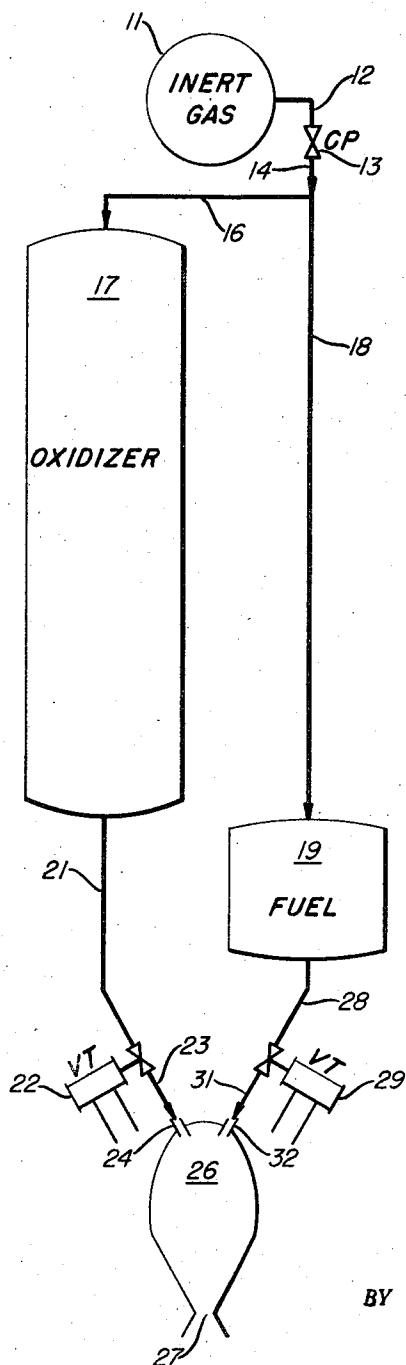


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ROCKET PROPULSION METHOD
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ROCKET PROPULSION METHOD

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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 contact 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 is markedly lower than the

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90% H₂O₂ 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 H₂O₂ has a freezing point of about -30° F. A so-called 80% H₂O₂-30% NH₄NO₃ 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 H₂O₂ solutions. Anhydrous hydrazine is usually considered to be the only fuel that is sufficiently hypergolic with concentrated H₂O₂ solutions to be practical; however, hydrazine has the disability of a comparatively high freezing point. Some fuels are operative with H₂O₂ solutions in the presence of a H₂O₂ decomposition catalyst. Furthermore, the prior art fuels are less effective with ammonium nitrate containing aqueous hydrogen peroxide than with aqueous hydrogen peroxide alone.

An object of this invention is a method of generating gas by the hypergolic 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 hydrocarbons, particularly non-hypergolic liquid hydrocarbons. A particular object is a method of generating gas by the hypergolic 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 organic sulfonyl halide and a defined hydrogen peroxide oxidizer when the fuel and the oxidizer are at lower atmospheric temperatures. 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 hypergolic fuel consisting essentially of an aliphatic sulfonyl halide containing from 1 to 4 carbon atoms wherein the halogen radical is selected from the class consisting of chlorine and bromine, and
- (2) An oxidizer selected from the class consisting of
 - (a) Aqueous hydrogen peroxide solutions which contain at least about 80 weight percent of H₂O₂ and the remainder is essentially water, and
 - (b) Aqueous hydrogen peroxide-inorganic salt solutions wherein the hydrogen peroxide-water portion contains at least about 80 weight percent of H₂O₂.

A mixed fuel which is hypergolic with hydrogen peroxide oxidizers which contain about 90 weight percent of H₂O₂ in the H₂O₂-water portion at temperatures on the order of +60° F. can be obtained by blending the more active aliphatic sulfonyl halides with a miscible hydrocarbon. The higher the temperature of operation the more hydrocarbon tolerable in the blend.

The aliphatic sulfonyl halides of this invention have a remarkable catalytic effect on the hypergolic activity with hydrogen peroxide oxidizers of alkyl mercaptans and di-

alkyl disulfides, which contain not more than 4 carbon atoms in the alkyl radical.

Certain sulfenyl halides ignite spontaneously when contacted with "hydrogen peroxide oxidizers." The various sulfenyl halides do not have equal hypergolic activity with the same oxidizer. However, by proper selection of the sulfenyl halide, it is possible to obtain a hypergolic reaction with a tolerable ignition delay when the sulfenyl halide and the oxidizer are at lower atmospheric temperatures at the moment of initial contact in the gas generating chamber.

These aliphatic sulfenyl halides have the generic empirical formula $R-S-X$ where S represents the element sulfur, X represents a halogen selected from the class consisting of chlorine and bromine, and R represents an aliphatic hydrocarbon radical containing from 1 to 4 carbon atoms.

The sulfenyl halides which are suitable for the purposes of this invention contain aliphatic hydrocarbon radicals which may be paraffinic, e.g., methyl, ethyl, propyl and butyl; or olefinic, e.g., ethenyl, propenyl, butenyl; or acetylenic, e.g., ethynyl and propynyl; and cycloaliphatic radicals, e.g., cyclopropyl, cyclopropenyl and cyclobutyl.

The most suitable sulfenyl halides for the purposes of this invention are the alkylsulfenyl halides wherein the alkyl radicals contain from 1 to 2 carbon atoms.

A mixed fuel which is suitable for the generation of gas can be made by mixing sulfenyl halides with miscible hydrocarbons. The minimum amount of sulfenyl halide necessarily present in said hypergolic mixed fuel will vary with the type of hydrocarbon, the desired temperature of operation and the type of H_2O_2 oxidizer. For example: In general petroleum hydrocarbon fractions are suitable materials as 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. The hypergolic activity of the mixed fuel can be improved at lower atmospheric temperatures by using as the hydrocarbon component olefinic hydrocarbons such as thermally cracked naphthas and gas oils or turpentine. Conversely, at higher atmospheric temperatures a hypergolic mixed fuel containing less sulfenyl halide is obtainable by the use of unsaturated hydrocarbons.

Alkyl mercaptans containing from 1 to 4 carbon atoms and dialkyl disulfides containing from 1 to 4 carbon atoms in the alkyl radical are active with hydrogen peroxide oxidizers. This activity varies from a mild hypergolicity to "reaction" as indicated by effervescence from the mixture of sulfur compound and oxidizer.

The addition of small amounts of the defined aliphatic sulfenyl halides to the defined mercaptans and disulfides results in a mixture possessing greatly increased hypergolic activity—the improvement is even more striking when using ammonium nitrate-aqueous hydrogen peroxide solutions as the oxidizer. The amount of sulfenyl halide needed will vary with the type of mercaptan and disulfide; the lower the activity toward hydrogen peroxide oxidizer the more sulfenyl halide needed to produce a fuel suitable for gas generation or rocket propulsion. When using methyl mercaptan, ethyl mercaptan, dimethyl disulfide or diethyl disulfide as the main fuel, it is preferred to have present between about 5 and 20 volume percent of methyl- or ethylsulfenyl halide, based on the blended fuel.

It is preferred to prepare the blended fuel by treating the mercaptan or disulfide main fuel with a halogenating agent selected from the class consisting of bromine, chlorine, sulfonyl chloride, SO_2Cl_2 ; sulfonyl bromide, SO_2Br_2 ; sulfinyl chloride, $SOCl_2$; and sulfinyl bromide, $SOBr_2$. Sufficient agent should be introduced into the main fuel to produce a blend containing the desired amount of sulfenyl halide. The preferred halogenating agent is sulfonyl chloride.

The oxidizers of this invention may be either concen-

trated aqueous hydrogen peroxide solutions or aqueous hydrogen peroxide solutions containing dissolved inorganic salts, for example, ammonium halides, sodium sulfate, sodium nitrate, etc.; for low temperature operation requiring a short ignition delay, ammonium nitrate must be used as the salt. 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. Commercially available 90% H_2O_2 solution is an excellent oxidizer for operation above 0° F. For low temperature operation it is preferred to use aqueous H_2O_2 -ammonium nitrate solutions, such as "90%—40%" or "80%—30%" solutions.

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 are commonly 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, potassium nitrate 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 -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 sulfenyl halides of this invention can be made from mercaptans by the method of Lecher and Holschneider Ber., 57B, 755 (1924), and Ber., 58B, 409 (1925), or in a corresponding manner using disulfide.

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 test illustrates the activity of the fuels of this invention and hydrazine with hydrogen peroxide oxidizers.

Test

A blended fuel was prepared by adding 5 volume percent of sulfonyl chloride to dimethyl disulfide at a temperature of about $+70^\circ$ F. The mixture was agitated

for a short time. This amount of SO_2Cl_2 corresponds to about 10 weight percent of methylsulphenyl chloride in the blend. The effectiveness of this "blend" and of other fuels was tested at $+70^\circ\text{F}$. using 0.5 ml. of 90% aqueous hydrogen peroxide oxidizer.

Run No.	Fuel	Fuel added, ml.	Ignition delay
1	Dimethyl disulfide	0.07	127 sec.
2	"Blend"	0.06	Short.
3	Hydrazine	0.05	Very short.
4	Ethylsulphenyl chloride ($\text{C}_2\text{H}_5\text{SO}_2\text{Cl}$)	0.10	No ignition.
5	Diethyl disulfide	0.07	No ignition (effervescence).

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 in aerial missiles which require a compact power plant that develops large amounts of energy over a very short period of time. Other examples of the use of this invention are: the rocket-assisted take-off or flight of aircraft; aerial missiles; boosters for surface vehicles.

The relative proportion of oxidizer-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 90%—40% hydrogen peroxide-ammonium nitrate solution as the oxidizer a blend of about equal parts of dimethyl disulfide and methylsulphenyl halide as the fuel, between about 3 and 4 volumes of oxidizer are needed 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., about $+30^\circ\text{F}$.

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 3.5 volumes of oxidizer per volume of fuel is 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 having the empirical formula RSX , wherein R is selected from the class consisting of aliphatic and cycloaliphatic groups containing not more than 4 carbon atoms, X is selected from the class consisting of chlorine and bromine 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 fuel.

2. The method of claim 1 wherein said fuel is methylsulphenyl chloride.

3. The method of claim 1 wherein said fuel is ethylsulphenyl bromide.

4. The method of claim 1 wherein said fuel is ethylsulphenyl chloride.

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

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

7. 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.

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 40 weight percent and the hydrogen peroxide-water portion consists of about 90 weight percent of H_2O_2 and the remainder essentially water.

9. 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 halide having the empirical formula RSX wherein R is selected from the class consisting of aliphatic and cycloaliphatic groups having not more than 4 carbon atoms, X is selected from the class consisting of chlorine and bromine, 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.

10. The method of claim 9 wherein said hydrocarbon is a liquid petroleum fraction boiling over the range of 300° and 600°F .

11. A method of generating gas, which method com-

prises injecting separately and essentially simultaneously into the combustion chamber of a gas generator (1) a hypergolic fuel consisting essentially of (a) a catalytically effective amount of a halide having the empirical formula RSX wherein R is selected from the class consisting of aliphatic and cycloaliphatic groups having not more than 4 carbon atoms, X is selected from the class consisting of chlorine and bromine and S is sulfur, and (b) a compound selected from the class consisting of aliphatic mercaptans and dialiphatic disulfides wherein the aliphatic group contains not more than 4 carbon atoms and (2) an oxidizer selected from the class 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 at 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.

12. The method of claim 10 wherein said halide is present in an amount between about 1 and 50 volume percent of said fuel.

13. The method of claim 10 wherein said halide is methylsulphenyl chloride.

14. The method of claim 13 wherein said compound is dimethyl disulfide.

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