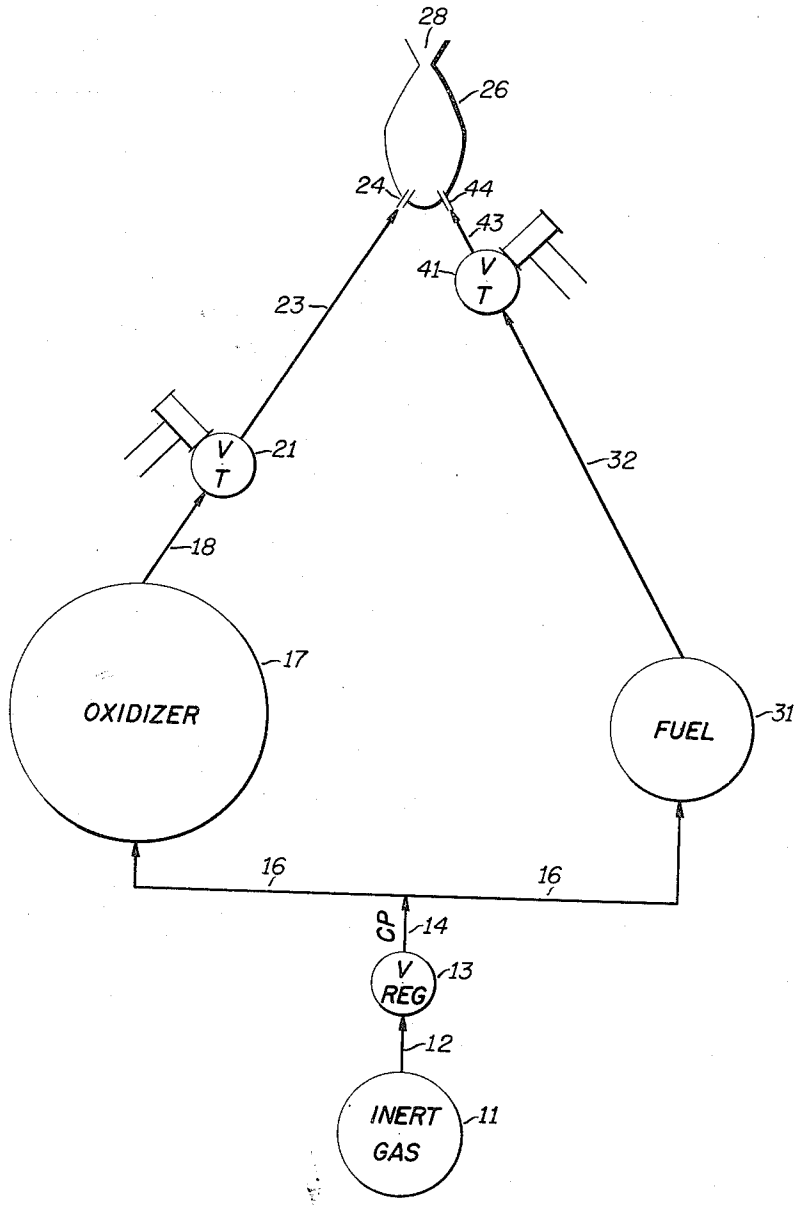
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LIQUID HYDROCARBON ROCKET FUEL

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LIQUID HYDROCARBON ROCKET FUEL

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This invention relates to reaction propulsion. More particularly, it relates to novel fuels that are spontaneously combustible, when contacted with an oxidizer, for the generation of hot gases in a rocket motor.

Rocket propulsion is now being used to assist airplanes in take-off or to attain bursts of speeds in excess of that attainable with the regular power plant. Also rocket propulsion is being used in the military projectile field, wherein an explosive container is air-borne by means of an attached rocket motor; the projectiles may be launched from the earth's surface or from an airplane in flight.

Rocket fuels, now in use, are either a single self-contained fuel—monopropellant—which may be either a solid or a liquid; or a separate fuel and a separate oxidizer—bipropellant. The bipropellant fuels are stored in separate tanks outside the rocket motor itself. The solid monopropellant fuels are stored in the combustion chamber of the rocket motor. The bipropellant rocket motor consists of a suitable combustion chamber provided with one or more pairs of nozzles adapted to inject therein the fuel and the oxidizer, separately and simultaneously. The combustion of the fuel and the decomposition of the oxidizer creates a mass of hot, burning gases which are ejected at high velocity through a suitable orifice; the reaction from this ejection provides the propulsive force. In general, the bipropellant rocket motor is more amenable to control and uses a somewhat more economical combustion chamber.

The ignition reaction between the fuel and the oxidizer may be initiated by an electric spark, a hot wire, a hot surface or may be spontaneous. A spontaneous combustion or self-ignition is preferred because of the possibilities of electrical and mechanical failure of the spark and hot surface methods of ignition. A fuel which is self-igniting when contacted with an oxidizer is called a hypergolic material.

Many materials which are hypergolic at temperatures of about +75° F. lose this property when the temperature is lowered. The temperature at the earth's surface may vary from a high of about +120° F. to a low of —40° F., and in the Polar and sub-Polar regions, to as much as —70° F. The temperature of liquids stored in ordinary tanks exposed to the sun may reach as much as +150° F. The temperatures encountered by airplanes at high altitude are often as low as —70° F. and, may be lower than —100° F. Thus a rocket motor using a hypergolic fuel may have to be started into operation with the fuel and oxidizer at a temperature as low as, or possibly lower than, —70° F. In this specification, the term "atmospheric temperatures" includes the entire range from about +120° F. to about —70° F.

An object of this invention is to obtain reaction propulsion by means of a hypergolic fuel and a nitric acid oxidizer. Another object is to provide a fuel for reaction propulsion which is hypergolic at atmospheric temperatures. Yet another object is to provide a relatively cheap

method of reaction propulsion. A particular object is a reaction propulsion method that is not dependent on auxiliary ignition devices for initiating combustion at very low temperatures.

Very briefly the hypergolic fuel of this invention consists of a liquid hydrocarbon oil boiling from about 100° to 400° F., which liquid has been derived from the light oil product of the pyrolysis of hydrocarbons at very high temperatures and at very short contact times by chilling said light oil to below at least about —10° F., preferably lower, and separating the hypergolic liquid product from the solid material.

The nitric acid oxidizers of this invention are: White fuming nitric acid—abbreviated WFNA—which normally contains less than about 2 weight percent of water. More dilute solutions have been utilized by fortifying the acid with nitrogen tetroxide—N_2O_4. Red fuming nitric acid—RFNA—normally contains less than about 5% of water and between about 5 and 20% of N_2O_4. Sodium and potassium nitrites and sodium and potassium nitrates are often added to WFNA to depress the freezing point; usually an aqueous solution of the salt is used. Liquid nitrogen tetroxide is an effective oxidizer when used above its freezing point. An excellent oxidizer for use at temperatures as low as about —65° F. is obtained by adding 10 to 30% of sulfuric acid (H_2SO_4) or about 1 to 30% of oleum to strong nitric acid. The particularly effective nitric acid oxidizers contain not more than about 5 weight percent of non-acidic material, such as, water or aqueous potassium nitrate solution. The preferred oxidizers, for very low temperature operation, are red fuming nitric acid and nitric acid-oleum mixtures. The use of the general term "nitric acid oxidizer" in this specification and in the claims is intended to include all the favorable compositions described in this paragraph.

One source of the hypergolic fuel of this invention is the light oil product from the pyrolysis of hydrocarbons in the vapor phase at temperatures from at least about 1250° to 1800° F., at pressures below about 100 p. s. i. a., usually below about 50 p. s. i. a., and at contact times from about 0.05 to 5 seconds, usually below about 2 seconds. Suitable feeds are ethane, propane, butane, propylene, butylene, naphthas, gas oils and other hydrocarbons which can be vaporized at the temperature of pyrolysis without an excessive amount of coke formation. The high temperature vapor phase pyrolytic reaction is normally used for the production of olefinic gases, such as, ethylene and propylene, and for the production of aromatic hydrocarbons, such as, benzene, toluene and xylene. In general, at a given temperature, the longer the contact time the greater the amount of aromatics produced. The gases from the cracking reaction are rapidly cooled, usually by quenching with water, to a temperature of about 400° F. A viscous tarry material condenses out of the gases during the quenching. The gases from the quenching are compressed and cooled; a light oil which boils between about 100° and 400° F. condenses out of the gases during this compression-cooling step. This light oil is commonly known as dripolene. The amount of tar and dripolene produced is dependent upon the feed, temperature, contact time and the pressure. The preferred operating conditions for the production of the hypergolic fuel of this invention are a temperature from about 1400° to 1550° F., a contact time from about 0.1 to 1 second, a pressure below about 35 p. s. i. a., and a feed consisting of ethane or propane, or mixtures thereof.

The readily condensible product is an extremely complicated mixture of hydrocarbons. The tar, which is defined as the material boiling above about 400° F., consists mainly of naphthalene and alkylated naphthalene; an appreciable amount of anthracene is present and the

remainder is thought to consist of condensed-benzene ring compounds. This tar is non-hypergolic with nitric acid oxidizers at atmospheric temperatures. The presence of tarry material in the dripolene should be avoided, because the tarry material is detrimental to hypergolic activity and has limited use at low temperatures.

The presence of a considerable amount of unsaturated linkages in the dripolene is evidenced by the maleic anhydride value of above about 60 and by the ease with which the dripolene can be resinified when using catalysts such as $AlCl_3$ or BF_3. Dripolene has never been completely analyzed because of its complexity. However, some of the components boiling below about 300° F. have been identified, to a considerable extent. These comprise minor amounts of propane, butane and pentane; some propylene and butylene; appreciable amounts of butadiene; cyclopentadiene and cyclohexadiene in fair amounts; cyclopentane and cyclopentene are also present; about one-half of the dripolene consists of benzene, toluene, xylene and ethylbenzene; styrene is present in appreciable amounts.

The material boiling above 300° F. is known to contain some dicyclopentadiene; the remainder is thought to consist of higher boiling alkylbenzenes, condensed cycloolefins and cyclodienes; in addition aromatics which have been alkylated with cycloolefins and/or cyclodienes are thought to be present. When the ASTM end point of the dripolene is about 400° F., a minor amount of naphthalene is usually also present. The presence of naphthalene is detrimental to the ferezing point of the dripolene and normally the dripolene is cut to an end point of about 375° F. to eliminate naphthalene.

Dripolene can be separated by a chilling technique into a liquid product having a freezing point about that of the temperature of separation and a product having a freezing point above the separation temperature. The chilling technique consists in cooling the dripolene until equilibrium is reached at the desired separation temperature and then separating the liquid product from the solid material by decantation, filtration or centrifuging. It has been discovered that the liquid product from chilling at at least about —10° F., preferably a lower temperatures, is hypergolic with nitric acid oxidizers. The liquid product from chilling at below about —70° F. is an extremely effective hypergolic fuel, at atmospheric temperatures, with certain nitric acid oxidizers.

While the high temperature pyrolysis of hydrocarbons, such as, ethane, propane, gas oil, etc. is the preferred source of the hypergolic fuel of this invention, other sources are available. These other sources produce in abundant supply very cheaply a light oil fraction which contains a hypergolic fuel equivalent to that obtained from dripolene. The more common sources are related to the carbonization of coal. A very good source is the light oil obtained from the carbonization of coal at low temperature, i. e., from about 1250° to 1600° F. Appreciable amounts of hypergolic fuel are obtainable from the light oil derived from the so-called high temperature carbonization of coal for the production of metallurgical coke. An excellent source is from the light oil derived from the production of coal gas, particularly when this process is carried out at from about 1250° to 1650° F.

Still another source of hypergolic fuel is the drip oil obtained from the manufacture of producer gas when using coal. An excellent source of hypergolic fuel is the drip oil obtained in the manufacture of carbureted water gas.

It is to be understood that the above list of sources of the fuel of this invention is not complete and that there are other lesser known sources. It is intended that the descriptive phrase "high temperature pyrolysis of hydrocarbons" includes all processes operating at a temperature of at least about 1250° F. to produce a light oil boiling from about 100° to 400° F., preferably below about 375° F., which light oil can be separated by chilling to —10° F., preferably below about —70° F. to obtain a liquid product having a maleic anhydride value of at least about 75.

By way of an example, a particular source of hypergolic fuel suitable for use in rocket propulsion is described below. In this particular example the feed to the pyrolysis consisted of ethane, 8 volume percent; propane, 90%; and butanes, 2%. The pressure at the inlet to the furnace was between about 35 and 45 p. s. i. g. and the exit pressure was about 11 p. s. i. g. The transfer line temperature was 1520° F. and the contact time in the high temperature zone in the furnace was about 0.2 second. The hot gases were quenched with water to eliminate tar. The dripolene fraction amounted to 3 weight percent of the product. The non-condensible product contained about 25 volume percent of ethylene and about 11 volume percent of propylene.

The dripolene was characterized as follows:

ASTM Distillation, ° F.:	
Initial	100
10%	158
20%	174
30%	186
40%	196
50%	210
60%	230
70%	264
80%	324
90%	366
Max	396
° API	35
Refractive index n_D^{20}	1.4830
Bromine number, cg. Br_2/g	89.4
Maleic anhydride value, mg. M. A./g	104.1

A sample of the dripolene was analyzed by conventional techniques for the presence of individual compounds or groups of closely related compounds. There are listed below the more or less positively identified components and the approximate amount present in volume percent.

Compound	Volume percent
Propane and propylene	0.7
Isobutane	0.1
Butylenes	2.
n-Butane	0.4
Butadiene	4.
Pentane	0.4
Pentadiene and cyclopentadiene	8.
Pentene and cyclopentene	6.
Benzene	35.
Toluene	8.
Xylenes	5.
Styrene	3.
Dicyclopentadiene	5.

The ignition characteristics of the dripolene and various fractions thereof were studied using a drop test method. This method utilizes a test tube, 1 in. x 4 in., containing 1 ml. of oxidizer. The fuel is added dropwise into the test tube by means of a syringe calibrated in 0.01 ml. markings. Usually 0.1 ml. of fuel is added per test; however, the feed usage may vary between 0.01 and 0.2 ml. per ml. of oxidizer. Low temperature tests were carried out by cooling the test tube and the oxidizer contained therein to the desired temperature by means of a dry ice-chloroform bath; a drying tube inserted into the top of the test tube excluded moisture. The fuel was cooled separately to the desired temperature. By supercooling it was possible to carry out tests at temperatures below the freezing point of the fuel and of the oxidizer. The time elapsing between the addition of the fuel to the oxidizer and ignition thereof—the ignition delay—was determined visually as either: very short, short, ig-

nition and no ignition. A very short delay corresponds to substantially instantaneous ignition.

Test 1

A sample of the dripolene described above was placed in a beaker which was immersed in a dry ice-chloroform bath. The beaker was chilled until the temperature of the dripolene had reached equilibrium at −70° F. The liquid product was then separated from the solid material by filtration. Two other samples of liquid products were obtained by chilling samples of the dripolene to −100° F. and −10° F., respectively. The hypergolic activity of the liquid product and the solid material from each dripolene separation was determined by the drop method. The test temperature was +75° F. and the oxidizer was WFNA, containing 2 weight percent of water. The results of the test are,

Chilling Temperature, ° F.	Product	Yield, Wt. Percent	Ignition
−10	Liquid	62	Short delay.
	Solid	38	None.
−70	Liquid	41	Very short delay.
	Solid	59	None.
−100	Liquid	26	Very short delay.
	Solid	74	None.

The liquid product obtained by chilling at −100° F. is slightly better in ignition delay than the liquid product from the chilling at −70° F. This fact plus the very desirably low freezing point of −100 makes the liquid product from the −100° F. chilling a preferred fuel.

The characteristics of the low freezing point hypergolic liquid products are,

	Liquid at −70° F.	Liquid at −100° F.
Boiling Range (1 atm.), ° F	100–400	100–400
Specific Gravity	0.872	0.876
Refractive Index, n_D^{20}	1.5048	1.5078
Freezing Point, ° F	<−70	<−100
Bromine Number	104.4	118.3
Maleic Anhydride Value	117.9	118.8

Test 2

The lowest temperature at which the −70° F. and −100° F. liquids from Test 1 were hypergolic with various oxidizers was determined.

	Minimum Hypergolic Temperature, ° F.	
	−70° F.	−100° F.
WFNA	+32	−20
RFNA (6.5% N_2O_4)	[1]<−65	[1]<−65
Mixed Acid [2]	[1]<−75	[1]<−75

[1] Supercooled.
[2] 80% of WFNA and 20% of 104.5% fuming sulfuric acid.

Test 3

For purposes of comparison a sample of commercial grade turpentine was measured as to hypergolic activity in the drop test at +75° F. The turpentine did not ignite with WFNA when as much as 0.2 ml. was used with 1.0 ml. of oxidizer. On the other hand only 0.15 ml. of the −70° F. liquid is required for ignition after a very short delay under the same conditions.

The invention is particularly advantageous when the fuel, oxidizer and combustion chamber are initially at atmospheric temperature as combustion begins without auxiliary ignition devices or without preheating of the combustion chamber. The nitric acid oxidizer and the fuel should be added to the combustion chamber separately and simultaneously so as to contact each other with considerable intermingling action. When using the hypergolic fuels of this invention about 3.5 to 6.0 pounds of RFNA are injected per pound of the fuel. While it is possible to vary the ratio during operation, it is preferred to maintain a constant ratio.

By way of example, this invention is applied to the driving of an air-to-air missile. The figure shows a schematic layout of the combustion chamber and bipropellant feed system of a reaction motor, such as is used in a military rocket projectile. In the figure, vessel 11 contains a quantity of inert gas under high pressure; nitrogen or helium is a suitable gas. Helium is passed through line 12, through a regulatory valve 13 which passes the helium into line 14 at a constant pressure. From line 14, the helium is passed into line 16 which is connected to the vessels containing the fuel and the oxidizer. Vessel 17 contains the oxidizer; the pressure of the helium from line 16 forces the oxidizer through line 18, through solenoid actuated throttling valve 21, through line 23, and through nozzle 24 into combustion chamber 26. Combustion chamber 26 is provided with a nozzle 28. Vessel 31 contains the main supply of fuel. The helium pressure forces the fuel out of vessel 31 through line 32, through solenoid actuated throttling valve 41, through line 43 and through nozzle 44 into combustion chamber 26. The nozzles 24 and 44 are so arranged that the streams of liquid violently impinge and thoroughly intermingle and ignite. The combustion of the fuel and the oxidizer results in the generation of a large volume of very hot gases which pass out of the combustion chamber through orifice 28; the reaction from this expulsion of gases drives the rocket.

The −100° F. fuel described in Test 1 is used in this example. The oxidizer is RFNA containing about 10% of N_2O_4; this is used because it is liquid at about −70° F. which the oxidizer and fuel will attain while being carried at high altitude by an aircraft looking for a target. The missile is launched by activating the solenoids on valves 21 and 41. The oxidizer and the fuel are forced into the combustion chamber in the weight ratio of 4.0 to 1. Instantly combustion takes place and the missile hurtles toward the target.

We claim:

1. A method of generating gas, which method comprises injecting separately and essentially simultaneously into the combustion chamber of the gas generator (1) a hypergolic liquid hydrocarbon fuel, which fuel is derived from the liquid product of the pyrolysis of a hydrocarbon selected from the class consisting of ethane, propane, butane, propylene, butylene, naphthas, and gas oils, in the vapor phase at a temperature between about 1250° and 1800° F., at a cracking zone pressure of not more than 100 p. s. i. a., for a cracking zone residence time between about 0.05 and 5 seconds, separating a liquid product from other cracking products, distilling said liquid product to obtain a light oil boiling over the range of 100° and 400° F., chilling said oil to a temperature of at least about −70° F. for a time sufficient to form a separate solid phase and removing said phase to obtain said liquid hypergolic fuel, which fuel is characterized by a freezing point of at least about −70° F., and (2) a nitric acid oxidizer containing not more than 5 weight percent of non-acidic materials, 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 oil boils over the range of 100° and 375° F.

3. The method of claim 1 wherein said oxidizer consists of red fuming nitric acid containing between about 5 and 20% of N_2O_4.

4. A method of generating gas, which method comprises injecting separately and essentially simultaneously into the combustion chamber of the gas generator (1) a hypergolic liquid hydrocarbon fuel, which fuel has been derived from the liquid product of the pyrolysis of a hydrocarbon consisting essentially of ethane in the vapor

phase at a temperature between about 1400° and 1550° F., at a cracking zone pressure of not more than about 35 p. s. i. a., for a cracking zone time between about 0.1 and 1 second, separating a liquid product from other reaction products and distilling said liquid product to obtain a light oil boiling over the range of 100° and 400° F., chilling said oil to a temperature of at least about −100° F. for a time sufficient to form a separate solid phase, and removing said solid phase to obtain said liquid hypergolic fuel, which fuel is charactized by a freezing point of at least about −100° F., and (2) a nitric acid oxidizer containing not more than about 5 weight percent of non-acidic materials, in an amount and at a rate sufficient to initiate a hypergolic reaction with and to support combustion of the fuel.

5. The method of claim 4, wherein said fuel boils over the range of 100° and 375° F.

6. The method of claim 4 wherein said oxidizer consists of red fuming nitric acid containiing between about 5 and 20% of N_2O_4.

7. The method of claim 1 wherein said oxidizer consists of 80% of white fuming nitric acid and 20% of 104.5% fuming sulfuric acid.

8. The method of claim 4 wherein said oxidizer consists of 80% of white fuming nitric acid and 20% of 104.5% fuming sulfuric acid.

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