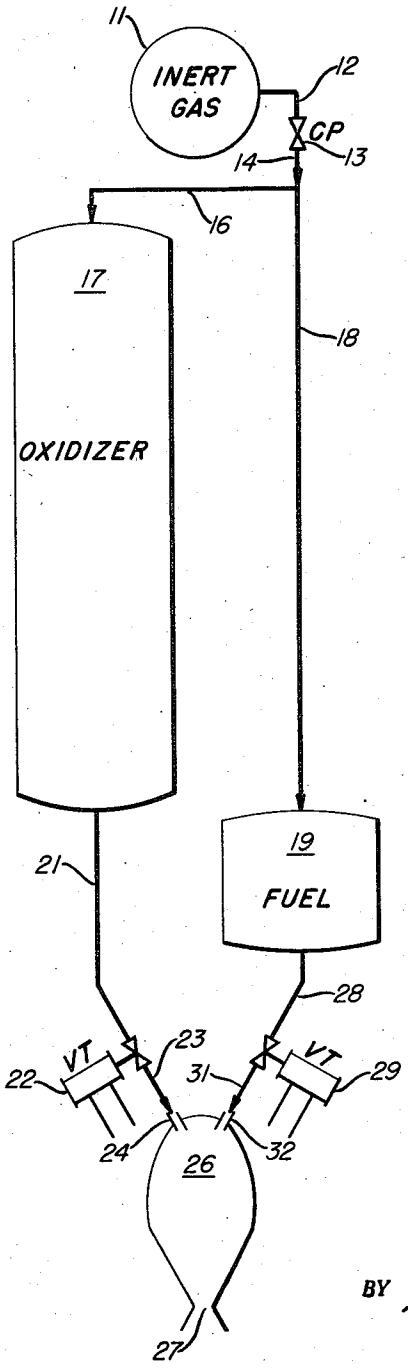
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ROCKET PROPULSION METHOD

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ROCKET PROPULSION METHOD

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This invention relates to the generation of gas. More particularly, it relates to reaction propulsion by the hypergolic reaction of a liquid fuel and a liquid oxidizer. Still more particularly, the invention relates to a method of rocket propulsion by the hypergolic reaction of a fuel and a hydrogen peroxide oxidizer, which materials spontaneously react to generate gas at high pressure and high temperature.

Reaction propulsion is now being used for many aerial purposes. For many uses it is necessary to operate with a fuel system which is not dependent on atmospheric oxygen. This fuel system may consist of a single self-contained propellant or it may consist of a separate fuel and a separate oxidizer, i.e., a bipropellant system.

In the bipropellant system the fuel and the oxidizer are introduced separately and essentially simultaneously into the combustion chamber of the reaction motor. The products of oxidation from the reaction of the fuel and the oxidizer are discharged through an orifice at the exit end of the combustion chamber and thereby produce the driving force. Because of the possibilities of electrical and/or mechanical failure of the auxiliary methods of ignition such as a spark or a hot surface, it is preferred to use a self-igniting fuel system. A fuel which is self-igniting, i.e., spontaneously combustible when contacted with an oxidizer, is known as a hypergolic fuel.

Temperature has an important effect on the hypergolic activity of fuels. The temperature at the earth's surface may vary from a high of about +125° F. to a low of as much as —65° F.; in general temperatures below about —20° or —30° F. are exceptional. Thus surface-to-air missiles or rocket-driven aircraft should be capable of operation when the temperature of the fuel and the oxidizer at the moment of initial contact in the combustion chamber of the rocket motor is on the order of —20° F. Temperatures at high altitudes are frequently on the order of —65° F. and are known to approach —100° F. Thus an air-to-air missile should be able to operate satisfactorily when the temperature of the fuel and the oxidizer at the moment of initial contacting in the combustion chamber is on the order of —65° F.

The more common oxidizers are white fuming nitric acid, red fuming nitric acid and nitric acid-sulfuric acid mixtures. While these nitric acid oxidizers operate satisfactorily over a wide range of atmospheric temperatures they have important drawbacks. The nitric acid oxidizers are extremely corrosive; they have poor storage stability; they give off toxic gases; and special precautions must be taken by personnel who handle these oxidizers.

Concentrated aqueous hydrogen peroxide solutions have excellent storage stability and do not give off harmful gas. However, these aqueous hydrogen peroxide solutions such as 90% hydrogen peroxide have the disadvantage of comparatively high freezing points, e.g., 90% hydrogen peroxide solution freezes at +12° F. The freezing point of 80% hydrogen peroxide is —9° F., but the activity of this solution toward the prior art fuels is markedly lower than the 90% H_2O_2 solution. The freezing point of aqueous hydrogen peroxide solutions can be depressed by dissolving therein inorganic salts, preferably ammonium nitrate. Thus a solution containing 40 weight percent of ammonium nitrate and in which the hydrogen peroxide-water portion contains 90 weight percent of H_2O_2 has a freezing point of about —30° F. A so-called 80% H_2O_2—30% NH_4NO_3 solution has a freezing point of below —70° F.

Concentrated aqueous hydrogen peroxide solutions have been used as monopropellants by catalytically decomposing the hydrogen peroxide, using such catalysts as potassium permanganate or copper oxide. Since the decomposition products contain free-oxygen the monopropellant system is inefficient. However, fuels which are hypergolic with nitric acid oxidizers may be much less active or even inactive with concentrated H_2O_2 solutions. Anhydrous hydrazine is usually considered to be the only fuel that is sufficiently hypergolic with concentrated H_2O_2 solutions to be practical; however, hydrazine has the disability of a comparatively high freezing point. Some fuels are operative with H_2O_2 solutions in the presence of a H_2O_2 decomposition catalyst. Furthermore, the prior art fuels are less effective with ammonium nitrate containing H_2O_2 than with H_2O_2 alone.

An object of this invention is a method of generating gas by the reaction of a fuel and a hydrogen peroxide oxidizer. Another object is a method of reaction propulsion by the hypergolic interaction of a fuel and a hydrogen peroxide oxidizer. Still another object is a method of reaction propulsion by the hypergolic interaction of a hydrogen peroxide oxidizer and a fuel which contains appreciable amounts of miscible hydrocarbons. A particular object is a method of generating gas by the interaction of a defined fuel and an oxidizer consisting of an aqueous hydrogen peroxide solution containing dissolved ammonium nitrate. Another particular object is a method of rocket propulsion by the hypergolic interaction of a defined fuel and a defined hydrogen peroxide oxidizer when the temperature of the fuel and the oxidizer is about +60° F. Other objects will become apparent in the course of the detailed description of the invention.

A method has been discovered for generating gas, which gas may be used as a substitute for compressed air for certain purposes or for driving the turbine of a jet engine or for rocket propulsion, which method comprises contacting

(1) A fuel consisting essentially of at least one member selected from the class consisting of liquid phosphorus halides and sulfur halides wherein the halogen radical is selected from the class consisting of chlorine and bromine,

(2) An oxidizer selected from the class consisting of

(I) Aqueous hydrogen peroxide solutions which contain at least about 80 weight percent of H_2O_2 and the remainder is essentially water, and

(II) Aqueous hydrogen peroxide-inorganic salt solutions wherein the hydrogen perixode-water portion contains at least about 80 weight percent of H_2O_2.

The above halides can be blended with miscible hydrocarbon to produce active mixed fuels with ammonium nitrate containing hydrogen peroxide solutions.

Certain inorganic halides ignite spontaneously when contacted with "hydrogen peroxide oxidizers." These various halides do not have equal hypergolic activity with the same oxidizer. However, by proper selection of the halide and oxidizer, it is possible to obtain a hypergolic reaction with a tolerable ignition delay when the halide and the oxidizer are at a temperature of about +60° F. at the moment of initial contact in the gas generating chamber.

Certain inorganic halides are useful for the purposes of this invention. These halides are the phosphorus halides and sulfur halides which are liquids at the temperatures suitable for hypergolic activity with hydrogen peroxide oxidizers, i.e., at temperatures above about —20° F. The halogen radicals are selected from the class consisting of chlorine and bromine. Examples of these halides are phosphorus trichloride, phosphorus tribromide, sulfur monochloride and sulfur dichloride. The phosphorus halides are preferred for lower temperature operation and for rocket propulsion.

A mixed fuel which is suitable for the generation of gas can be made by mixing a liquid phosphorus halide with a miscible hydrocarbon. An effective amount of halide must necessarily be present in the mixed fuel in order to obtain the hypergolic reaction. This amount will vary with both the type of hydrocarbon and the oxidizer. The higher the initial temperature of the fuel and the oxidizer, the more hydrocarbon tolerable in the mixed fuel. In general petroleum hydrocarbon fractions are suitable materials, for example, those fractions boiling between about 300° and 600° F. which correspond to the fuel requirement of military jet engines. Aromatic hydrocarbons which boil below about 600° F. are suitable hydrocarbons for this purpose. It is preferred to use unsaturated liquid hydrocarbons such as thermally cracked naphthas and gas oils which boil below about 600° F. or turpentine.

The oxidizers of this invention may be either concentrated aqueous hydrogen peroxide solutions or aqueous hydrogen peroxide solutions containing dissolved inorganic salts, for example, ammonium halides, sodium sulfate, sodium nitrate, etc. The concentrated aqueous hydrogen peroxide solutions should contain at least about 80 weight percent of H_2O_2; the remainder of the solution is essentially water. The hypergolic activity of the aqueous hydrogen peroxide solution is improved by increasing the concentration of the peroxide.

Concentrated aqueous hydrogen peroxide solution as made commercially is virtually only H_2O_2 and water. In order to improve storage stability small amounts of stabilizers may be added to the solution, e.g., sodium stannate, tetrasodium pyrophosphate, adipic acid, tartaric acid; in general only trace amounts of stabilizers are added so that the solution consists essentially of hydrogen peroxide and water.

In order to depress the freezing point of aqueous hydrogen peroxide solutions soluble inorganic salts are dissolved therein, e.g., sodium nitrate, ammonium chloride and ammonium nitrate have been used. These salt-containing solutions are commonly designated in terms of the weight percent of salt in the total solution and the weight percent of hydrogen peroxide present in the aqueous portion of the solution, e.g., 90% H_2O_2—40% NH_4NO_3 indicates that the total aqueous hydrogen peroxide-nitrate solution consists of 40 weight percent of ammonium nitrate and 60 weight percent of aqueous hydrogen peroxide composed of 90 weight percent of H_2O_2 and the remainder essentially water. This particular solution has a freezing point of about —30° F. A temperature of —70° F. is attainable with an 80% H_2O_2—30% NH_4NO_3 solution.

It is preferred to operate in the presence of ammonium nitrate because of the pronounced favorable effect on the hypergolic activity of the fuels of this invention.

The ignition characteristics of various fuels were studied using a "drop" test. This method utilizes a test tube, 1 in. x 4 in., containing about 0.5 ml. of oxidizer. The fuel to be tested was drawn into a hypodermic syringe. It was then ejected forcibly against the oxidizer surface by depressing the syringe plunger. By this method amounts of fuel of as little as 0.01 ml. can be added. Low temperature tests were carried out by cooling the test tube and the oxidizer contained therein by means of a bath; a drying tube inserted into the top of the test tube excluded moisture. The fuel was cooled separately to the desired test temperature. By supercooling it was possible to carry out tests at temperatures below the freezing point of the fuel and/or the oxidizer.

The "ignition delay," which is the time elapsing between the addition of fuel to the oxidizer and visual ignition thereof, was determined as either (*a*) very short which corresponds to substantially instantaneous ignition, (*b*) short which corresponds to substantially less than 1 second, and (*c*) more than 1 second, which time was determined by a stop watch.

The following tests illustrate the activity of some of the halides of this invention and of other materials with hydrogen peroxide oxidizers.

Test 1

In this test the runs were made at about +70° F. temperatures using 0.5 ml. of various H_2O_2 solutions as the oxidizer.

Run No.	Fuel	Fuel added, ml.	Oxidizer, H_2O_2, percent	Ignition delay, seconds
1	PCl_3	0.06	90	14.
2	PBr_3	0.02	90	4.
3	PBr_3	0.05	80	11.
4	S_2Cl_2	0.10	90	No ignition.[a]
5	$TiCl_4$	0.06	90	Do.[b]
6	$SiCl_4$	0.20	90	Do.
7	BCl_3	0.10	90	Do.[a]
8	Hydrazine	0.05	90	Very short.
9	do	0.03	80	Short.

[a] Vigorous effervescence.
[b] Effervescence.

Test 2

In order to observe the effect on the activity of the materials of test 1 of the presence of ammonium nitrate in the hydrogen peroxide oxidizer, runs were made at +70° F. using 0.5 ml. of aqueous hydrogen peroxide-ammonium nitrate solutions as the oxidizer.

Run No.	Fuel	Fuel added, ml.	Oxidizer H_2O_2—NH_4NO_3, percent	Ignition delay, seconds
10	PCl_3	0.03	90–5	6.
11	PCl_3	0.03	80–30	Short.
12	PBr_3	0.05	80–20	Do.
13	S_2Cl_2	0.10	90–40	32.
14	$TiCl_4$	0.06	90–40	No ignition.[a]
15	$SiCl_4$	0.20	90–40	(b).
16	Hydrazine	0.03	90–40	Very short. [c]

[a] Vigorous effervescence.
[b] Some effervescence after 4 minutes' delay.
[c] Less flame than in run 8.

These data show that the presence of ammonium nitrate in the oxidizer markedly improves the activity of the halide containing materials.

Test 3

The activity of the phosphorus halides and hydrazine at lower temperatures was tested using 0.5 ml. of various oxidizers.

Run No.	Fuel	Fuel added, ml.	Oxidizer H_2O_2—NH_4NO_3, percent	Temp., ° F.	Ignition delay, seconds
17	PCl_3	0.03	80–30	+70	Short.
18	PCl_3	0.05	80–30	−20	25.
19	PBr_3	0.05	90–40	0	24.
20	PBr_3	0.05	80–20	+70	Short.
21	PBr_3	0.10	80–20	0	23.
22	Hydrazine	0.10	80– 0	+14	No ignition (effervescence).
23	do	0.03	90– 0	+14	Very short.
24	do	0.03	90–40	+14	No ignition (effervescence).

These data show that at lower atmospheric temperatures the phosphorus halides are much more active than

is hydrazine, i.e., at these temperatures the order of activity is reversed.

It is obvious from the data presented above that this invention can be used to generate gas at high pressure. This gas can be used for operating machinery such as "compressed air hammers" or for aircraft catapults; another important use for this high pressure gas is in the starting of the turbines of jet-type engines. The invention is particularly useful for operations which require a compact power plant that is able to produce a large amount of energy over a short period of time, when the fuel and oxidizer are at moderate atmospheric temperatures. Other examples of uses of this invention are: the rocket-assisted takeoff of aircraft; boosters for surface vehicles.

The relative proportion of oxidize-to-fuel used will depend upon the type of operation, the temperature of operation and the type of fuel and oxidizer being used. When using a "80% H_2O_2—30% NH_4NO_3" solution as the oxidizer and phosphorus trichloride as the fuel, between about 1.4 and 2.5 volumes of oxidizer may be used per volume of fuel.

By way of example this invention is applied to the propulsion of a surface-to-air missile. The annexed figure which forms a part of this specification shows schematically the bipropellant feed system and the motor of this missile. This missile is suitable for operations wherein the fuel and the oxidizer can be maintained at a temperature high enough to insure at least a short ignition delay, e.g., when using the above oxidizer and fuel combination, a temperature of about +60° F.

In the drawing 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 chamber at the launching site. 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 example 2 volumes of 80%–30% solution per volume of phosphorus trichloride are introduced into the combustion chamber. 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 method of generating gas, which method comprises injecting separately and essentially simultaneously into the combustion chamber of a gas generator (1) a hypergolic fuel consisting essentially of a member selected from the class consisting of PX_3, SX_2, and S_2X_2 wherein X is selected from the class consisting of chlorine and bromine, S is sulfur and P is phosphorus and (2) an oxidizer selected from the class consisting of (*a*) aqueous hydrogen peroxide solutions consisting of at least about 80 weight percent of H_2O_2 and the remainder essentially water and (*b*) aqueous hydrogen peroxide-ammonium nitrate solutions wherein the hydrogen peroxide-water portion consists of at least about 80 weight percent of H_2O_2 and the remainder essentially water, in an amount and at a rate sufficient to initiate a hypergolic reaction with and to support combustion of the fuel.

2. The method of claim 1 wherein said fuel is phosphorus trichloride.

3. The method of claim 1 wherein said fuel is phosphorus tribromide.

4. The method of claim 1 wherein said fuel is sulfur monochloride.

5. The method of claim 1 wherein said fuel is sulfur dichloride.

6. The method of claim 1 wherein said oxidizer consists of about 80 weight percent of H_2O_2 and the remainder essentially water.

7. The method of claim 1 wherein said oxidizer consists of about 90 weight percent of H_2O_2 and the remainder essentially water.

8. The method of claim 1 wherein said oxidizer consists of a solution of hydrogen peroxide, water and ammonium nitrate, wherein the nitrate content is about 30 weight percent and the hydrogen peroxide-water portion consists of about 80 weight percent of H_2O_2 and the remainder essentially water.

9. The method of claim 1 wherein said oxidizer consists of a solution of hydrogen peroxide, water and ammonium nitrate, wherein the nitrate content is about 40 weight percent and the hydrogen peroxide-water portion consists of about 90 weight percent of H_2O_2 and the remainder essentially water.

10. A method of generating gas, which method comprises injecting separately and essentially simultaneously into the combustion chamber of a gas generator (1) a hypergolic mixed fuel consisting essentially of (I) a liquid miscible hydrocarbon and (II) a member selected from the class consisting of PX_3, SX_2 and S_2X_2 wherein X is selected from the class consisting of chlorine and bromine, P is phosphorus and S is sulfur and (2) an oxidizer selected from the class consisting of (*a*) aqueous hydrogen peroxide solutions consisting of at least about 80 weight percent of H_2O_2 and the remainder essentially water, and (*b*) aqueous hydrogen peroxide-ammonium nitrate solutions wherein the hydrogen peroxide-water portion consists of at least about 80 weight percent of H_2O_2 and the remainder essentially water, in an amount and at a rate sufficient to initiate a hypergolic reaction with and to support combustion of the mixed fuel.

11. The method of claim 10 wherein said hydrocarbon is a liquid petroleum fraction boiling over the range of 300° and 600° F.

No references cited.