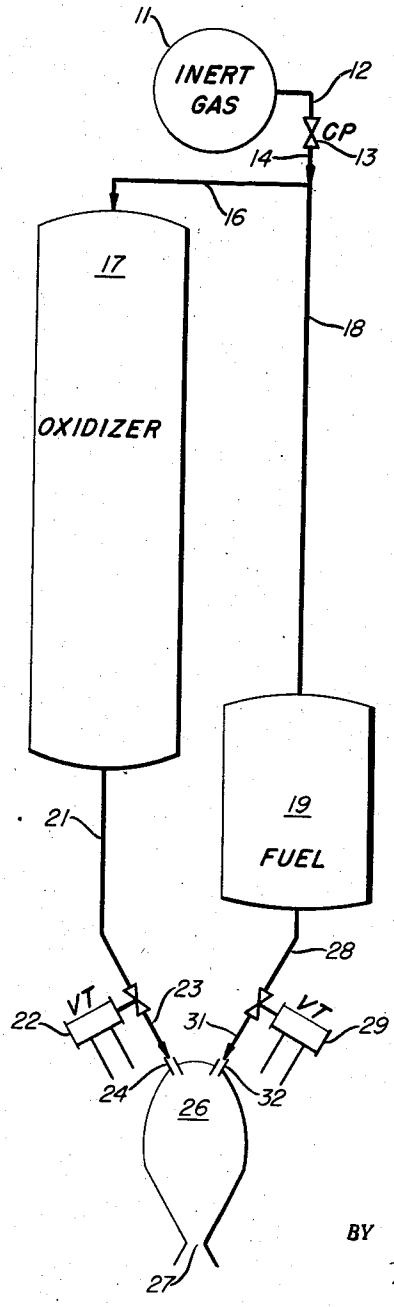
Aug. 11, 1959 D. R. CARMODY ET AL 2,898,735

ROCKET PROPULSION METHOD

Filed Aug. 12, 1954



INVENTORS:
Evan A. Mayerle
Don R. Carmody

BY Michael Dofiney

ATTORNEY

United States Patent Office 2,898,735 Patented Aug. 11, 1959

2,898,735

ROCKET PROPULSION METHOD

Don R. Carmody, Crete, and Evan A. Mayerle, Lansing, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application August 12, 1954, Serial No. 449,398

3 Claims. (Cl. 60—35.4)

This invention relates to the generation of gas. More particularly it relates to a method of reaction propulsion by the hypergolic reaction of a nitric acid oxidizer and a liquid fuel.

Reaction propulsion or rocket propulsion operates with a fuel system that is not dependent on atmospheric oxygen. The fuel system may consist of a single self-contained propellant, i.e., mono-propellant system or it may consist of a separate fuel and a separate oxidizer, i.e., bi-propellant system.

A bi-propellant rocket carries the fuel and the oxidizer in separate tanks. The fuel and the oxidizer are introduced separately and substantially simultaneously into the combustion chamber of the rocket motor. The gaseous products of the reaction of the fuel and the oxidizer are discharged through an exit nozzle; the forward thrust is developed by the passage of these gaseous products through the nozzle. A self-igniting fuel system is preferred because of the possibilities of failure when using auxiliary methods of ignition, such as a spark plug or a glow plug. A fuel which is self-igniting or spontaneously combustionable when contacted with an oxidizer is known as a hypergolic fuel.

Temperature has an important bearing on the hypergolic activity of fuels. The earth's surface may vary in temperature from a high of about +125° F. to a low of about —65° F. Temperatures below about —30° F. are exceptional. Surface-to-air missiles or rocket driven air craft must be capable of operation at temperatures on the order of —30° F.; this means that a hypergolic reaction must take place when the temperature of the fuel and the oxidizer at the moment of initial contact in the combustion chamber are at a temperature of about —30° F. High altitude temperatures are normally on the order of —65° F. and are known to reach —100° F. An air-to-air missile must be able to operate at these very low atmospheric temperatures; that is, the fuel and the oxidizer must react hypergolically even though at the moment of initial contacting in the combustion chamber of the rocket motor they are at a temperature of about —65° F. or even lower.

An object of the invention is a method of generating gas by the hypergolic reaction of a fuel and a nitric acid oxidizer. Another object is a method of reaction propulsion or rocket propulsion by the use of the hypergolic reaction of a fuel and a nitric acid oxidizer. Still another object is a method of rocket propulsion by the use of the hypergolic reaction of a nitric acid oxidizer and a fuel which contains appreciable amounts of hydrocarbons, particularly those hydrocarbons which are essentially non-hypergolic at ordinary temperatures. Yet another object is a novel class of organic compounds. Other objects will become apparent in the course of the detailed description of the invention.

The novel composition 2-chloro-1,3,2-oxathiaphospholane undergoes a hypergolic reaction with nitric acid oxidizers at atmospheric temperatures to produce gaseous products of decomposition. This fuel can be used in

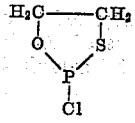
rocket propulsion by injecting the fuel and a nitric acid oxidizer separately and substantially simultaneously into the combustion chamber of a rocket motor and discharging the gaseous decomposition products from said combustion chamber through an exit nozzle.

The composition of this invention is hypergolic with nitric acid oxidizers at ordinary temperatures, such as about 75° F. At temperatures on the order of 0° F., a hypergolic reaction takes place with nitric acid oxidizers containing as much as 5 weight percent of non-acidic materials. The non-acidic materials generally are used to depress the freezing point of high purity nitric acid. The most common materials are water itself or aqueous solutions of potassium nitrate or nitrite. These non-acidic materials have an adverse influence on the hypergolic activity of the nitric acid and therefore nitric acid containing large amounts of these materials cannot be used at very low atmospheric temperatures. Commercial grade white fuming nitric acid—WFNA—which contains about 2 percent of water can be used down to its freezing point of about —40° F. WFNA is the preferred oxidizer at temperatures above its freezing point. Red fuming nitric acid, which consists of nitric acid and dissolved N_2O_4 is usable over the entire range of atmospheric temperature. In general, RFNA contains 7 percent or more of N_2O_4. For operation at very low atmospheric temperatures, i.e., below about —65° F., the preferred oxidizer is RFNA containing at least about 16 percent of N_2O_4.

Nitric acid oxidizers suitable for use at very low temperatures can be obtained by mixing WFNA with various strong oxidizing acids. A suitable nitric acid oxidizer consists of WFNA and oleum. Oleum consists of sulfuric acid and dissolved SO_3. A blend containing about 80 percent of WFNA and about 20 percent of oleum containing about 10 percent of SO_3 is suitable for use at temperatures on the order of —65° F. Blends of WFNA and alkanesulfonic acids containing not more than 4 carbon atoms in the alkane group are particularly suitable for use at very low atmospheric temperatures. For example, a blend consisting of 85 percent WFNA and 15 percent methanesulfonic acid is usable at temperatures of —73° F.; a blend consisting of 84 percent WFNA and 16 percent ethanesulfonic acid is usable at temperatures of —64° F.

It is to be understood that while all nitric acid oxidizers are not suitable for use over the entire range of atmospheric temperatures, the term "nitric acid oxidizer" is intended to include those oxidizers which are suitable at the desired temperatures of initial contacting of the fuel and the oxidizer.

The novel fuel of this invention is a heterocyclic compound having the empirical formula C_2H_4OSPCl. The structural formula is:



This compound is named: 2-chloro-1,3,2-oxathiaphospholane.

The oxathiaphospholane can be blended with liquid hydrocarbons to produce hypergolic fuels that are useful for gas generation or rocket propulsion. An economical fuel is obtained with an essentially non-hypergolic liquid hydrocarbon, i.e., one that does not react with a nitric acid oxidizer to produce a visible flame, although gaseous products may be produced, at ordinary temperature, i.e., at about 80° F. Examples of such essentially non-hypergolic liquid hydrocarbons are heptane, octane, heavy naphtha, kerosene, jet plane

fuel, diesel oil, cracked naphtha, diisobutylene, propylene tetramer, and butylene trimer.

The olefin polymers made by polymerizing butylenes or propylenes and co-polymerizing butylenes and propylenes are particularly suitable essentially non-hypergolic liquid hydrocarbons.

In general, the mixed fuel of this invention consists essentially of between about 25 and 75 volume percent of the oxathiaphospholane and the remainder a liquid hydrocarbon. For operation at very low atmospheric temperatures, it is preferred to use a fuel consisting essentially of about equal volumes of an olefin polymer containing about 8 carbon atoms and the oxathiaphospholane.

The novel composition of this invention and the results obtainable therewith are set out in the following illustrative example.

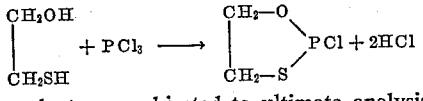
The ignition delays set out below were determined by means of an apparatus which permitted the measurement of the delay in milliseconds. (The ignition delay is defined as the time between the mixing of the fuel and the oxidizer and the appearance of a visible flame.) The delays were determined by cooling the fuel and the oxidizer separately to the desired temperature and introducing these into the apparatus which had also been cooled to the desired temperature. The WFNA used in the examples contained about 2 weight percent of water. The RFNA used in the examples contained about 22 weight percent of N_2O_4.

Example I

The apparatus consisted of a 500 ml., three-necked round bottomed flask equipped with a stirrer, a vent and an upward slanting watercooled condenser. At the upper end of the condenser was a Y tube with dropping funnels connected to the two upper arms of the Y tube.

Approximately 1.25 moles each of phosphorus trichloride and mercaptoethanol were separately added dropwise from the dropping funnels through the arms of the Y tube. As the liquids came in contact, reaction took place and the liquids entered the slanting condensed and flowed by gravity into 250 ml. of dry methylene chloride in the flask. The condenser removed some of the heat liberated in the reaction and the hydrogen chloride formed was continuously vented. During the addition (30–45 minutes) and for about 15 minutes afterwards, the methylene chloride was stirred continuously.

After addition and reaction were complete, the methylene chloride was stripped out of the reaction mixture. During this operation, a yellow-orange solid appeared in the reaction mixture. The supernatant liquid was decanted from the solid and distilled under vacuum. Approximately 16.4 grams of distillate was obtained. The reaction can be expressed by the equation:



The product was subjected to ultimate analysis. The composition was compared on the basis that the compound was 2-chloro-1,3,2-oxathiaphospholane.

	Actual	Theoretical
Carbon	17.12	16.85
Hydrogen	3.10	2.83
Chlorine	27.09	24.87
Sulfur	22.85	22.49
Phosphorous	21.15	21.73
Oxygen		11.22

The physical characteristics of the compound are:

Boiling point, ° C.	42–45 at 1.5 mm.
Melting point	Below −100° F.
Density, g./ml. at 21° C.	1.473.
Refractive index, 20° C.	1.5973.

The ignition delays of this compound were determined at various temperatures as set out in the following tabulation:

Temperature	Oxidizer	Ignition delay, milliseconds
−40° F.	WFNA	43.9
−65° F.	RFNA	15.8

Example II

In this example, blends of the oxathiaphospholane were made with diisobutylene. The diisobutylene showed no hypergolic activity with WFNA at +75° F. The ignition delays were determined visually at +75° F. when dropping th fuel into WFNA.

Blend—Percent		Ignition Delay
Oxathiaphospholane	Diisobutylene	
100	0	Very slight.
50	50	slight.
30	70	slight.
10	90	no ignition.

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

In the figure 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, 4.5 lbs. of 22% RFNA are introduced into combustion chamber **26** per pound of fuel. Herein the fuel consists of 70 volume percent of 2-chloro-1,2,3-oxathiaphospholane and 30 volume percent of diisobutylene. The oxidizer and the fuel react almost instantaneously upon contact in the combustion chamber; a large volume or 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.

The extremely good ignition delay of oxathiaphos-

pholanes makes them excellent igniter fuels. Where economy is desirable or high thrust is necessary, the main fuel may be one of relatively low hypergolic activity but possessing high thrust. Examples of these fuels are turpentines and cracked naphthas. These fuels are relatively non-hypergolic at very low atmospheric temperatures. However, once the combustion chamber of the rocket motor has been heated by the reaction of an oxidizer and a fuel, these relatively non-hypergolic fuels are able to maintain the reaction in the combustion chamber. The reaction is begun by passing into the combustion chamber an igniter fuel which is readily hypergolic at very low atmospheric temperatures. The igniter fuel and the oxidizer react to generate a large volume of those gaseous decomposition products which heat rapidly the combustion chamber. The main fuel is then injected into the hot combustion chamber and reacts under these conditions with the oxidizer to continue the gas generation. The flight of the missile is then determined by the thrust characteristics of the main fuel and the oxidizer. For example, in a small size ground-to-air missile only about a pint of igniter fuel is necessary.

It is to be understood that the fuel and the oxidizer must be contacted in a ratio sufficient to initiate the hypergolic reaction, and the ratio of fuel to oxidizer must be regulated at such a point to maintain the hypergolic reaction after it has begun. The ratio may vary over a relatively wide range, dependent on the type of fuel, the oxidizer and the initial temperature of contacting.

Thus, having described the invention, what is claimed is:

1. A method of propelling a rocket, which method comprises bringing together separately and substantially simultaneously into the combustion chamber of a rocket motor, a nitric acid oxidizer and 2-chloro-1,3,2-oxathiaphospholane and discharging the gaseous decomposition products from said combustion chamber through an exit nozzle, under conditions of temperature and oxidizer/fuel ratio such that a hypergolic reaction occurs.

2. A method of rocket propulsion, which method comprises bringing together separately and substantially simultaneously into the combustion chamber of said rocket motor a nitric acid oxidizer and a mixed fuel consisting essentially of 2-chloro-1,3,2-oxathiaphospholane, in an amount between about 25 and about 75 volume percent and the remainder a liquid hydrocarbon, and discharging gaseous decomposition products through an exit nozzle, wherein the ratio of oxidizer and fuel is sufficient to initiate and to maintain decomposition of the fuel.

3. The method of claim 2 wherein said hydrocarbon is diisobutylene.

References Cited in the file of this patent

UNITED STATES PATENTS

2,573,471	Malina et al.	Oct. 30, 1951
2,645,657	Rudel et al.	July 14, 1953
2,655,786	Carr	Oct. 20, 1953
2,693,483	Tolkmith	Nov. 2, 1954