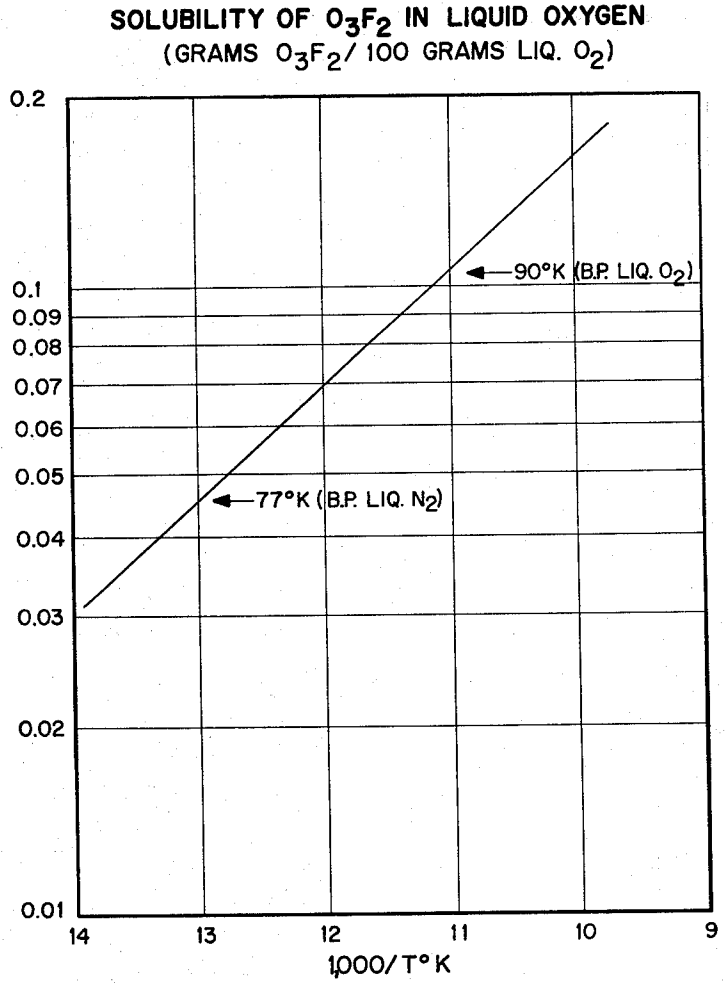
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USE OF O_3F_2 AS A HYPERGOLIC ADDITIVE FOR LIQUID OXYGEN

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USE OF O_3F_2 AS A HYPERGOLIC ADDITIVE FOR LIQUID OXYGEN

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This invention relates to a method of operating rocket engines. In particular, this invention pertains to an improvement in the operation of bipropellant liquid rocket motors and liquid oxidizer compositions especially useful in the operation of such rocket motors.

The method of operating bipropellant liquid rocket motors is old in the art. Generally, a bipropellant liquid rocket engine comprises a fuel tank, and oxidizant tank, an injection system, a combustion chamber, and an exhaust nozzle. The fuel and oxidizer are fed from their respective tanks through the injector into the combustion zone where they react to produce gases at high temperature and pressure. These gases are ejected through the exhaust, thus, producing a thrust which propels the rocket. The actual thrust produced by such a motor is obviously dependent on many variables. Illustrative of these variables are the particular fuel and oxidizer, the ratio of fuel to oxidizer, and the rate at which the oxidant and fuel are fed to the combustion chamber.

If the fuel and oxidizer are not hypergolic, then it is necessary to provide some means of igniting the propellants in the combustion chamber. The necessity of having to incorporate a means of ignition is undesirable since another possible area of rocket failure is thereby introduced. Moreover, when the fuel and oxidizer ignite spontaneously on contact, there is less possibility of an excess of fuel and oxidizer accumulating in the combustion chamber prior to ignition. Too large an excess of fuel and oxidizer when finally ignited can explode resulting in the damage or destruction of the rocket.

Most of the hypergolic fuels now available depend upon white fuming nitric acid, red fuming nitric acid, nitric acid, and mixtures of nitric and sulfuric acids as the oxdizers. Among the fuels which are hypergolic with these oxidizers are mixtures of mercaptans and alkenyl monoamines such as tertiary-butyl mercaptan, dienes such as 2-methyl-1, 3-butadiene, acetylenic compounds such as proparkyl alcohol, and ethylene imine. However, these fuels are relatively costly in comparison to the cheaper hydrocarbon fuels when the large volumes necessary for use in rockets are considered. Moreover, the acid oxidizers create many additional problems in handling, storage, and use because of their toxicity and corrosive characteristics.

One answer to the above problem is the use of liquid oxygen as the oxidizer and the inexpensive hydrocarbon fuels such as gasoline. The liquid oxygen is non-toxic and non-corrossive in addition to being superior as an oxidizer. Furthermore, the hydrocarbon fuels are easily handled and stored. Another fuel also being studied for use with liquid oxygen is liquid hydrogen. The liquid hydrogen-liquid oxygen bipropellant system can theoretically develop a specific impulse in excess of 340 seconds.

A hinderance in the bipropellant systems using liquid oxygen is the lack of practical hypergolic fuels. While sudden pressurization may cause mixtures of liquid oxygen and commercial oils or organic materials to detonate or explode, the smooth spontaneous combustion on contact at ambient pressures necessary to achieve suitable rocket propellant ignition is absent.

It has been discovered that almost any fuel including the hydrocarbons and liquid hydrogen will spontaneously ignite when brought into contact with liquid oxygen having dissolved therein a small amount of trioxygen difluoride, O_3F_2. Therefore, to the advantages of bipropellant liquid rocket systems employing liquid oxygen previously mentioned hereinabove, it is now possible to add the advantage of spontaneous ignition. This advantage precludes the necessity of an ignition means in the rocket motor or may be used as a safety factor in conjunction with other ignition means. This is of particular usefulness when it is desired to cease combustion and reignite the propellants during flight of the rocket.

In accordance with the foregoing, it is an object of the invention to set forth a composition of matter comprising trioxygen difluoride dissolved in liquid oxygen.

It is a further object of this invention to describe a means of improving the method of operating bipropellant liquid rocket engines which employ liquid oxygen as an oxidizer by substituting therefor a solution of trioxygen difluoride in liquid oxygen.

It is a still further object of this invention to describe a method of operating a bipropellant liquid rocket engine employing a solution of trioxygen difluoride in liquid oxygen and a fuel hypergolic therewith.

Another object of the invention is to stabilize combustion of the fuel in the combustion chamber of bipropellant liquid rocket motors employing liquid oxygen by adding trioxygen difluoride to the liquid oxygen.

These and other objects will become apparent from the detailed description of the invention presented hereinbelow.

The graph illustrates the solubility of trioxygen difluoride in liquid oxygen at various temperatures.

Trioxygen difluoride, or ozone fluoride as it is sometimes referred to in the prior art, is a compound melting at 83° K. into a blood-red viscous liquid having a density of 1.800 gm./ml. The compound undergoes spontaneous decomposition to dioxygen difluoride and oxygen at approximately 120° K. The dioxygen difluoride further decomposes to oxygen and fluorine at about 200° K. Trioxygen difluoride can be distilled at a pressure of 0.1 to 1.5 mm. of mercury and a temperture of 96° K. to 114° K. The pure compound can be evaporated rapidly, refluxed, or thermally decomposed without explosion. However, in contact with oxidizable matter, combustion or explosion may occur. At the boiling point of liquid nitrogen (77° K.), decomposition of trioxygen difluoride is negligible and it may be stored for extended periods as a solid at this temperature. At the boiling point of oxygen, it decomposes at the rate of about 4% each 24 hours. Trioxygen difluoride is safer and easier to handle than either ozone or fluorine since ozone is shock sensitive and fluorine is highly corrosive. An electric spark in trioxygen difluoride or solutions of trioxygen difluoride in liquid oxygen causes only smooth, slow decomposition, due to thermal energy.

The solutions of trioxygen difluoride in liquid oxygen are made by thoroughly mixing the two components. Trioxygen difluoride can be employed in an amount up to the quantity necessary to achieve a saturated solution. These amounts can be determined from the graph. For

example, at 90° K., the boiling point of oxygen, 0.11 gram of trioxygen difluoride will dissolve in each 100 milliliters of liquid oxygen; at 77° K., 0.046 grams will dissolve per 100 milliliters of liquid oxygen.

It is apparent that the temperatures of the solution during preparation and storage should preferably be maintained slightly below the boiling point of liquid oxygen to reduce loss of oxygen. Liquid nitrogen and/or liquid oxygen baths for the mixing apparatus can be employed to facilitate temperature control.

Glassware, such as Pyrex glassware, can be used as containers for storage and mixing. The solutions are best stored under an inert atmosphere such as helium. This is a safety measure to prevent contact with oxidizable materials. Moreover, the solutions are conveniently pumped under by means of helium pressure.

As would be expected from the solubility of trioxygen difluoride as shown in the graph, cooling a saturated solution, from 90° K. to 77° K. for example, results in the precipitation of the excess trioxygen difluoride. Likewise, oxygen boil-off of a saturated solution results in some trioxygen difluoride coming out of solution. For this reason, it is advisable to employ solutions containing less than the saturation quantity of trioxygen difluoride.

In practical application, the liquid oxygen-trioxygen difluoride solutions will be at the boiling point of liquid oxygen (90° K.) when in the liquid oxygen tanks of the rockets, since it is usually impractical to maintain a temperature less than this. It has been found that a solution of 0.05% by weight trioxygen difluoride in liquid oxygen will ignite spontaneously when brought in contact with most rocket fuels including amines, hydrocarbons, alkanols, and hydrogen. At this concentration, 50% of the liquid oxygen can boil from the solution at 90° K. without any precipitation of trioxygen difluoride. Furthermore, as the boil-off concentrates the solution, the percent by weight trioxygen difluoride increases. Thus, there is no loss in the ability to spontaneously ignite in contact with fuels. In fact, this ability is increased with the increase in the percent by weight trioxygen difluoride.

One particularly beneficial characteristic of the solutions of 0.05% by weight trioxygen difluoride in liquid oxygen is the density. The density difference between liquid oxygen and the trioxygen difluoride-liquid oxygen solution is less than 0.03%. Therefore, little if any design changes will be necessary in present rocket motors with the use of the solution of trioxygen difluoride in lieu of liquid oxygen.

Initial studies of the spontaneous ignition of various fuels were made by means of a series of open cup tests. Essentially this test comprised placing five cubic centimeters of the fuel to be tested in an aluminum cup. Then a few milliliters of 0.05% O_3F_2 in liquid oxygen was added. The results of such a series of tests are given below in Table I.

Table I

[Open cup tests of 0.05% of O_3F_2 with various fuels]

Fuel	Vol. of fuel, ml.	Vol. of oxidizer, ml.	Reaction time, sec.	Remarks
JP-4	5	5	3.4	Fire.
JP-4	5	10	12.4	Explosion.
UDMH (Unsymmetrical Dimethyl Hydrazine).	5	5	0	Instantaneous ignition.
U-DETA*	5	1	0	Do.
50% (by vol.) UDMH in JP-4.	5	3	0	Do.
10% (by vol.) UDMH in JP-4.	5	3	0	Do.
5% (by vol.) UDMH in JP-4.	5	5	0	Do.
1% (by vol.) UDMH in JP-4.	5	5	0	Do.

*50% by volume UDMH–50% by volume diethylene triamine.

The fuels listed in Table I are by no means all that are hypergolic with the trioxygen difluoride-liquid oxygen solutions of the invention. In fact, all fuels tested were found to be hypergolic. Any of the JP or RP type of fuels such as JP–3 and JP–4 function satisfactorily. Apparently any conventional fuel is hypergolic with the trioxygen difluoride-liquid oxygen solutions. Examples of suitable specific fuels are diethylene triamine, hydrazine, kerosene, furfuryl alcohol, aniline, orthotoluidine, trimethylamine, propargyl alcohol, ethanol, butanol, methylvinylpyridine, diethyl ether, propane, butane, and octane. It is obvious to those skilled in the art that, to be used successfully in a bipropellant rocket engine, the fuels should be liquids or gases. However, the trioxygen diflunride-liquid oxygen mixture is hypergolic with most solid combustible materials.

The results of the open cup tests clearly demonstrated that spontaneous ignition in a rocket motor is possible when a solution of trioxygen difluoride is employed. Nevertheless, to verify this conclusion and obtain more data as to the performance of the new hypergolic additive, additional tests were performed in small test motors. Typical results of these tests in 7.5 atmosphere micro-rocket motors using conventional fuels are tabulated below. Table II gives the results using a liquid oxygen oxidizer containing 0.10% by weight O_3F_2 while Table II gives the results of tests utilizing 0.05% by weight O_3F_2 in liquid oxygen.

Table II

[Ignition Tests 0.1 Wt. % O_3F_2 in LOX]

Fuel	Starting Pressure		Injector*	Remarks
	Fuel	Oxidizer		
Ethyl alcohol (100%).	10	70	3 Fuel on 1 Oxidizer.	Immediate ignition.
Propane (at −78° C.).	10	70	-----do-----	Ignition outside chamber.
JP-4	4	20	3 Fuel on 3 Oxidizer.	Immediate ignition.
U-DETA	4	20	-----do-----	Do.

*All injectors were fuel cooled.

Table III

[Ignition Tests of 0.05% O_3F_2 in LOX]

Fuel	Starting Pressure		Injector*	Remarks
	Fuel	Oxidizer		
Ethyl alcohol	4	20	3 Fuel on 1 Oxidizer.	Instantaneous ignition.
JP-4	4	20	-----do-----	Instanteous ignition in each of 3 runs.
U-DETA	4	20	-----do-----	Do.
H_2 (gas at 90° K.).	75	20	1 Fuel on 1 Oxidizer, water-cooled.	Instantaneous ignition in both of 2 runs.

*Unless otherwise noted all injectors were fuel cooled.

Propane ignited outside the combustion chamber as seen from Table II. This was the result when a high-pressure start was employed. However, utilizing a low-pressure start, the pressure on the fuel and oxygen tanks was easily regulated and the proper ratio of fuel to oxidizer was easily maintained. The low-pressure starts gave instantaneous ignition inside the combustion chamber. When the pressure on the fuel and oxidizer was again increased, the flame was blown out. The failure at high pressure was due to the inability to control the ratio of fuel to oxidizer in the combustion chamber since, in the micro-motor system, high pressure applied to the fuel and oxidizer could not be properly regulated so as to maintain the desired flow of fuel and oxidizer into the combus-

tion chamber. In the operation of larger motors, fuel and oxidizer pressure is easily regulated thus providing correct flow of fuel and oxidizer into the combustion chamber and assuring hypergolic ignition.

The hydrogen test result given in Table III was obtained by cooling hydrogen gas in coiled copper tubing immersed in liquid nitrogen and then introducing the hydrogen into the combustion chamber. Under maximum flow conditions (.003 lb./sec.) their cooling systems maintained the gas at a temperature of from 85° K. to 90° K.

To facilitate the achievement of dependable hypergolic ignition, the fuel and oxidizer should be injected into the combustion chamber in such a manner as to allow thorough mixing of the two while at the same time providing maximum evaporation of oxygen from the liquid oxygen-trioxygen difluoride solutions. This results in the concentration of trioxygen difluoride and, thus, as previously explained hereinabove, assists hypergolic ignition. In view of this, the injector employed with the liquid oxygen-trioxygen difluoride solution can be of considerable assistance in achieving spontaneous ignition. Typical specifications of injectors employed in some of the micro-motor tests are given in Table IV below.

Table IV

[Injector data]

Fuel	Injector	Angle of Impingement, degrees	Fuel No. and size of holes	Oxidizer No. and size of holes
Hydrogen	1 Fuel on 1 Oxidizer.	45	1 at 0.055 in.	1 at 0.038 in.
JP-4	3 Fuel on 3 Oxidizer, 1 on 1 Impingement.	45	3 at 0.0145 in.	3 at 0.025 in.

Nevertheless, injector design can be varied considerably as the particular motor may require. A two-port injector having an impingement angle of 90° allowed hypergolic ignition of JP-4 and liquid oxygen containing 0.05% by weight trioxygen difluoride.

In addition to providing hypergolic ignition, the solution of trioxygen difluoride in liquid oxygen provides improved combustion stability over the fuel and liquid oxygen alone. This was evidenced not only from visual observation and high speed photography, but also from the combustion chamber pressures traces.

No significant differences in specific impulse values were obtained experimentally between the liquid oxygen-trioxygen difluoride solutions and pure liquid oxygen. However, it is expected that a slight, insignificant increase in specific impulse occurs.

In order to investigate the handling characteristics of the trioxygen difluoride-liquid oxygen solutions, open-cup compatibility tests were made with those engineering materials frequently used in liquid oxygen systems. These tests were conducted by placing the material in shallow aluminum cups and pouring 10 milliliters of the solution (0.05% and 0.10% by weight trioxygen difluoride in liquid oxygen) on the material. The solution was allowed to evaporate completely, thus exposing the material to the original solution as well as dinitrogen difluoride and finally fluorine vapor for short times as the solution warmed in air. Such tests, while purely qualitative, are very severe.

Since the test results could be affected by condensed moisture coating the materials being studied, the tests were repeated taking care to exclude moisture. The results were identical with the test results where moisture was not excluded. Table V gives the results of these tests.

Table V

[Open cup compatibility tests of engineering materials with 0.05% O_3F_2 in liquid oxygen]

Class	Material	Remarks [a]
Metal	Stainless steel, No. 303	No appreciable reaction.[b]
	do	Do.
	Stainless steel, No. 316	Do.
	Stainless steel, No. 321	Do.
	Stainless steel, No. 347	Do.
	Aluminum	Do.
	Copper	Do.
	Brass	No appreciable reaction; surface pitted on continued exposure.
	Stainless steel carpenter 20 cb[c].	No appreciable reaction.
	Titanium alloy beta-120-VCA[c].	Do.
	Magnesium-lithium (14.1%) alloy.[c]	Do.
	Magnesium-thorium alloy X.K31.	Do.
Packing gasket	Kel-F elastomer (plasticized).	Delayed (50 sec.) slight reaction.
	Allpax 500	No appreciable reaction.
	Allpax 500 (fluorolube T-80 treated).	Do.
	Teflon	Do.
	JM 76	Do.
	Duroid 3400[c]	Do.
	JM "Lo-Flo"	Do.
	Polyethylene film	Delayed (60 sec.) ignition.
Lubricants and Sealants.	Fluorolube T-80 (T-45)	No appreciable reaction.
	Halocarbon, series 11-14	Delayed (50 sec.) slight reaction.
	Kel-F oil, alkane No. 464.	Do.
	Molykote "Z"[b]	No appreciable reaction.
	Oxylube 702[b]	No appreciable reaction.[c]
	AR-1F, LOX lube	Delayed (50 sec.) slight reaction.

[a] No appreciable reaction indicates no fire, flame, or other visible evidence of reaction.

[b] These samples were tested additionally by being immersed in 0.11% O_3F_2/LOX solution, which was cooled with liquid nitrogen for a specified time, then allowed to warm up until the solution evaporated. These samples again showed no tendency to react.

[c] The residue indicated a possible reaction, although no obvious reaction took place during evaporation of solutions.

The results of the above mentioned test as seen from Table V showed that with the possible exception of some chlorotrifluoroethylene base materials (Halocarbon No. 11-15, Kel-F elastomer, Kel-F alkone No. 464 oil), the trioxygen difluoride-liquid oxygen solutions do not react with the materials most frequently employed in space vehicle liquid oxygen propulsion systems.

Thus, it is seen that trioxygen difluoride not only offers the advantage of a hypergolic additive, it is compatible with rocket motor materials and stabilizes combustion within the motor. At the same time, no loss in specific impulse is encountered. If anything, an increase in the specific impulse, though negligible in amount, is to be expected. The combination of advantages makes trioxygen difluoride an especially suitable additive for liquid oxygen to be employed as an oxidizer in bipropellant liquid rocket systems.

The above detailed description is for the purpose of illustration only and is in no way to be considered a limitation of the invention. Many obvious modifications may be applied to the invention without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. In the operation of bipropellant liquid rocket engines which employ liquid oxygen as the oxidizer for the fuel, the improvement which comprises substituting for said liquid oxygen a solution of from about 0.05% to 0.10% by weight of trioxygen difluoride in liquid oxygen.

2. The improvement according to claim 1, wherein a solution of about 0.05% by weight of trioxygen difluoride in liquid oxygen is substituted for said liquid oxygen.

3. A method for operating a bipropellant liquid reaction motor which comprises bringing together in a combustion zone of said motor a solution of about 0.05% to

0.10% by weight trioxygen difluoride in liquid oxygen and a fuel which is hypergolic with said solution.

4. The method according to claim 3, wherein the solution of liquid oxygen and trioxygen difluoride is about 0.05% by weight trioxygen difluoride.

5. A method for operating a bipropellant liquid reaction motor which comprises bringing together in a combustion zone of said motor a solution of about 0.05% to about 0.10% by weight trioxygen difluoride in liquid oxygen and a fuel selected from the group consisting of ethanol, propane, unsymmetrical dimethyl hydrazine, hydrogen, unsymmetrical dimethyl hydrazine-diethylene triamine mixture, and JP–4.

6. The method according to claim 5, wherein the solution of liquid oxygen and trioxygen difluoride is about 0.05% by weight trioxygen difluoride.

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