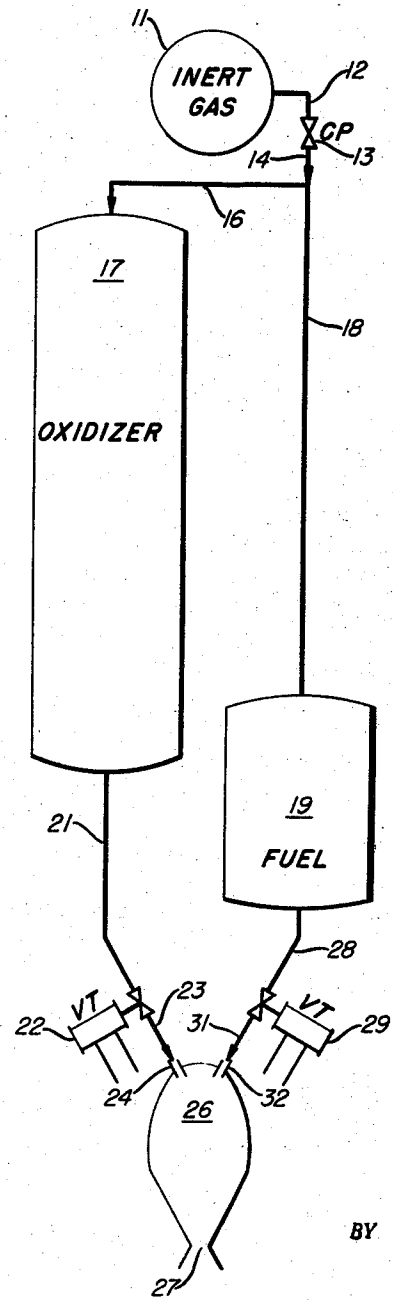
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ROCKET PROPULSION METHOD

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ROCKET PROPULSION METHOD

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This invention relates to the generation of gas. More particularly it relates to 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 aircraft 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, which hydrocarbons 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 compositions having the general formula $R_2NP(OR)_2$ wherein R is selected from the class consisting of alkyl and alkenyl and the total number of carbon atoms in the composition is not more than 16, and preferably not more than 5 carbon atoms are present in

any R group, 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 compositions of this invention are 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 nitrite or nitrate. 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 temperatures. 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 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 temperature of initial contacting of the fuel and the oxidizer.

The novel fuel of this invention has the general formula $R_2NP(OR)_2$ wherein R is selected from the class consisting of alkyl and alkenyl and the total number of carbon atoms in such fuel is not more than 16. This composition is designated hereinafter, as mono-(dialiphaticamino)-dialiphaticphosphite wherein the total number of carbon atoms is not more than 16 and the aliphatic groups are selected from the class consisting of alkyl and alkenyl. It is preferred that not more than 5 carbon atoms be present in any aliphatic group. Examples of the alkyl derivatives are mono(dimethylamino)-dimethylphosphite, mono(dimethylamino) - di-n-propylphosphite, mono(di-n-butylamino) - di-n-propylphosphite and mono(diethylamino)-dimethylphosphite. For very low temperature operation the compositions containing methyl groups, ethyl groups and mixtures thereof are preferred.

The phosphite compositions can be blended with essen-

tially non-hypergolic liquid hydrocarbons to produce hypergolic fuels that are useful for gas generation or rocket propulsion. An essentially non-hypergolic liquid hydrocarbon is defined as 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 these essentially non-hypergolic liquid hydrocarbons are heptane, octane, heavy naphtha, kerosene, jet plane fuel, diesel oil, cracked naphtha, di-isobutylene, propylene tetramer, and butylene trimer.

At ordinary temperatures, blends of saturated hydrocarbons, i.e., paraffins and cycloparaffins with the defined phosphites possess, in general, hypergolic activity substantially equal to blends of the defined phosphites and unsaturated hydrocarbons such as olefins and cycloolefins. The low temperature activity of the two blends is surprisingly different. Blends of the defined phosphites and olefins containing from about 7 to about 20 carbon atoms are much more active at low temperature than are the corresponding saturated hydrocarbons. 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 defined phosphite and the remainder an essentially non-hypergolic liquid hydrocarbon; preferably, an olefin containing between about 7 and 20 carbon atoms. 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 defined phosphite containing methyl groups only, ethyl groups only, or a mixture of methyl and ethyl groups.

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

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

Mono(dimethylamino)-di-n-propylphosphite was prepared as follows: Phosphorus trichloride was reacted with 1-propanol in pentane solution. The HCl formed in the reaction was removed with dimethylaniline. The amine salt was removed by filtration and the pentane was distilled from the reaction mixture.

The pentane-free reaction product mixture was carefully distilled under vacuum. Two fractions distilling between 115 to 130° C. and 130 to 150° C. at 120 mm. were used for the subsequent reaction. These two fractions represented about 30% of the theoretical yield of di-n-propyl chlorophosphite.

The chlorophosphite was dissolved in pentane and reacted with a very large excess of dimethylamine. The amine hydro chloride formed by reaction of the excess amine with the HCl was removed by filtration. Pentane was stripped from the filtrate and the reaction product mixture distilled under vacuum. The yield of the fraction identified as mono(dimethylamino)-di-n-propylphosphite was about 76% of theory.

The product was subjected to ultimate analysis. The composition as calculated on the basis that the compound was mono(dimethylamino)-di-n-propylphosphite is compared below with the analytical results.

	Actual, percent	Theoretical, percent
Carbon	59.5	60.6
Hydrogen	11.7	11.6
Oxygen	9.5	11.5
Nitrogen	4.9	5.1
Phosphorous	11.0	11.2

The physical characteristics of mono(dimethylamino)-di-n-propylphosphite are:

Boiling point, ° C. ---------- 88–90.5 at 18 mm.
Melting point ---------- Below −100° F.
Density, g./ml. at 20° C. ---------- 0.935.
Refractive index, 20° C. ---------- 1.4379.

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

Temperature	Oxidizer	Ignition delay, milliseconds
75° F.	WFNA	23.1
75° F.	RFNA	26.9
−40° F.	WFNA	31.7
−40° F.	RFNA	35.0
−65° F.	RFNA	38.1
−100° F.	RFNA	53.8

Example II

Mono(di-n-butylamino)-di-n-propylphosphite was prepared in the same manner as described in Example I except that the amine used was di-n-butylamine. The ultimate analysis of the product taken as the mono(di-n-butylamino)-di-n-propylphosphite and the theoretical analysis are given below:

	Actual, percent	Theoretical, percent
Carbon	51.3	49.7
Hydrogen	10.6	10.4
Oxygen	17.1	16.6
Nitrogen	5.6	7.2
Phosphorous	14.8	16.0

The physical properties of mono(di-n-butylamino)-di-n-propylphosphite are:

Boiling point, ° C. ---------- 90.5–100 at 0.3 mm.
Melting point ---------- Below −100° F.
Density, g./ml. at 20° C. ---------- 0.900.
Refractive index, 20° C. ---------- 1.4444.

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

Temperature	Oxodizer	Ignition delay, milliseconds
75° F.	WFNA	49.8.
75° F.	RFNA	71.5.
−40° F.	WFNA	69.4.
−40° F.	RFNA	No ignition

For low temperature operation an ignition delay of about 100 milliseconds is acceptable. These data indicate that this compound, which contains 14 carbon atoms, is acceptable when used with white fuming nitric acid oxidizer.

Example III

Mono(dimethylamino)-dimethylphosphite was prepared in a manner similar to that set out in Example I, except that sodium methylate was used instead of the methanol and no dimethyl aniline was used. By the use of the sodium methylate, good yields of the desired chlorophos-

phite were obtainable. The physical characteristics of the mono(dimethylamino)-dimethylphosphite are:

Boiling point, ° C.	82–90 at 120 mm.
Melting point	Below −100° F.
Density, g./ml. at 20° C.	0.963.
Refractive index, 20° C.	1.4422.

This compound is very fluid at −100° F. It supercools easily and remains fluid at temperatures far below −100° F.

The ignition delays obtained at various temperatures with this compound are set out below:

Temperature	Oxidizer	Ignition delay, milliseconds
75°	WFNA	7.7
75° F	RFNA	10.6
−40° F	WFNA	15.6
−40° F	RFNA	17.7
−65° F	RFNA	19.3
−100° F	RFNA	22.6

The defined aminophosphites react more readily with white fuming nitric acid than they do with red fuming nitric acid. This characteristic is of considerable value since WFNA is a more desirable oxidizer than RFNA because of its lower volatility and greater ease of pumping.

Example IV

In this example, blends of mono(dimethylamino)-dimethylphosphite were made with n-heptane and di-isobutylene. Each blend contained 60 volume percent of the defined aminophosphite. The n-heptane and the di-isobutylene showed no hypergolic activity with WFNA at +75° F. The ignition delays in milliseconds of the two blends at various temperatures are set out below:

Temperature	Oxidizer	n-Heptane Blend	Di-isobutylene Blend
75° F	WFNA	29.1	5.9
−40° F	WFNA	50.3	23.4
75° F	RFNA	49.6	21.1
−40° F	RFNA	50.0	33.0
−65° F	RFNA	No ignition	29.6
−100° F	RFNA	do	36.3

The mixed fuels were chilled in liquid nitrogen until they had attained a temperature well below −100° F. Both blends showed no phase separation, i.e., the two components are miscible at this low temperature. Both blends were extremely fluid at these temperatures. The di-isobutylene blend is noteworthy in that the ignition delay at very low temperature is only slightly higher than the ignition delay of the aminophosphite itself.

The data of Example IV show that a mixed fuel can be obtained which has an ignition delay of below about 100 milliseconds, preferably 50 milliseconds, that is suitable for rocket propulsion purposes at very low atmospheric temperatures.

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 bi-propellant 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 oxider.

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 45 volume percent of a mono(diethylamino)-diethylphosphite and 55 volume percent of the di-isobutylene. 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.

The extremely good ignition delay of these phosphites 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 for generating gas, which method comprises contacting, in a reaction chamber, a nitric acid oxidizer and a fuel having the general formula

$$R_2NP(OR)_2$$

wherein R is selected from the class consisting of alkyl and alkenyl and the total number of carbon atoms in said fuel is not more than 16, under conditions of temperature and oxidizer/fuel ratio such that a hypergolic reaction occurs to produce gaseous decomposition products.

2. 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 a mono(dialiphatic-amino)-dialiphaticphosphite, wherein the aliphatic groups are selected from the class of alkyl and alkenyl and the total number of carbon atoms in said phosphite is not more than 16 in an amount and at a rate sufficient to initiate a hypergolic reaction and to support combustion of the fuel, and discharging the gaseous decomposition products from said combustion chamber through an exit nozzle.

3. The method of claim 2 wherein said fuel is mono(dimethylamino)-dimethylphosphite.

4. The method of claim 2 wherein said fuel is mono(dimethylamino)-di-n-propylphosphite.

5. The method of claim 2 wherein said fuel is mono(di-n-butylamino)-di-n-propylphosphite.

6. The method of claim 2 wherein said oxidizer is white fuming nitric acid.

7. The method of claim 2 wherein said oxidizer is red fuming nitric acid.

8. A method of initiating combustion in a rocket motor, which method comprises bringing together in the combustion chamber, a nitric acid oxidizer and mono(dimethylamino)-dimethylphosphite, wherein the relative amounts of oxidizer and fuel are sufficient to initiate a spontaneous combustion of the fuel.

9. 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 (*a*) a mono(dialiphaticamino)-dialiphaticphosphite containing not more than 16 carbon atoms and wherein said aliphatic groups are selected

from the class consisting of alkyl and alkenyl, in an amount between about 25 and about 75 volume percent and (*b*) the remainder an essentially non-hypergolic liquid hydrocarbon in an amount and at a rate sufficient to initiate a hypergolic reaction and to support combustion of the fuel, and discharging gaseous decomposition products through an exit nozzle.

10. The method of claim 9 wherein said hydrocarbon is an olefin containing between about 7 and 20 carbon atoms.

11. The method of claim 9 wherein said hydrocarbon is diisobutylene.

12. A method of rocket propulsion, which method comprises bringing together 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 and red fuming nitric acid and a mixed fuel consisting essentially of about equal volumes of (*a*) mono(dimethylamino)-dimethylphosphite and (*b*) an olefin polymer containing about 8 carbon atoms, said oxidizer and said fuel being present in an amount sufficient to initiate and to maintain the spontaneous combustion of said fuel and discharging gaseous combustion products through an exit nozzle.

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