ON THE USE OF HYDROGEN PEROXIDE AS OXIDIZER IN HYBRID SYSTEMS

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ABSTRACT. This paper deals with the use of hydrogen peroxide as an oxidizer in hybrid propulsion systems, the ignition being assured by hypergolic reactions.

The laboratory study of its hypergolic qualities shows that the metallic hydrides and borohydrides, in particular the alcaline compounds, give short ignition time-lags. The mixture 70% paratoluidine 30% potassium borohydride, tested in a microthruster in the presence of a metatoluene diamine-based fuel, gave an ignition time-lag of six millisec.

A performance comparison of this same fuel in the presence of nitric acid, nitrogen peroxide and hydrogen peroxide shows for this last oxidizer higher regression rates, leading to higher characteristic mixture ratios. As a consequence, new fuels appear that are specific to this oxidizer; they contain polymers and plastic binders. To their good combustion qualities they add excellent mechanical properties. Among them, carboxyl-polybutadiene has been used as a base for studying the combustion of metals.

The couple carboxyl polybutadiene-hydrogen peroxide is particularly well suited to frontal combustion, as it permits, among other qualities, a thermochemical decomposition of the hydrogen peroxide.

I. General Considerations on Hybrid Combustion

Hybrid combustion brings into play propellants of differing physical pro-   /16*
perties. As a general definition, an oxidizing liquid is passed over as solid
fuel. Though modified, and even opposite, concepts are possible, we will only
examine in this article the strict case of a classical system. The fundamental

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* Numbers in the margin indicate pagination in the original foreign text.

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principles of operation of these engines have been treated in various publications [1 -3]. We will only recall them in general outline, limiting ourselves to the case of a liquid oxidizer and a solid fuel. Figure 1 gives the general concept of a thruster using this type of combustion. The oxidizer contained in the tank (pressurized to a value p_i), is injected into the chamber containing the solid fuel. Combustion, generally hypergolic, proceeds rapidly as pressure stabilizes itself to a value p_0, such that the total output passing through the throat of section Ac is equal to $\dot{m}_t = \frac{p_o A_c}{c^*} \dot{m}_t$, which is the sum of the outputs of the oxidizer $\dot{m}_0$ and of the fuel $\dot{m}_H$ and c^*, the characteristic velocity of the couple under consideration. It is known that the fuel output depends on conditions present in the chamber, such as its physical and chemical state. It is connected to the combined output in the central channel by a law of the form $\dot{m}_H = k_1 (\rho u)^\alpha$, and the parameter α varies between 0.4 and 0.8 depending on flow conditions [4]. In the majority of tests- on the thruster, the parameter α is of the order of 0.5, a value, it might be mentioned, different from that observed in configurations in which the flow and boundary layer are better defined. The influence of pressure on this fuel output is still under discussion; within certain limits it obeys a law of the form $\dot{m}_H = k_2 (\rho u) p_o^\beta$, β being small, between 0.2 and 0.5.

Several ignition-injection geometries can be envisaged, the most familiar being the cylindrical configuration with one or two channels. In the tests described in this article, we have experimented with the single-channel system. This simple shape is eminently suitable for hybrid combustion. To obtain operation at constant exhaust concentrations, the relation P/A_p^n must be constant, with A_p being the cross section of perimeter P. Since the majority of tests at fixed points have shown that n is in the vicinity of 0.5, the central cylindrical channel with a circular section is well adapted to this type of propulsion.

II.   Influence of Hydrogen Peroxide from an Energy Viewpoint.

Hydrogen peroxide leads to couples which present interesting specific impulses. A comparison between standard specific impulses calculated for various solid fuels in association with hyrodgen peroxide, or with nitrogen

peroxide, is shown in Figure 2. These values are classified as a function of the specific mass ρ of the total propellant. With a simple fuel like polyethylene, the standard impulse is 278 sec. With polybutadiene, which has the advantage of being cast and polymerized easily, the impulse reaches 274 sec. It rises to 290 sec. with the addition of 50% aluminum. The gain is more significant if the metal introduced is beryllium; calculations indicate an impulse of 315 sec., at optimum conditions. With beryllium hydride, production of which has not yet passed the laboratory stage, impulses should be higher than 350 sec. Solid fuel/ hydrogen peroxide couples rank high on the scale of possible impulses obtainable /17 from storable propellants, beryllium or its hydride being the chosen metal for this oxidizer. [5-6].

III. Present State of Readiness and the Stability of Hydrogen Peroxide [7]

Among the numerous methods used to prepare hydrogen peroxide (the action of acids on peroxides, oxydo-reduction of quinones, direct synthesis, complete and incomplete combustion of hydrocarbides) few are commercially useful. The electrolytic method is the one most often employed. A solution, either of sulphuric acid, ammonium sulphate, or potassium in excess sulphuric acid, is used. Hydrogen peroxide is obtained as a result of oxidizing effects in the vicinity of the anode, where it forms as intermediate substances, from persulphuric acid or the persulphate. Hydrogen peroxide in the gaseous state is separated from the by-products, concentrated, and extracted in a chamber over the anode compartment. Yields are better when the persulphate is used.

La Société d'Électrochimie (Ugine) was the first French plant to make hydrogen peroxide by electrolysis. In 1931, the Pierre Bénite plant near Lyon, a member of the same group, was able to ensure production for all France.

Oxygenated water, or hydrogen peroxide, is made to a concentration of approximately 75 p.p.100. To obtain superior concentrations, distillation and fractional crystallization are used.
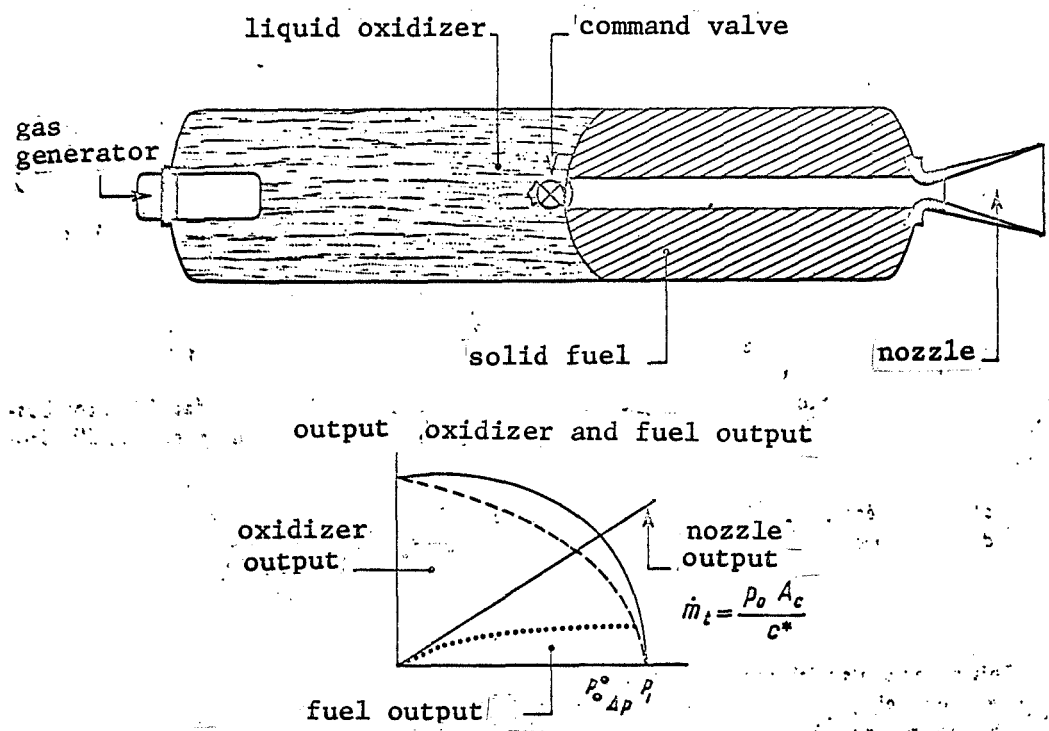
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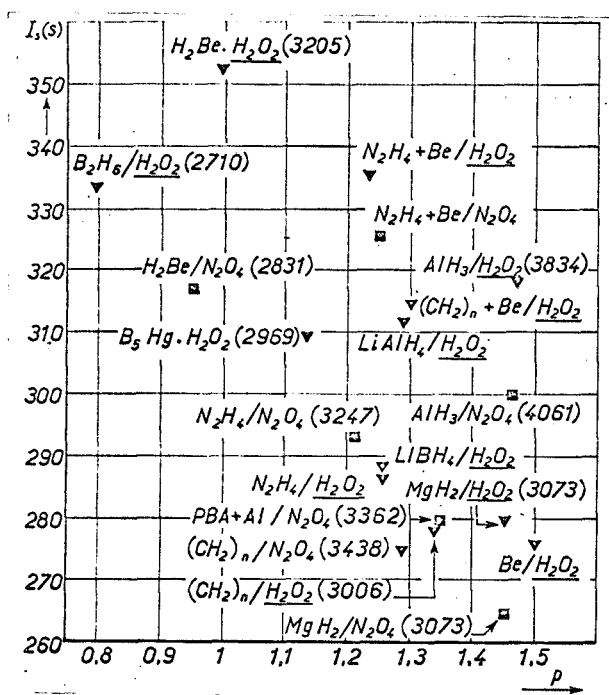Figure 1. Schematic of a lithergol rocket

Figure 2. Performances and combustion temperatures
with two oxygenated oxidizers.

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A process of double distillation allows the elimination of impurities and the production of 90% concentrations. Better concentrations are possible by fractional crystallization of these 90% solutions.

Hydrogen peroxide thus obtained is very pure, and loses less than 1% of its strength annually when stored at moderate temperatures — the loss being due to its decomposition into oxygen and water.

An experimental study of its preservation over a period of time in a five-liter jar showed a difference in concentration of only 0.5%; it declined from 95.5% to 95% in 18 months.

Storage over long periods is mainly done in high-purity aluminum vats. These tanks are provided with an air cover with a safety membrane, which prevents dangerous pressure overloads due to slow decomposition of the peroxide. Filters reduce the possibility of contamination.

Every hydrogen peroxide container must be placed in an isolated, well-ventilated location, far from all materials which might be combustible or might possibly contain decomposition catalysts; a source of water must also be close, to allow dilution should it become necessary.

As a general practice, surfaces in contact with this compound should be extremely well-polished, in order to reduce the surface of contact as much as possible. This is a most important point. These surfaces should then, with equal care, be cleaned and rendered inert with a solution of nitric acid (density 1.4), and with stronger and stronger concentrations of hydrogen peroxide liquid.

The high concentration hydrogen peroxide sued in this study (96%), was supplied by the Laboratories of Air Liquide de Lyon.

IV. Methods of Use of Hydrogen Peroxide in Thrusters.

Interest has been shown in the use of hydrogen peroxide as an oxidizer in rocket propulsion. Some of the factors favorable to its utilization are that it possesses high density and boiling point, a low viscosity, and significant oxidizing properties. On the other hand, its relatively high crystallization temperature can be a hindrance in some applications.

It decomposes under the influence of heat, or, at ordinary temperatures, under the influence of catalysts. Accordingly, it can be used in two ways:

— in a monopropellant form,
— as an oxidizer, through catalytic predecomposition.

Further, because of its oxidizing power, it can be injected directly into the chamber, to produce fuel ignition by hypergolic reactions.

IV.1. Catalytic Decomposition.

Hydrogen peroxide can be decomposed by itself, under temperature increase alone, into oxygen and water. The temperature of the products formed depends on the concentration and the initial state of the solution.

This decomposition can also be produced at ordinary temperatures in the presence of catalysts. In this case, the equation:

$$H_2O_2 \text{ liq.} \xrightarrow{(100\%)} H_2O_{gas} + 1/2 \ O_2 - 12,95 \ Kcal/Mole$$
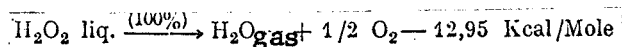
liberates energy corresponding to a temperature (in the gaseous mixture) of 1273°K, at one atmosphere.

Decomposing catalysts can be:

Homogeneous: consisting of metallic cations of iron and copper, and of chromate and vanadate anions precipitated by stabilizers in complex form;

Heterogeneous: consisting of metals in a pure, finely divided state, or their oxides: Pt, Mn, Hg, Fe, Cu, Cs, Ag, Ni.

The most usual agent for solutions of concentration less than 95% is silver, /18 for which a plateau of decomposition rates exists over a large range of temperatures. In practice, it is set on grilles of nickel coated with crude electrolytic silver.

This rapid decomposition illustrates its possible use of a monopropellant. As such, it was the subject of numerous studies. Specific impulses, a function of the concentration, are for 90% hydrogen peroxide, of the order of 134 sec. at a pressure of 20 bars, and 141 sec. at 35 bars. This type of decomposition is best used in auxiliary guidance thrusters.

The decomposition of hydrogen peroxide was also studied as a gas generator in a supply system of rocket engines with hybrid propellants.

G. E. Moore and Kurt Berman first proposed the use of this oxidizer in hybrid thrusters through a catalytic predecomposition [1].

Hydrogen peroxide of 90% concentration is injected over a decomposition pile of silver-based catalyst. The products formed, $H_2O + O_2$, are next passed into an annular combustion chamber made of two concentric cylinders of polyethylene. The combustion reactions take place between the gas and the surface of the solid; the standard theoretical specific impulse is 278 sec.

In classic hybrid thrusters made solely of one cylindrical block (grain) with a single channel (perforation) in the center, one can visualize a

surrounding deposit of active material catalyzing the decomposition of the hydrogen peroxide, which is being injected directly into the chamber.

The work in this article only deals with hybrid combustion initiated by hypergolic reactions in a certain manner. A compound (whose hypergolicity with hydrogen peroxide produces sufficient energy to initiate combustion of the solid fuel over all its surface), is deposited along the interior of the central channel.

Figure 3 shows a system of two classic hybrid thrusters, one with catalytic predecomposition, the other with hypergolic combustion.

IV.2. Direct Injection of Hydrogen Peroxide into the Chamber — Hypergolic Reactions.

The hypergolic nature of hydrogen peroxide with liquid fuels was also studied in Germany at the end of the Second World War, and had military applications in V2's. Later, the English did work of interest on ignition from hydrogen peroxide. Hydrazine and ethyl alcohol ignite with it on contact, but this ignition requires the presence of a catalyst. Specific impulses obtained with 90% concentration hydrogen peroxide and hydrazine are 242 sec. at 21 bars, and 257 sec. at 35 bars. With ethyl alcohol, impulses are 230 sec. and 245 sec. for the same pressures. The hypergolic properties of the couple 98% H_2O_2 — Aerosine 50 would be ideal for the thruster operating on impulse. In the field of hybrid systems, there still does not exist, at least to our knowledge, work on hypergolic combustion in the presence of liquid hydrogen peroxide. For this reason it seemed useful to us to publish certain results obtained at the O.N.E.R.A. relative to the study of the hypergolicity of liquid hydrogen peroxide in the presence of various solids, and to the development in microthrusters of couple performances using H_2O_2 as an oxidizer.
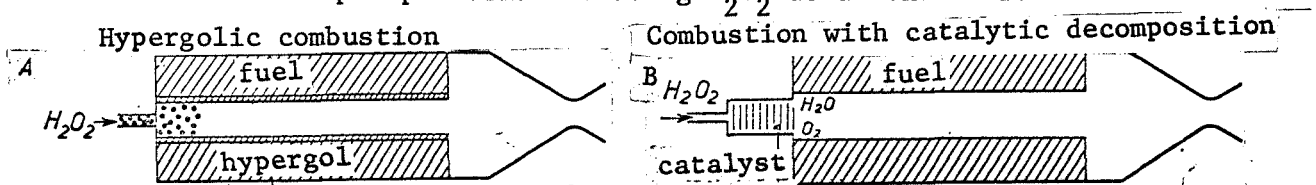

Figure 3. Hybrid combustion with hydrogen peroxide

V. Direct Injection of Hydrogen Peroxide in the Chamber.

V.1. Study of Hypergolicity in the Laboratory.

Preliminary studies lead to the following conclusions:

— the hydrides, the metallic borohydrides , notably the alkaline compounds, have short ignition delays.
— the solid aromatic amines: paratoluidine, metatoluidine, and paraphenylene diamine, have a combustion delay better than a second;
— the complex dimethylhydrazine-diborane has a slower reaction with liquid hydrogen peroxide, leading to explosion after a second of contact,
— the ignition delays of the more interesting compounds have been measured with a piston apparatus. Listing the results recorded gives the following values:

Lithium hydride (HLi)	2 msec.
Lithium anhydride (NH_2Li)	6 msec.
Lithium borohydride (BH_4Li)	1 msec.
Lithium aluminohydride (AlH_4Li)	7 msec.
Sodium borohydride (BH_4Na)	8 msec.
Potassium borohydride (BH_4K)	2 msec.

For the complex dimethylhydrazine-diborane, 150 msec. was obtained. Amorphous borax powder ignites on contact with hydrogen peroxide, but with a delay of about 1 sec.

Potassium borohydride was retained in preference to other compounds as an initiator of combustion; it is both stable in air, and very reactive in the presence of the oxidizer. For purposes of reaction, it is placed in suspension with a paraanisidine-paratoluidine mix. These combinations, studied in various concentrations, possess the following ignition delays:

{ Potassium Borohydride (10%)		48 msec.
{ Paratoluidine (90%)		
{ Potassium Borohydride (30%)	.	35 msec.
{ Paratoluidine (70%)		
{ Potassium Borohydride (30%)		59 msec.
{ Paraanisidine (70%)		

All of these values are satisfying, and the use of these suspensions can be considered in the ignition of solid fuels for thrusters. The composition having the lowest ignition delay — i.e., potassium borohydride (30%) paratoluidine (70%) — was, by preference, retained.

All ignition delays have been measured with a hydrogen peroxide concentration of 96%. When this is reduced, delays lengthen dangerously.

V.2. Study of Ignition in the Microthruster MT-15.

The suspension of 30% potassium borohydride in 70% paratoluidine solvent is spread at the rate of 0.05 gm/sq. cm. on the surface of the channel in the fuel grain. It changes after solidification into a very adhesive white film.

The fuel grain itself is composed of 96% active element (metatoluene diamine) and 4% binder (nylon made plastic with cyclohexylphtalate). Its dimensions are: 90 mm. length, 60 mm. diameter, 30 mm. threshhold chamber, and a weight on the order of 300 gm.

The microthruster MT-15 allows a detailed study of ignition; it is relatively easty to operate, and does not use large quantities of material.

Adapted to measure ignition delay and hydrogen peroxide consumption, (Figure 4) it comprises:
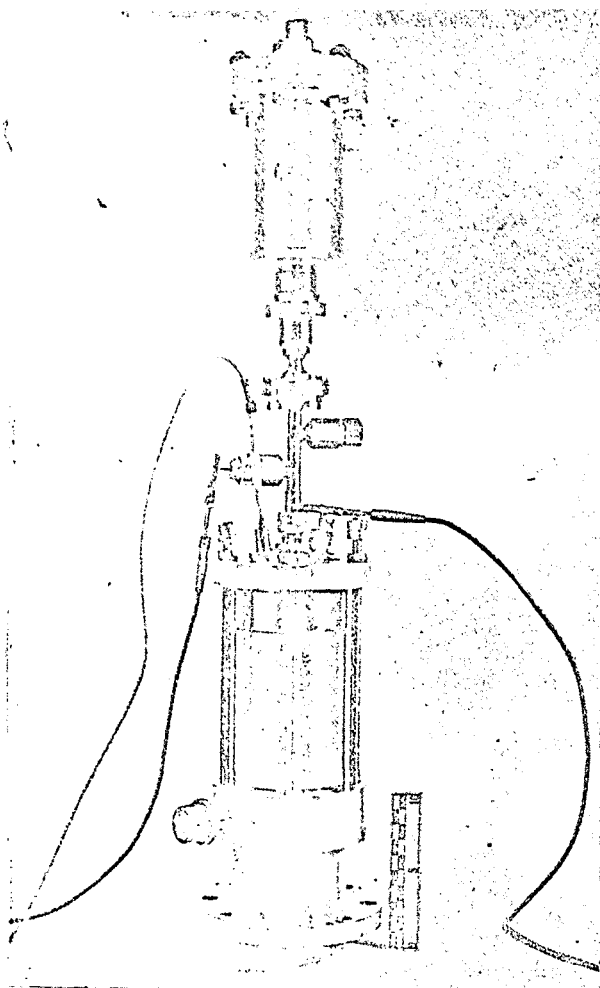
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Figure 4. Ignition delay measurement on thruster.

— a tank of aluminum alloy, with a carefully polished interior, and with a capacity of 300 cm;

— a connection between the tank and the thruster, made of stainless steel (the period of contact with the peroxide being limited). It is supplied with a blowout valve of polyethylene, of 0.1 mm thickness, secured between two circular plates, one of which has a torsion joint;

— a probe registering the arrival of the oxidizer, isolated and situated above the injector,

— finally, the microthruster itself, in three parts:

a) the injection head, equipped with a spray injector, and a tubular chamber which is used to hold a germanium type OAP12 cell, to detect rises in temperature;

b) the combustion chamber, enclosing the solid fuel;

c) the nozzle, having a diameter of 5 mm at the throat, with a pressure gauge at the convergent section.

The readings of ignition delay and the rise in pressure at ignition appear simultaneously on a dipolar oscilloscope, where the light intensity of the signals is modulated to 1000 Hz. Pressure is similarly recorded on a slow-motion recorder (2 cm/sec.), equipped with galvanometers.

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V.2.1. Results Obtained

The results obtained are condensed in Table I[(*)].

TABLE I.

Firing information (mass of H_2O_2 in g)	Physical delay (msec.)	Chemical delay (msec.)	Global delay (msec.)	P_0 max. at ignition (bars)	p during test (bars)
I 100 . . .	6	2	8	9	27
II 200 . . .	6	2	8	19	28.6
III 200 . . .	9	2	11	16	28.2
IV 200 . . . 24 hours after being placed in the initiation chamber, and exposed to air.	6	2	8	10	28.5

[(*)] Measurements of ignition delay and the interpretation of results have been examined on several occasions; the reader is asked to check the references himself [8, 9].

For these tests, injection pressure is 30 bars; the firing release is controlled by an electrical switch in the tank, which is pressurized with nitrogen.

An examination of Table 1 and the readings in Figure 5 indicate a satisfactory ignition without pressure points. The activity of the ignition catalyst is unchanged even after deliberate exposure to air, without special protection, for 24 hours. Also to be noted is the high reaction rate: τch = 2 msec.
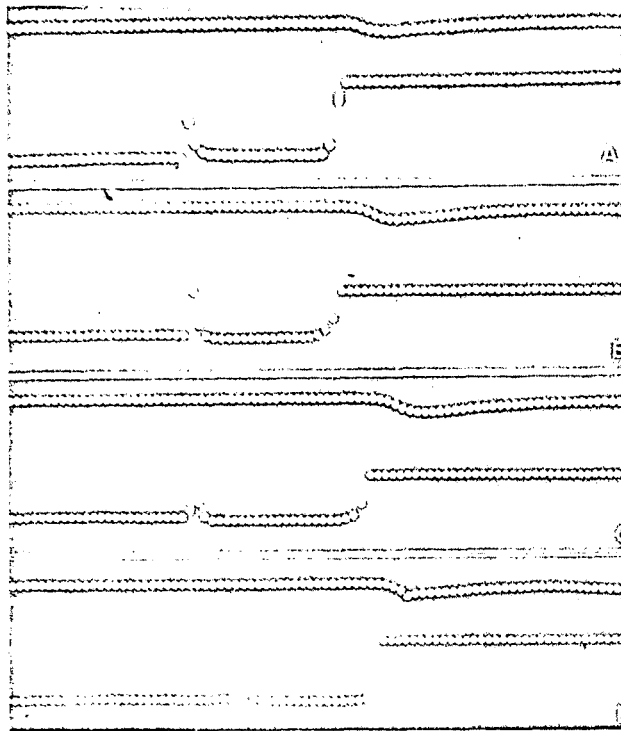
Figure 5. Recordings of ignition delay
and chamber pressure.

Time base 1.10 sec.
Time count 12.10 sec.

A — No. 1 firing, B — No. 2 firing
C — No. 3 firing, D — No. 4 firing

V.3. Non-hypergolic Reactions. Choice of Fuel.

The tests carried out in the laboratory indicated that some solid aromatic amines react with hydrogen peroxide, and could be ignited after a second of contact. These amines make excellent active bases for fuels in the presence of this oxidizer.

The microthruster MT-15 (described in the preceding section) then allowed us to make a preliminary series of measurements, having as their aim:

1. As a first step, to make a comparison of the combustion characteristics of standard lithergol NMTD (metatoluenediamine-nylon-cyclohexyl-phtalate) in the presence of hydrogen peroxide, nitric acid, and nitrogen tetroxide;

2. To define new, specific fuels for this oxidizer, especially those which would have high ablative rate. In effect, this meant new compounds compatible with hydrogen peroxide, since poor results were obtained with nitric acid and nitrogen tetroxide. A wide selection of fuels is thus produced, which would react in the presence of highly concentrated hydrogen peroxide as an oxidizer. The standard mixtures with an amine base, supplemented by a series of polymers, including binders and plastic resins, such as polybutadiene, araldite D, the polyesters, plexiglass, araldite EM1, nylon, and polyethylene. All these compounds combine good combustion characteristics with excellent mechanical strength.

A second series of tests was performed on a more significant scale with the microthruster MT-32, with 30 daN thrust, in order to:

1. Check whether the results obtained on lithergol NMTD were repeated on this scale;

2. Study the variations in the relation between the mixture and the characteristic velocity as a function of the length of the fuel;

3. Show the influence of the variation of chamber pressure on performance, particularly on regression rates of the fuel.

VI. Experimental Microthrusters MT-15 and MT-32

VI.1. Description

The microthruster MT-15 has been described in the section on ignition studies. For combustion tests, the cell and probe detecting the arrival of the oxidizer were not used.

The microthruster MT-32, shown schematically in Figure 6, develops a thrust of approximately 30 daN. The diameter of the nozzle throat is 10 mm. The configuration is the same as for the MT-15 microthruster; for practical convenience the oxidizer tank is above the thruster, and separated from it by a blowout valve. The dimensions of the fuel grain are: 140 mm long, 105 mm exterior diameter, and 40 mm threshhold diameter.

VI.2. Experimental Technique and Monitoring. Calculation of
Performance and Regression Rate.

For the MT-15 engine, the hydrogen peroxide tank capacity is 1000 cm. and the fuel grain mass is 300 gm.

The MT-32 engine has an oxidizer capacity of 2000 cm., and the fuel a mass of about 1 kg.

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1. Nitrogen entrance
2. Stop valve
3. Tank
4. Oxidizer
5. Blowout valve
6. Injector
7. Fuel
8. Durestos casing
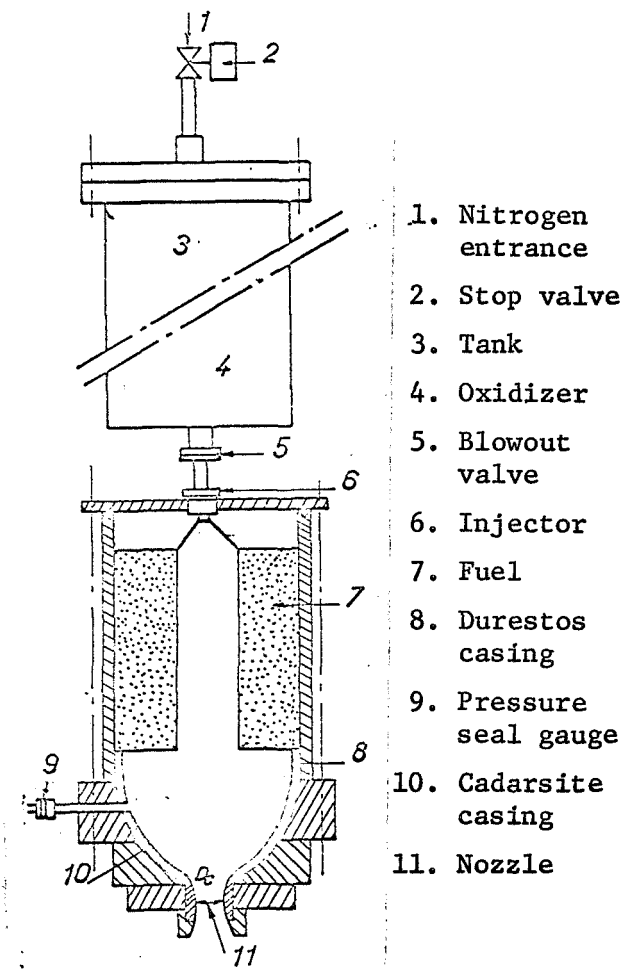9. Pressure seal gauge
10. Cadarsite casing
11. Nozzle

Figure 6.

Experimental techniques are the same in both cases. After removing the fuel grain from its enclosing duralinox mold, the ignition catalyst is spread on the surface of the thresh-hold. The whole apparatus is carefully weighed, and then inserted into the combustion chamber; the latter is re-assembled in two parts, lower and upper (or, in terms of flow, downstream and upstream), consisting of the injectors, and the convergent section of the noz-zle. The entire unit is placed ver-tically in its support on the test bench. The pressure seals are stan-dardized; the hydrogen peroxide is agi-tated in the tank some moments before the firing. At the last instant, it is put under pressure.

An important point must be noted: hydrogen peroxide being a monopropel-lant, it is essential to prevent any possibility of combustion products re-entering the tank, and providing a pressure overload at the moment of ignition.

The parameters describing each firing are as follows:

m_0(g): total mass of oxidizer consumed, obtained by weighing the tank before and after firing;

m_H(g): total mass of fuel consumed, obtained by weighing the grain before and after firing;

p_i, p_0(bars): injection pressure and chamber pressure, measured at the same instant on the same strip at a velocity of 2 cm/sec., with a photographic recorder ACB, equipped with galvanometers, on a mobile frame. The preliminary pressure standardization is also recorded on the same strip;

t_b(sec.): combustion time, registered on the pressure record strip;

τ(msec.): the time elapsing between the two rises in injection and chamber pressure, measuring the ignition delay.

These values determine the performance of the propellant:

a) the relationship of the mixture m:

$$m = \frac{m_{II}/t_b}{m_o/t_b} = \frac{\dot{m}_{II}}{\dot{m}_o}.$$

Note: For outputs of nitric acid and nitrogen tetroxide, instantaneous measurements were available. In the following experiments, an output meter was not inserted into the circuit, and the average output is calculated from the total mass consumed. The values are obtained indirectly from oxidizer waste at the beginning and the end of firing.

b) the relationship of the characteristic mixture ϕ:

$$\phi = m/m_s$$

where m_s is the stoichometric mixture relation;

c) the characteristic velocity C*:

$$C^* = \frac{p_o A_c}{\dot{m}_{ch} + \dot{m}_o} \quad \text{and} \quad \overline{C}^* = \frac{A_c \int_0^{t_b} p_o dt}{m_{II} + m_o},$$

where A_c is the throat section. The combustion wastes noted have an effect on the characteristic velocity, which is therefore less than in practice, but this amount can serve as a basis of comparison between propellents.
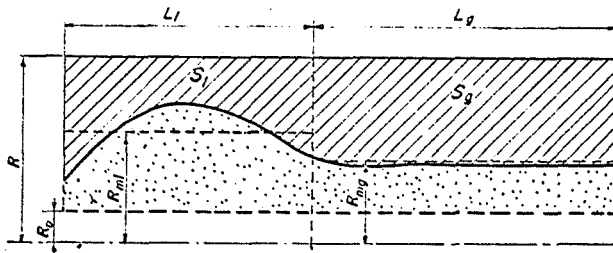
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Figure 7. Test monitor. Determination of average regression rates.

Results obtained on the MT-32 are much closer to their real values than those obtained on the MT-15. Dimensions and operating times of the latter are smaller than the MT-32, and the short period of occupation is not favorable to the attainment of high combustion. Still, its easier operation makes it more suitable for preliminary comparisons;

d) the average rate of regression is obtained by two methods:

— in the first, the average radius of the fuel grain after the firing is calculated, knowing its mass loss Δm, its specific mass ρ, its length L, and its initial radius R_0, by the relation:

$$R_m = \left(\frac{\Delta m}{\rho \pi L} + R_0^2\right)^{\frac{1}{2}}$$

and its rate of regression for a combustion time t_b is given by:

$$\bar{v} = \frac{R_m - R_o}{t_b},$$

or:

$$\bar{v} = \frac{1}{t_b}\left[\left(\frac{\Delta m}{\rho \pi L} + R_0^2\right)^{\frac{1}{2}} - R_o\right];$$

— the second, valid in some experiments, consists of making a longitudinal section in the fuel grain after combustion, following the diameter, and recording the surfaces obtained on graph paper. After graphical integration, the average radius is calculated. The record of one test is shown in Figure 7. Two very distinct zones can be discerned: in the region affected by the injector, the wear on the block is more significant than in the zone below. This phenomenon, which occurs in much the same way with all fuels, is more pronounced in the presence of hydrogen peroxide. The two combustion phases, liquid and gaseous, are therefore distinguishable in the calculation of regression rates. The most probable lengths corresponding to each of them is determined: L_t and L_g.

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Their remaining surfaces are measured between the outer wall and the combustion zone, using graphical integration. They give radii R_{ml} and R_{mg}, and thus regression rates $\bar{v}_l$ and $\bar{v}_g$.

It would have been possible to use a more precise method of monitoring, giving the regression rate at time t and a given section X of the grain — for example, stopping the thruster at ever-increasing operating times, and calculating at each abscissa X the variation of the radius R as a function of time. This is generally of the form:

$$R^n(x) = R_0^n + Kt$$

where n and K are determined empirically. The rate of regression v(x, t) is equal to:

$$v(x, t) = \frac{K}{n}[R(x)]^{1-n}.$$

For fuel comparisons, it is simpler to use $\bar{v}$.

VI.3. Techniques for Preparing Lithergol Grains

These techniques differ according to the physical properties of the compounds used. In the case of the lithergol NMTD, its constituents have a relatively low fusion point, and casting can be employed. The components are introduced cold into the receptacle, in the proportions to be used in the experiment. The mixture is heated to about 150-160°C, at which temperature it is completely liquid. It is then poured into the mold appropriate to the microthruster being used. By recooling, a homogeneous, resistant grain is obtained.

For binders, and plastic resins, procedures are as follows:

— the carboxyl polybutadiene, diethylene carbide, having 0.45 carboxy component in a mass of 1000 gm, is warmed in an oven to 60°C, with an imino-derivative, while in the mold. The compound hardens thermally. The polymerized product has a rubbery appearance, and excellent mechanical properties;

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— araldite D forms part of the series of epoxy resins resulting from the action of glycol epichlorhydrine on a polyalcohol; it casts and hardens easily;

— araldite EM1, a mixture of epikotes which, polymerized and molded, is much more plastic than the preceding form, and shows a certain amount of elasticity;

— stratyl, a polyester currently in use, is polymerized by the action of a peroxide, directly in the mold;

— polyethylene is machined from a cylindrical block;

— plexiglass (polymetacrylate) is also machined;

— nylon (polyamide) is similarly formed by machining.

VII. Results of Firings

VII.1. Experiments with Microthruster MT-15

VII.1.1. Comparative study of the combustion of NMTD in the presence of hydrogen peroxide, nitric acid, and nitrogen tetroxide.

This comparative study was made by varying the principal constituents, both amine and its supporting components, in the standard lithergol NMTD. The results of firings in the presence of hydrogen peroxide are condensed in Table II.

A quite significant increase can be noticed in the mixture relation. Figure 8 shows the development of this mixture ratio as a function of amine /23 concentration for two oxidizers, hydrogen peroxide and nitric acid. A noticeable increase in exhaust concentration occurs when the proportion of amine increases, with a significant divergence in favor of hydrogen peroxide, a divergence which becomes more obvious for greater quantities of support material.
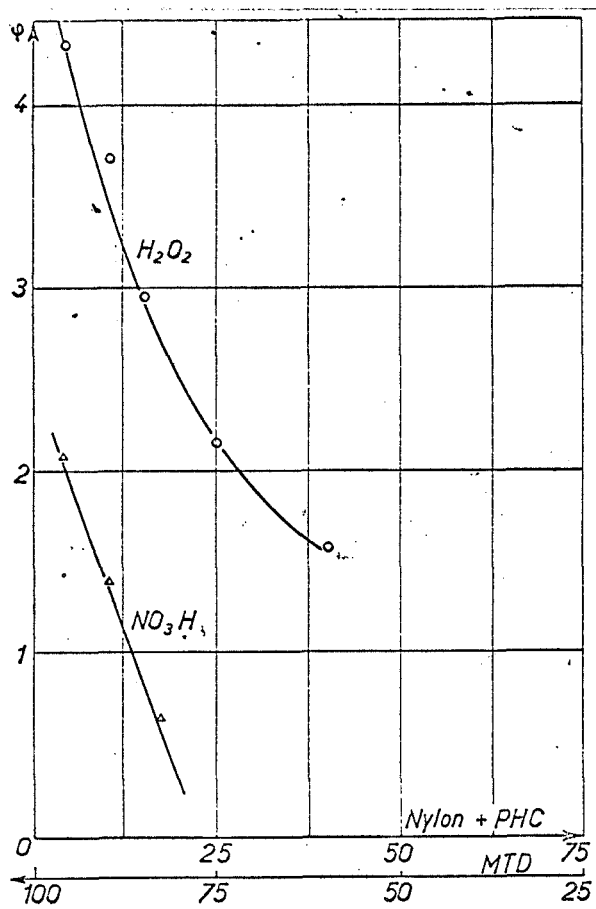
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Figure 8. Development of a characteristic
mixture relation as a function of
amine concentration.

Two firings made with a fuel based
on metatoluene diamine one with nitric
acid, and one with nitrogen tetroxide,
under identical conditions, gave the
following respective values — 1160 and
1240 m/sec. for the characteristic
velocity. With hydrogen peroxide, 1366
m/sec. was obtained.

VII.1.2. Study of combustion of
fuels made exclusively
from plastics.

Table III shows the results obtained
from these compounds:

TABLE III

Fuel	$\dot{m}_H$ (g/s)	$\dot{m}_o$ (g/s)	p_o (bars)	φ	C* (m/s)
Polybutadiène . .	8,72	29,79	27,5	2,03	1400
Araldite D	6,73	28,85	27,8	1,35	1531
Polyester	5,85	30,49	27,9	0,94	1505
Plexiglass	5,67	30,93	27,5	0,78	1473
Araldite EM$_1$	5,30	30	27,7	1,02	1538
Nylon	4,31	31,58	26,7	0,74	1458
Polyéthylène . . .	3,98	30,86	28	0,99	1575

TABLE II.

MTD	N = PHc	t_b(s)	$\dot{m}_H$(g/s)	$\dot{m}_o$(g/s)	p_o(bars)	φ	C*(m/s)
96	2 + 2	6,4	24,14	31	28,6	4,32	1016
90	5 + 5	6,2	21,61	32,25	28,2	3,72	1026
85	10 + 5	6,1	17,54	32,78	27,7	2,97	1079
83	12 + 5	6,6	16,51	30,30	27,5	3	1151
75	20 + 5	6,2	13,95	31,45	27,7	2,16	1169
60	35 + 5	9,6	9,37	30,52	27,8	1,69	1366

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An examination of the table indicates that these new fuels, while not usable in the presence of other oxidizers, have here excellent combustion characteristics. Mixture ratios range from 0.7 to 2.

A comparison between the combustion of polybutadiene in the presence of hydrogen peroxide and nitric acid is shown by pressure chamber readings (Figure 9). Excellent stability in the presence of hydrogen peroxide is apparent. In this case, values remain high (27.5 bars); they are much lower and more unstable in the presence of nitric acid.

If the regression rates obtained with these various fuels are now examined, it can be seen that they are relatively high, and lead to correct mixture ratio values for this microthruster. Figure 10 shows photographs of the grains of these compounds after combustion. Again in this instance, one can differentiate between the regression rates in the liquid and gaseous phase.

The following results (Table IV) are graded in terms of increasing values of regression rate in the liquid phase.

TABLE IV

Type of Binder	Liquid phase	Gas phase	Flexible araldite	Carboxyl polybutadiene
Nylon	40	50	0,42	0,095
Polyéthylène . .	41,5	48,5	0,46	0,195
soft araldite	45	45	0,558	0,29
Plexiglass . . .	48	42	0,58	0,21
Stratyl	43	47	0,695	0,366
Araldite D . .	50	40	0,71	0,275
Polybutadiene carboxyl . .	50	40	1,053	0,532

The rates are again produced in Figure 11. By introducing very reactive charges in these binders, values are increased. Thus, araldite D with 10% potassium borohydride has a regression rate of 0.88 in the liquid phase, and 0.59 in the gaseous phase.
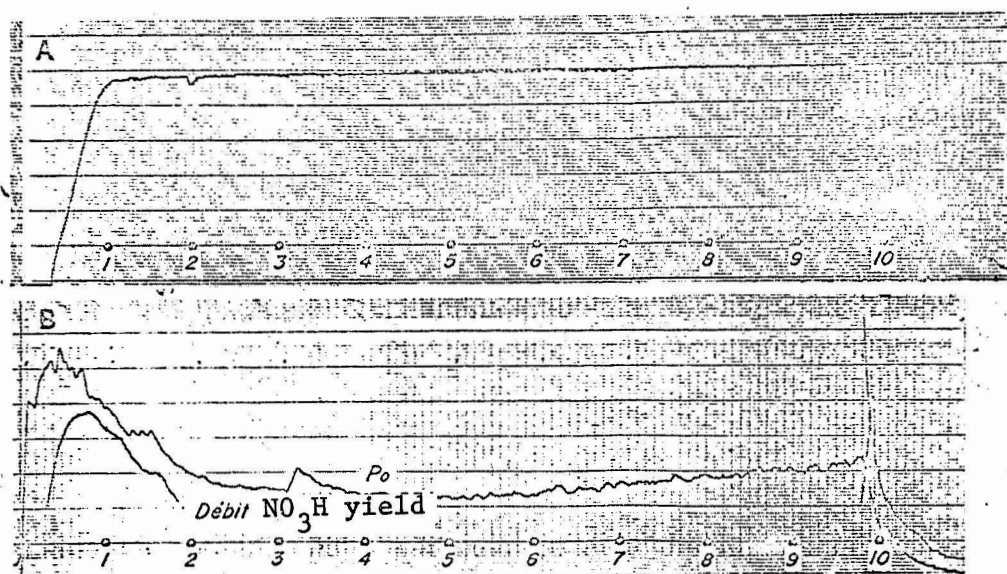
Figure 9. Comparison: hydrogen peroxide and nitric acid firings, in
the presence of carboxyl polybutadiene.

A. Carboxyl polybutadiene with hydrogen peroxide
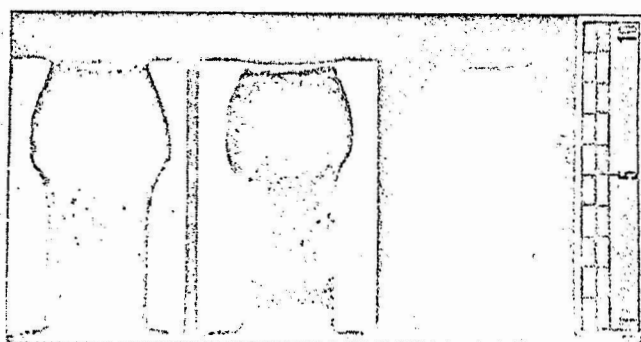B. Carboxyl polybutadiene with nitric acid.

Fig. 10 A.

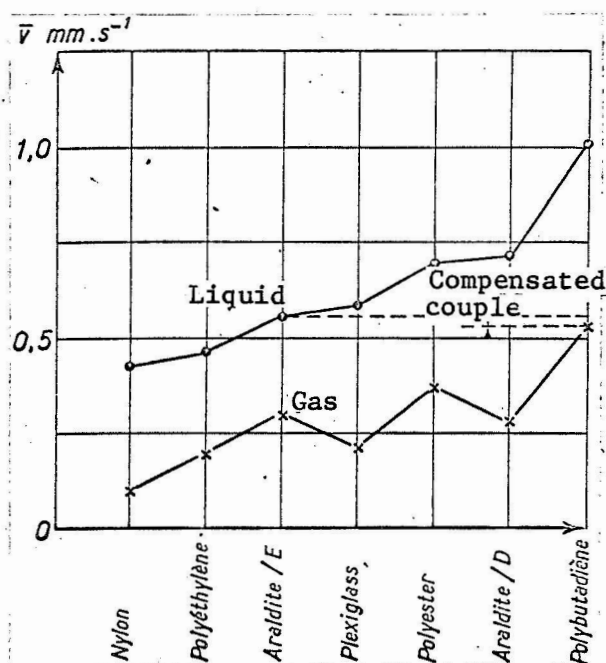Figure 10. Photographs of resin grains
after their combustion.

Figure 11. Regression rates obtained
on resin grains.

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VII.2. Tests on the Microthruster MT-32

VII.2.1 Verification on a larger scale of premininary results
obtained with NMTD.

The same study was performed with different concentrations of amine in
the NMTD fuel. Table V gives results obtained, and allows comparison of two
firings, performed under the same conditions, with hydrogen peroxide and nitrogen
tetroxide.

In comparison to the MT-15 microthruster, higher values are immediately
apparent for characteristic velocities for some concentrations, and for
identical mixture ratios. Next, the two firings (one in the presence of
hydrogen peroxide, the other in the presence of nitrogen tetroxide, both for
the same composition (90% NMTD, 10% support material), show an increase in
exhaust concentration, indicating a higher regression rate.

The result of this comparison is important, and strongly confirms the
behavior observed for the microthruster MT-15. A significant increase can thus
be seen in the rate of regression, in the presence of hydrogen peroxide.
The curves of Figure 12 show the development of these rates as a function of
amine concentration, and one can compare these with values of Figure 8,
showing the increase in mixture relation with increase in amine proportion.

VII.2.2 Influence of the length of the fuel.

The results produced in Table IV have been obtained with the following
fuel composition: MTD 83%, PHc 5%, Nylon 12%.

It is interesting to note that, as the length of the fuel progressively
diminishes, the exhaust concentration approaches a value corresponding to   /25
the maximum of the characteristic velocity. On the other hand, with other
oxidizers and their consequent smaller regression rates, it would be necessary
to increase the length of the same fuel to approach the optimum.

TABLE   V.

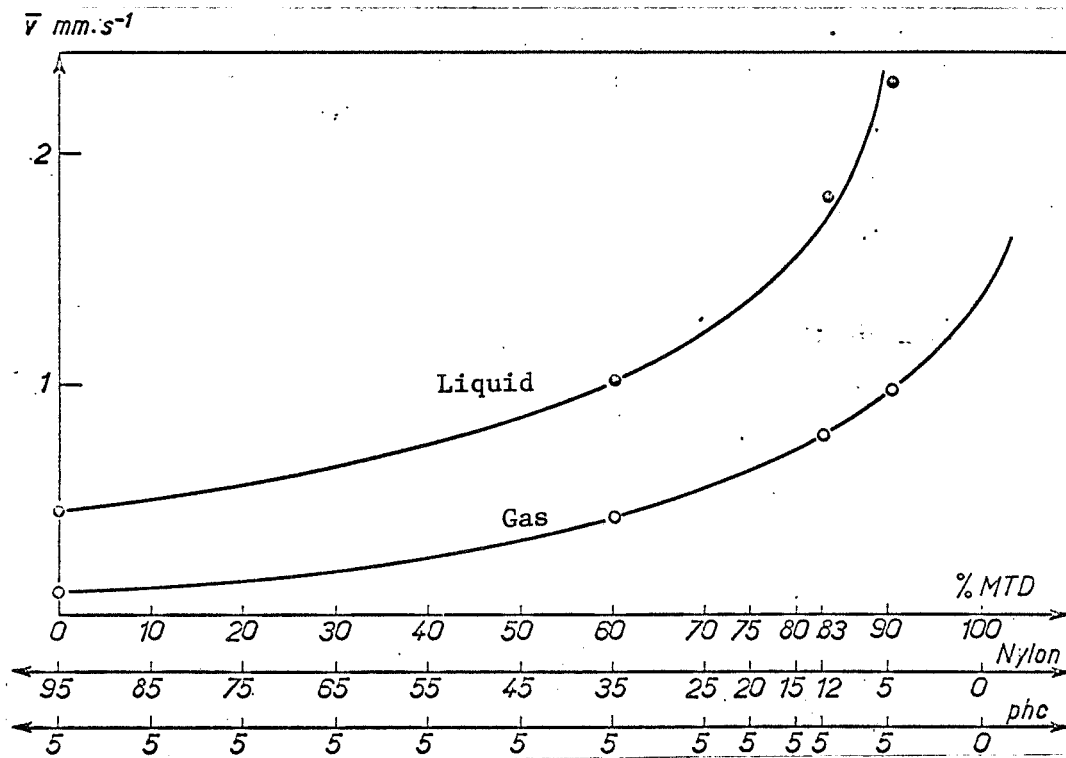| Fuel	Oxidizer	t_b(s)	$\dot{m}_o$(g/s)	$\dot{m}_H$(g/s)	p_o(bars)	φ	C*(m/s)	L_l (mm)	L_g (mm)	$\bar{v}_l$ (mm/s)	$\bar{v}_g$ (mm/s)
MTD 90 N + PHc 10	N_2O_4	6,1	162,95	30,98	25,6	0,68	1026				
MTD 90 N + PHc 10	H_2O_2	8,5	115,29	60,23	27,8	2,9	1232	90	50	2,32	0,98
MTD 83 N + PHc 17	H_2O_2	8,7	114,37	45,29	27,4	2,19	1334	85	55	1,82	0,77
MTD 75 N + PHc 25	H_2O_2	8,6	115,70	35,93	28	1,71	1450	64	76	1,715	0,721
MTD 60 N + PHc 40	H_2O_2	7,5	130	24,40	26,8	1,03	1363	50	90	1,0266	0,413

Figure 12.   Development of regression rates in liquid and gaseous phases as a function of amine concentration.

After each test, the grains are systematically examined in longitudinal sections. For the last 60 mm. of length, combustion occurs solely in the liquid phase.

VII.2.3. Influence of Chamber Pressure.

Polybutadiene was chosen for these measurements, because it is simple to prepare, in a non-shrinking, compact grain, by hardening in the actual mold. The same injector was kept, and injection pressure P_i was varied between 20 and 40 bars. The total mass of fuel used remained constant in all tests. The following performances and regression rates were obtained (Table VI).

TABLE VI

Length mm	$t_b(s)$	$\dot{m}_H(g/s)$	$\dot{m}_o(g/s)$	p_o(bars)	φ	$C^*(m/s)$
140	8,7	45,29	114,37	27,4	2,19	1334
120	8,6	43,95	115,70	27,5	2,10	1333
100	8,8	39,54	113,07	27,5	1,93	1415
80	8,7	36,90	113,90	27,5	1,79	1432
60	8,6	27,56	115,70	27,5	1,31	1508

At an injection pressure of 20 bars, fluctuations in chamber pressure occur, which are due to small deviations Δp, between the two pressures. For larger Δp, chamber pressure is stable. A high characteristic velocity is obtained, 1597 m/sec., for a chamber pressure of 26.8 bars. These figures are a result of a significant increase in the regression rate of fuels in the presence of hydrogen peroxide. If the curves of Figure 13 are examined, we can see that, for the same throat diameter:

— the regression rate in the injection zone (liquid phase) is proportional to the pressure. In the zone of the gaseous phase, it is closely proportional to the square root of the pressure. In the tests described, we find:

$$v_g = Kp_0^{0.52} \quad \text{(Figure 14)}$$

It is therefore interesting in this case to produce modulations in thrust, in the region of small chamber pressure values, for example, between values of a bar and 10 bars. At this latter value, the difference between the two

regression rates is 0.06 mm/sec., or 16% of the regression rate in the liquid phase. In a later section, frontal compensated combustion will be examined. Combustion takes place in this case essentially in the liquid phase, and one must be able to modulate the pressure without producing significant repercussions on the mixture ratio.

VII.3. Classification of Various Fuels as a Function of Ablation Rates. Possible Compensations for Ablation Rates.

The following basic conclusion results from this study:

Regression rates increase noticeably with the use of hydrogen peroxide, and this permits the use of pure plastic polymers. Among these, polybutadiene lends itself well to operative techniques, and at all times gives an interesting performance. Moreover, a high combustion yield is generally obtained without the use of special devices.

Regression rates are increased still more by the introduction of fusible or more reactive charges, such as metatoluene diamine in nylon, and, at low concentrations, potassium borohydride in epoxy resins.

Moreover, since these regression rates are different in liquid and gaseous phases, a fuel with compensated regression rates in the two zones can be considered. Two compositions should be chosen in which rates of regression are close, or equal, one in the wet section near the injector, and the other in the more distant section.

Examination of the preceding tables allows us to envisage a series of neutral couples, shown as follows (Table VIII):

TABLE VII

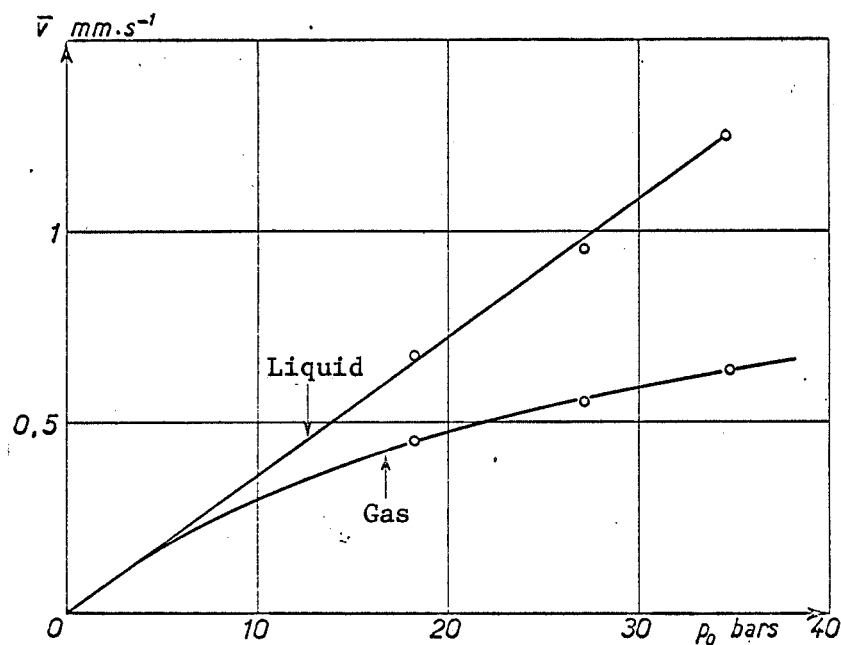| p_i(bars)	t_b(s)	$\dot{m}_{H}$(g/s)	$\dot{m}_o$(g/s)	p_o(bars)	φ	C^*(m/s)	L_i(mm)	L_g(mm)	$\bar{v}_i$(mm/s)	v_g(mm/s)
20	26,7	18,28	74,72	18,4	1,74	1554	75	65	0,68	0,44
30	17,8	19,72	112,08	26,8	1,23	1597	75	65	0,938	0,529
40	12,7	23,38	157,09	34,5	1,04	1502	70	70	1,236	0,622

Figure 13. Variation of regression rates in liquid and gaseous phases
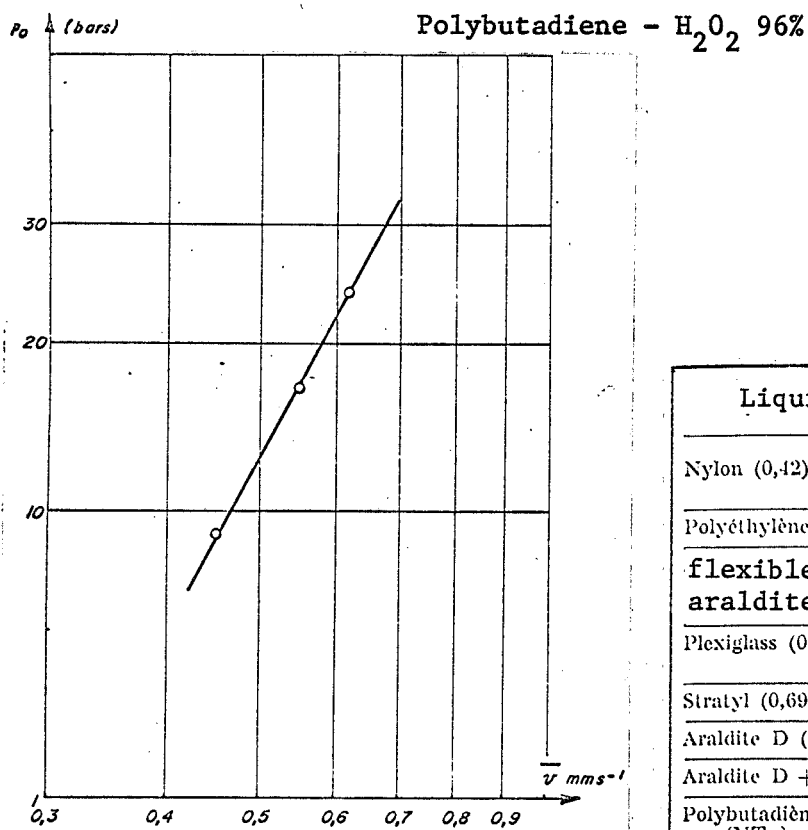for polybutadiene as a function of chamber pressure.

Polybutadiene - H_2O_2 96%

Figure 14. Variation of regression
rate in gaseous phase as a
function of chamber pressure.

TABLE VIII

Liquid zone	Gaseous zone
Nylon (0,42)	Stratyl (0,366) NMTD 60-35-5 (0,413)
Polyéthylène (0,46)	»
flexible (0,558) araldite	Araldite D + 10 % BH₄K (0,59) Polybutadiène (0,532)
Plexiglass (0,58)	Araldite D + 10 % BH₄K (0,59).
Stratyl (0,695)	NMTD 75-20-5 (0,721)
Araldite D (0,71)	NMTD 75-20-5 (0,721)
Araldite D + 10 % BH₄K	»
Polybutadiène (0,938) (MT₃₂) Polybutadiène (1,05) (MT₁₈)	NMTD 90-5-5 (0,98) (MT₃₂)

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Among these, two couples can be selected:

1) polybutadiene for the liquid phase (0.938) (1.05)
   NMTD 90-5-5 for the gaseous phase (0.98)

2) flexible araldite for the liquid phase (0.558)
   carboxyl polybutadiene for the gaseous phase (0.532).

This second combination of two polymers is noted in Figure 11.

Tested in the microthruster, under normal conditions, these two couples gave the following results:

For the first: $t_b : 8,2$ s; $\varphi : 1,36$; $\dot{m}_{II} : 26,5$ g/s; $\dot{m}_o : 122,0$ g/s; $C^* : 1\,434$ m/s; $L_l : 75$ mm; $\bar{v}_l : 0,923$ mm/s; $L_g : 92$ mm; $\bar{v}_g : 0,97$ mm/s.

For the second: $t_b : 7,5$ s; $\varphi : 0,87$; $\dot{m}_{II} = 17,71$ g/s; $\dot{m}_o : 133,31$ g/s; $p_u : 27$ bars; $C^* : 1\,404$ m/s. $L_l : 45$ mm; $\bar{v}_l : 0,493$ mm/s; $L_g : 92$ mm; $\bar{v}_g : 0,48$ mm/s.

For these two couples, it can be seen that regression rates $\bar{v}_1$ and $\bar{v}_g$ are close. Photographs taken after combustion of sections of the carboxyl polybutadiene-araldite couple in Figure 15 show a continuous combustion surface profile. Based on this, a thruster formed from two fuels with similar regression rates in the two zones can be considered.

VIII. Combustion in the Presence of Metals: Comparison of Results with Theory.

The addition of finely divided metals, notably powders of aluminum or magnesium-aluminum alloys, has a double effect. On the one hand, the characteristic velocity, and above all the specific impulse (increase in the coefficient of thrust) are improved. On the other hand, the volumetric mass of the fuel is higher. Its increase can reach 50% when the percentage of metal in the litergol is 60%. However, partial combustion of metallic particles leads to a significant drop in performance. This is the case in combustion with nitric acid, when aluminum is used without special treatment. With
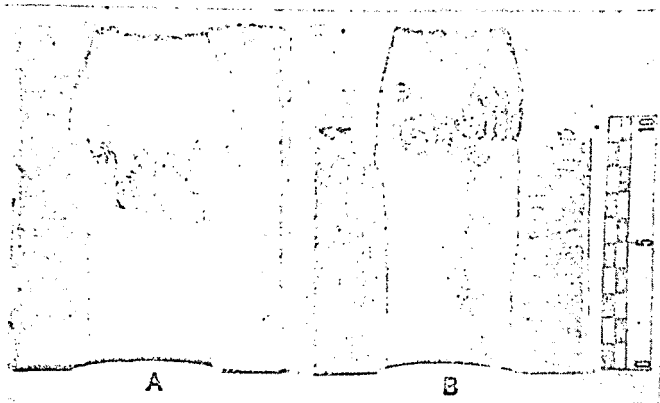
28

Figure 15.   Comparision of photographs
after combustion, of sections of
polybutadiene and an araldite-poly-
butadiene couple. A-polybutadiene;
B- couple: araldite-polybutadiene.

nitrogen peroxide N_2O_4, combustion is improved, but the high temperature produced in the chamber leads to rapid destruction of hard nozzles.

VIII.1.   Choice of Base Fuel.

Polybutadiene was chosen as a base fuel; its performance and mechanical behavior already made it a lithergol of interest. Further, its high viscosity allows it to maintain a homogeneous particulate suspension during polymerization.

VIII.2.   Results Obtained with Aluminum Powder in 5μ diameter Spherical Particles.

Percentages of 20, 30, 40, 50, and 60% aluminum were tested, and the results of firings are recorded in Table IX. For aluminum percentages less than or equal to 40%, there is no increase in characteristic velocity. The diameter of the throat of the tungsten nozzle remains virtually the same. When the aluminum introduced reached 50%, the nozzle rapidly deteriorated. This makes determination of the experimental characteristic velocity very uncertain. None of the various materials used for nozzle construction were resistant; this was notably the case with pryolitic graphite, and with rokidized graphite (protected by a projection of zirconium oxide plasma).

VIII.3.   Protection of the Nozzle by Fuel Flow.

The technique consists of molding, a plastic fuel material in the body of the convergent section preceding the nozzle, with a circular passage orifice of a diameter equal to 1.5 times that of the throat (Figure 16). The results obtained are significant, since the tungsten nozzles were resistant for 20 sec. of firing, with concentrations of 60% aluminum in the fuel, the diameter of the throat increasing by only 0.4 mm. The increase in the characteristic mixture ratio due to fuel removal in the convergent section remains acceptable. Since the characteristic velocity exceeds 1600 m/sec., the double influence of the addition of metals to litergols is retained (increase of specific impulse and
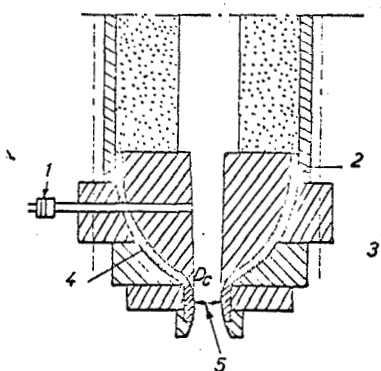
Figure 16. Microthruster MT-32 equipped for firings with H_2O_2 and lithergols. Metallic powder charges — protection of the nozzle.

1. pressure seal gauge P_0
2. durestos protector
3. molded plastic: polybutadiene or polyester or araldite.
4. cadarsite protector
5. nozzle.

volumetric mass of the fuel).

Several materials were tested in this way, and molded into the convergent section; the results have been satisfactory with polybutadiene, stratyl (polyester) and above all, araldite. Figure 17 shows the states of nozzles after 20 sec. firing, and Table X gives the results of firings performed with 60% 5μ aluminum.

Combustion yield is excellent, especially when we are always dealing with average characteristic velocity calculated over a relatively short firing time. (Standard specific impulse would be of the order of 260 sec.).

VIII.4. Results Obtained with Al-Mg Alloy(50%) Powder.

The granulometry of these particles in greater than that of the aluminum p particles used (70 μ approx.), but the presence of magnesium gives them better inflammability. As for aluminum, maximum gain is near 50% metal in the fuel, but only for the pressure of 30 bars in the chamber. There is only a 5% gain in specific impulse, (270 sec.), and nothing for characteristic velocity.

Results of firings are (Table XI):

TABLE IX

% Al	t_b(s)	$\dot{m}_{u}$(g/s)	$\dot{m}_o$(g/s)	p_o(bars)	φ	C*(m/s)	$\frac{C^* exp.}{C^* th.}$	M_v	Φ col (mm)
20	16,7	21,44	119,76	27	1,04	1532	0,94	1,05	10,1 → 10,1
30	18,6	24,19	107,53	26	1,18	1536	0,94	1,11	9,96 → 9,96
40	17,8	28,65	112,55	27	1,23	1534	0,94	1,23	9,96 → 10,1
50			Destruction of nozzle					1,32	
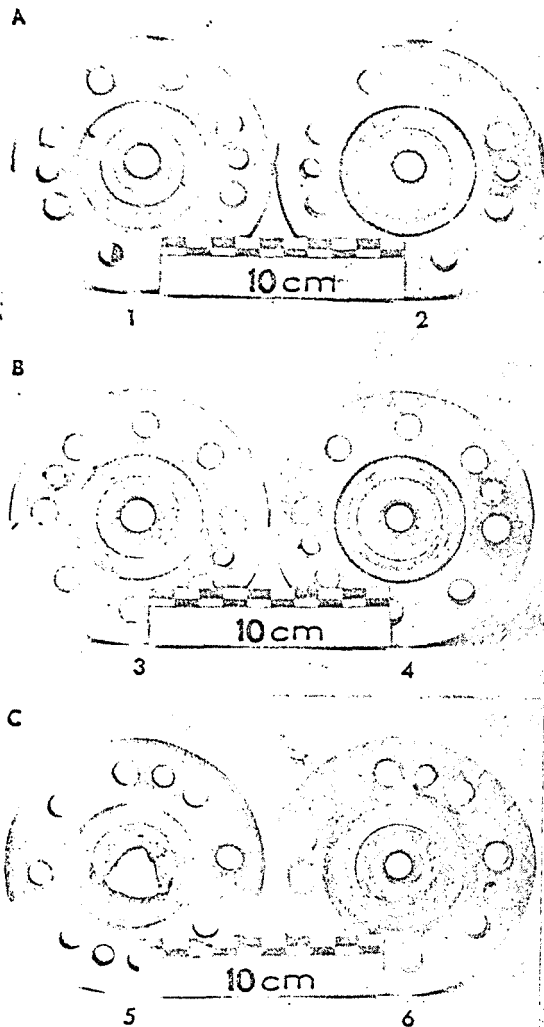
Figure 17. Throats of rokidized graphite .

A1. without protection ⌀ 10 → 14,2.
  2. with araldite protection
     ⌀ 10 → 12, Al : 60 %.
B. graphite throats
  3. without protection ⌀ 10 → 13,6.
  4. with araldite protection
     ⌀ 10 → 11,8, Al : 60 %.
C. tungsten throats
  5. unprotected
  6. with araldite protection.
     ⌀ 10 → 10,4.

As for aluminum alone, combustion yield increases with the metal content. Figures given only concern characteristic velocities. Since the increase in the thrust coefficient is still more important, a propellant can be used, with a volumetric mass close to 1.5, whose standard specific impulse easily reaches 260 sec., in a imple engine, without combustion devices.

IX. Combustion in Other Configurations.

IX.1. Frontal Microthruster.

Researches on the hybrid couple HLi-ClF have led to consideration of a particular mode of combustion. In this configuration, only a portion of the fuel is subjected to the action of the liquid oxidizer. It is diagrammed in Figure 18. The grain is subjected to a force derived from the difference between the injection pressure of the oxidizer, and the chamber pressure $(P_i - P_0)$. It is thus locked in its support within the combustion chamber, and maintains this position by gradually sliding downward until the grain is consumed. This arrangement has the advantage of maintaining the dimensions of the combustion chamber at constant values, and simplifies extrapolatory calculations, both in thrust and time, for hybrid thrusters.

TABLE X

Fuel moulded in convergent section.	l_b(s)	$\dot{m}_{\mathrm{H}}$(g/s)	$\dot{m}_o$(g/s)	p_o(bars)	φ	C*(m/s)	$\dfrac{C^* \text{ exp.}}{C^* \text{ th.}}$	Φ col (mm)
Polybutadiène	20,4	49,66	98,04	27	1,98	1590	0,98	9,9 → 11
Araldite D	19,3	55,57	103,63	27	2,09	1609	0,99	10 → 12
Araldite EM₁	21,2	46,84	94,34	28,5	1,94	1650	1	10 → 10,4

TABLE XI

Al-Mg %	l_b(s)	$\dot{m}_{\mathrm{H}}$(g/s)	$\dot{m}_o$(g/s)	p_o(bars)	φ	C*(m/s)	$\dfrac{C^* \text{ exp.}}{C^* \text{ th.}}$	M_v	Φ col (mm)
10	18,4	22,23	108,69	26	1,16	1545	0,96	0,97	9,96 → 9,96
20	19,4	22,73	103	25,3	1,13	1565	0,97	1,00	10 → 10
30	20	24,7	400	25,4	1,16	1600	0,98	1,06	10 → 10
40	19,6	29,43	102,04	27,2	1,22	1624	1,0	1,17	9,96 → 10
50	18,8	39,47	106,38	26,6	1,42	1610	0,99	1,25	9,96 → 10,6

Hydrogen peroxide allows the use of fuels having mechanical properties favorable to this type of combustion. For example, polybutadiene, by virtue of its excellent elastic properties, ensures an airtight fit between the two surfaces undergoing pressures p_i and p_0. Two firings performed in the MT-32 chamber, the first at a chamber pressure of 11.2 bars for 20 sec., and the second at 7.5 bars for 34 sec., show that combustion is very stable, and that a high combustion yield is attainable. The regression rate of the grain is very close to 1 mm/sec. In the second firing, a characteristic velocity of 1570 m/sec., was achieved for an exhaust concentration of 1.84.

Hydrogen peroxide can be used in a compensated frontal combustion system, and its auto-combustion favors ease of combustion. It is thus possible to devise a thruster with small thrust, but large operating time. For example, a thrust of 50 daN was obtained in a vacuum for 10 minutes from a grain 160 mm. in diameter and 600 mm long, and fuel being carboxyl polybutadiene. The
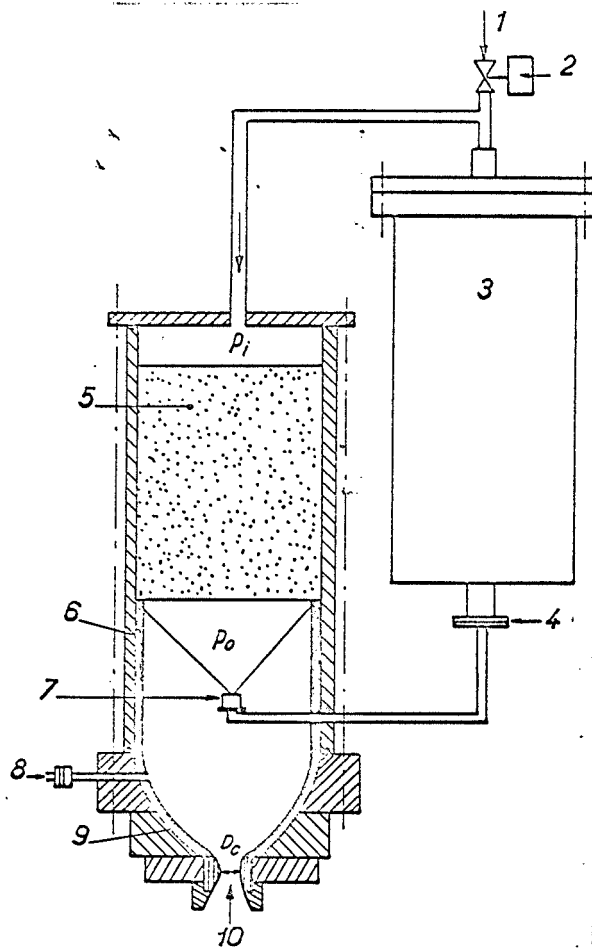
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Figure 18. Diagram of thruster with frontal combustion.

1. nitrogen entry
2. stop valve
3. oxidizer tank
4. blowout valve
5. polybutadiene grain
6. durestos protector
7. injector
8. pressure seal gauge p_0
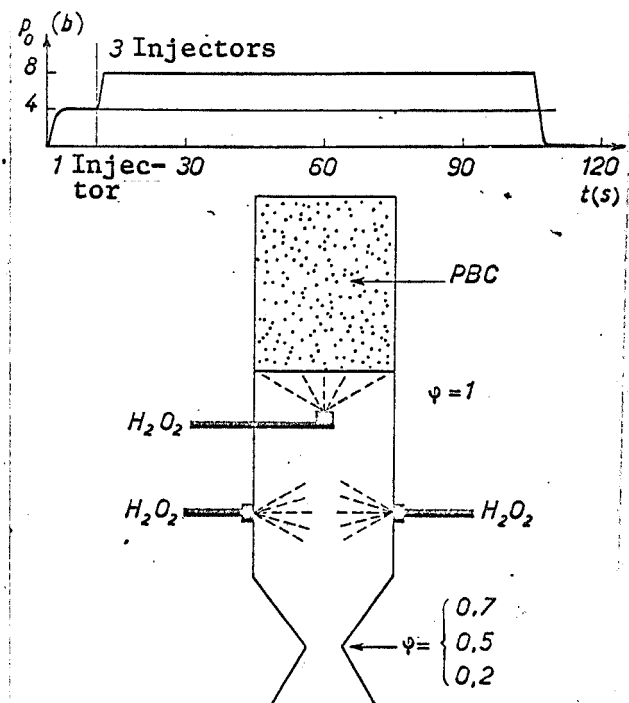9. caradsite protector
10. nozzle

Figure 19. Thermochemical decomposition of hydrogen peroxide.

standard theoretical specific impulse (70/1) of this couple was nearly 280 sec., and interesting applications can be imagined.

IX.2. Thermochemcial Decomposition.

A variant of this system is possible, in which thermochemical decomposition of hydrogen peroxide could be induced.

Figure 19 shows the principle. The first injector ensures combustion with the fuel "in the region of combined characteristic mixture ratio of unity". Below this, other injectors disseminate the hydrogen peroxide, which decomposes

in front of the throat. The experiment was done on a microthruster of diameter 60 mm, while the secondary injection was adjusted in such a way as to obtain small exhaust concentration values (0.7 to 0.2). For this last value, a firing of several minutes was carried out, performances being superior in this case to those obtained through catalytic decomposition of hydrazine. One can, then, by regulating the global mixture ratio, produce any performance between the limits of simple decomposition of hydrogen peroxide, and the maximum value of the hydrogen peroxide-fuel couple, the choice being determined by the temperature tolerated by the throat.

The advantage of this solution in relation to the standard system of catalytic decomposition is to suppress aging of the catalyst, to have a constant transfer function, and short response times, and to produce higher performance while operating at a concentration determined by the state of the throat.

X. Conclusion

Hydrogen peroxide can be used for purposes of propulsion in three ways:

1. as a monopropellant, using catalytic or thermal decomposition;
2. as an oxidizer by a preliminary catalytic predecomposition;
3. as a liquid oxidizer, by direct injection into the chamber over a hypergolic substance.

The last case forms the object of this study, in its application to hybrid thrusters.

The following results are obtained:

— solid compounds, strongly hypergolic with hydrogen peroxide, are more difficult to react with other oxidizers, such as nitric acid or nitrogen tetroxide, even at very strong concentrations. Among the compounds studied, potassium borohydride was retained because of its short ignition delay in the piston apparatus — 2 msec. Tested while in an amine suspension, and deposited

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on the perforation of a solid fuel in a microthruster MT-15, this compound gave a delay of 6 msec. As an initiator it is stable and insensitive to humidity.

— A comparative study of the standard amino lithergol NMTD in the presence of hydrogen peroxide, nitric acid, and nitrogen tetroxide in the microthrusters MT-15 and MT-32 led to an important result: regression rates are distinctly higher in the presence of hydrogen peroxide, and a new series of very rich plastic binder fuels is contemplated. These compounds combine good qualities of combustion with excellent mechanical properties. Among them, carboxyl polybutadiene, easy to mold and polymerize, was taken as a basis for study of pressure and performance obtainable through addition of metals.

— Longitudinal sections of litergol grains after their combustion in the presence of hydrogen peroxide show a different appearance to those obtained with other oxidizers; the lack of similarity between the two combustion zones, liquid-solid and gas-solid, are more pronounced in the presence of hydrogen peroxide, and regression rates are definable in these two zones. These, calculated by a method of graphical integration, allow the prediction of a lithergol with a constant combustion profile. This is obtained by the superposition of two fuels, one of which possesses the same regression rate in the gaseous phase as the other does in the liquid phase.

— Hydrogen peroxide of high concentration (greater than 95%) allows excellent combustion of metals incorporated in plastic materials. In the case of aluminum or aluminum-magnesium alloy powders, one can obtain, without recourse to sepcial devices, combustion products (calculated from characteristic velocities) of 0.94 and 0.99. This results is quite remarkable, and prompts consideration of the possible combustion of beryllium with this oxidizer.

— The configuration of the frontal microthruster is particularly well adapted to polybutadiene-hydrogen peroxide combustion, and on this principle a thruster with small thrust and large operating time is conceivable.

On the same principle, thermochemical decomposition of hydrogen peroxide is possible, using the heat derived from a primary hydrogen peroxide-fuel reaction in a stoichometric relation, and by adding secondary injectors. One can conclude that hydrogen peroxide is an oxidizer well adapted to hybride combustion. In the stable form in which it is used, it is simple to manipulate, and can be stored in tanks, previously rendered inert, with only a small amount of waste.

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