteristics of the trithiophosphites that the melting point line in Figure 1 is a reasonably accurate representation of the facts.

The data show a startlingly favorable change in the melting point of the blends of ETP and MTP as compared with the high purity compounds themselves. These data show that it is perfectly feasible to operate under conditions wherein the liquid fuel is at a temperature far lower than that tolerable with either triethyl trithiophosphite or trimethyl trithiophosphite.

Example II

In this example the hypergolic activity of the high purity trithiophosphites and various blends of the two were measured in terms of ignition delay. The ignition delay is defined as the time between mixing the fuel and the oxidizer and the visible ignition thereof. The ignition delay in this example was determined by means of an apparatus which permitted the measurement of the ignition delay in milliseconds. In this example the oxidizer was red fuming nitric acid containing 22% of N_2O_4 . The ignition delays were determined by cooling the fuel and the oxidizer to the desired temperature before mixing the two. The data derived in these tests are set out below:

Composition, Vol. Percent		Ignition Delay, Milliseconds		
ETP	MTP	-40° F.	-65° F.	-80° F.
0	100	7.6	7.9	12.9
10	90	-----	8.7	-----
20	80	9.7	6.4	16.1
30	70	-----	7.7	-----
50	50	9.9	-----	-----
100	0	9.4	18.0	20.6

It is considered that an ignition delay of 75 milliseconds is satisfactory for missile usage. A delay of below about 50 milliseconds is desired. It is apparent that the ignition delays of the compositions of this in-

vention are more than satisfactory for very low temperature operation.

By way of illustration the composition of this invention is applied to the propulsion of an air-to-air missile. Figure 2 which forms a part of this specification shows schematically the bipropellant fuel system, the motor and other parts of such a missile.

In Figure 2 vessel 11 contains a quantity of gas at high pressure; this gas must be inert with respect to the oxidizer and the fuel; suitable gases are nitrogen and helium. Herein helium is used as the inert gas. Helium from vessel 11 is passed through line 12 and through valve 13 which regulates the flow of gas to maintain a constant pressure beyond valve 13. From valve 13 helium is passed through lines 14 and 16 into vessel 17 and simultaneously through line 18 into vessel 19.

Vessel 17 contains the oxidizer. Helium pressure forces the oxidizer out of vessel 17 through line 21 to valve 22. Valve 22 is a solenoid actuated throttling valve. Suitable electrical lines connect valve 22 to an electrical source and operating switch (not shown) at the control panel of the aircraft. The oxidizer is passed through line 23 and injector 24 into combustion chamber 26. Combustion chamber 26 is provided with an outlet nozzle 27.

Vessel 19 contains the fuel. Vessels 17 and 19 are constructed to withstand the high pressure imposed by the helium gas. The gas pressure forces fuel from vessel 19 through line 28 to solenoid actuated throttling valve 29. Valve 29 is similar in construction and in actuation to valve 22. The fuel is passed through line 31 and injector 32 into combustion chamber 26.

Valves 22 and 29 are of such a size and setting that a predetermined ratio of oxidizer-to-fuel is passed into combustion chamber 26. Injectors 24 and 32 are so arranged that the streams of oxidizer and fuel converge and contact each other forcibly, resulting in a very thorough intermingling of the fuel and the oxidizer.

The missile is launched by activating the solenoids on valves 22 and 29. In this illustration 2.5 lbs. of 22% RFNA are introduced into combustion chamber 26 per pound of fuel. Herein the fuel consists of 25 volume percent of triethyl trithiophosphite and 75 volume percent of trimethyl trithiophosphite. The oxidizer and the fuel react almost instantaneously upon contact in the combustion chamber; a large volume of very hot gas is produced in the combustion chamber, which gas escapes through orifice 27. The reaction from this expulsion of gas drives the missile toward its target.

Thus having described the invention, what is claimed is:

1. A composition suitable for use as a liquid rocket fuel at very low temperatures which consists of between about 15 and about 50 volume percent of triethyltrithiophosphite and the remainder essentially only trimethyltrithiophosphite, which composition is characterized by a melting point lower than about -120° F.

2. A composition suitable for use as a liquid rocket fuel at very low temperatures which consists of about 25 volume percent of triethyltrithiophosphite and about 75 volume percent of trimethyltrithiophosphite, which composition is characterized by a melting point lower than about -170° F.

3. A method of rocket propulsion which comprises injecting separately and substantially simultaneously into the combustion chamber of a rocket motor a nitric acid oxidizer selected from the class consisting of white fuming nitric acid containing about 4% of potassium nitrate and 4% of water and red fuming nitric acid containing at least about 16% of N_2O_4 and a liquid rocket fuel consisting of (a) between about 15 and about 50 volume percent of triethyltrithiophosphite and the remainder essentially only trimethyltrithiophosphite, in an amount and at a rate sufficient to initiate a hypergolic reaction with and to support combustion of the fuel, wherein said

method is characterized by operability at temperatures lower than -100° F.

4. The method of claim 3 wherein said fuel consists of about 25 volume percent of triethylthiophosphite and about 75 volume percent of trimethyltrithiophosphite. 5

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