NON-TOXIC HOMOGENEOUS MISCIBLE FUEL (NHMF) DEVELOPMENT FOR HYPERGOLIC BIPROPELLANT ENGINES

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Abstract*

The authors have collaborated to conduct rocket engine firings of a newly discovered non-toxic homogeneous miscible fuel (NHMF) with 91% hydrogen peroxide. The synthesis of the NHMF and purification of the high test peroxide, as well as the preliminary spot-plate testing, were accomplished at the Naval Air Warfare Center Weapons Division, China Lake, California. The rocket engine firings were conducted at the Mojave Test Facility of HMX Incorporated located at the Mojave airport. These engine tests represent a continuation and enhancement of research started under a technology feasibility study.

The synthesized fuels were found to be true polar solutions, were non-toxic, economical, and, most importantly, had actual hypergolic ignition delays in the millisecond region. These candidate fuels are applicable for use in divert/attitude control system, orbit transfer, and large launch vehicle applications.

Nomenclature

ACS	Attitude Control System
CRADA	Cooperative Research and Development Agreement
DACS	Divert/Attitude Control System
HTP	High Test Peroxide
Isp	Specific Impulse
MMH	Monomethyl Hydrazine
NAWCWPNS	Naval Air Warfare Center Weapons Division, China Lake, CA
NHMF	Non-toxic Homogeneous Miscible Fuel
NTO	Nitrogen Tetroxide
O/F	Oxidizer-to-Fuel *[ratio]*
TBMD	Theater Ballistic Missile Defense

Background

In 1993, the Naval Air Warfare Center Weapons Division (NAWCWPNS), China Lake, California, began evaluating divert/attitude control system (DACS) approaches that were shipboard compatible and provided energy on demand to support future Navy Theater Ballistic Missile Defense (TBMD) intercepts. As a result of these studies, NAWCWPNS' researchers identified a combination of concentrated hydrogen peroxide and JP-10 derivative fuels as a potential DACS candidate.[1]

In 1994, NAWCWPNS' investigators demonstrated the feasibility of combusting 70% hydrogen peroxide and JP-10 in a 400-lbf thruster. The engine used a heterogeneous catalyst to decompose the 70% hydrogen peroxide into superheated steam and oxygen which then axially entered the combustion chamber and mixed with the radially injected JP-10 fuel. The mixture was then ignited downstream by an oxygen/hydrogen torch. The ignition source was necessary because the actual decomposition temperature, with flow cooling, proved to be less than the ignition temperature of the JP-10.

In 1995, NAWCWPNS conducted a series of studies that incorporated the chemical catalyst into the fuel (homogeneous), along with ignition boosters. This change allowed direct single-phase injection of the fuel and oxidizer into the combustion chamber, which, in turn, allowed the hydrogen peroxide/fuel streams to

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mix and react. During these demonstrations, 70% hydrogen peroxide and 85% high test peroxide (HTP) were used; this combination helped the ignition problems experienced earlier. The ignition delays were still pronounced, and backup igniters had to be used.[2]

The 1996 demonstrations provided definitive confirmation that the hydrocarbon fuels selected could yield stable and good performance in a closed combustion chamber with 90% HTP. Total propellant flows were in the 0.079 lbm/s range, and chamber pressure was varied from 64 to 220 psia. Some tests exhibited true hypergolicity, but ignition usually occurred past the combustion chamber, which implied a long ignition delay. Spark ignition was again required to ignite the mixtures to ensure ignition within the combustion chamber. With the spark ignition, combustion was always instantaneous, repeatable, and stable.[3]

It was postulated that the ignition problems could be traced to the immiscibility of the fuel and oxidizer streams and to the high (6.5) oxidizer-to-fuel (O/F) ratio needed. Both of these factors generally give poor mixing, hence poor ignition. The next phase of the research concerned the use of a new class of fuels, the non-toxic homogeneous miscible fuel (NHMF) species, which, in principle, would minimize ignition delays to the region of true hypergolicity within the combusion chamber of a rocket engine.

Introduction

Navy TBMD missions place great demands on kill vehicle divert and attitude control propulsion systems. Success of these missions mandate that the DACS provide fast, reliable, and controlled propulsion to accommodate location errors and guide the interceptor to a successful direct hit at the appropriate incoming warhead location. Trade-off studies[1] show that liquid propulsion systems provide many of the operating characteristics needed to accomplish this mission for the Navy—mainly good performance, energy on demand (minimum energy wasted during null or low thrust cycles), fast response, and good insensitive munitions characteristics. Traditionally, conventional hypergolic bipropellants with all of these attributes would have been selected; however, Navy TBMD requirements also include the necessity to meet shipboard safety and environmental regulations. Because existing hypergolic propellants are either extremely toxic or carcinogenic, the logistic and operational impact of using them is prohibitive.

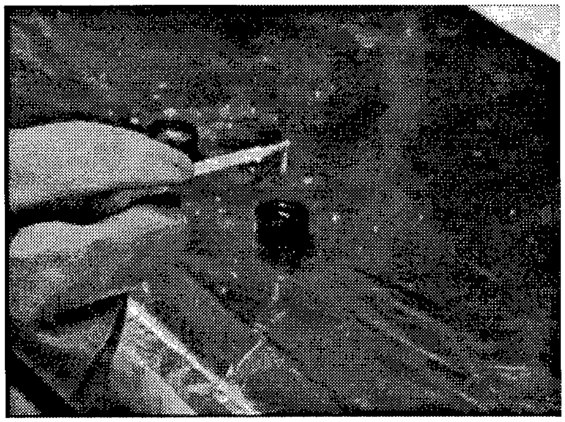
The results of the 1993 through 1996 studies conducted at China Lake[1-3] stimulated a significant number of inquiries from government and commercial activities for a diverse number of applications. This interest led to a realignment of the research to study both heterogeneous catalyst power generation devices such as monopropellant thrusters, turbines, and biphasic bipropellants, and homogeneous catalyst bipropellant rocket engines. In order to effectively evaluate the new concepts, a Cooperative Research and Development Agreement (CRADA) was established between HMX Incorporated and the United States Navy. The CRADA proved extremely beneficial to both parties, as data and resources were shared to obtain a common goal. This joint development allowed the verification of a new fuel, which not only exhibited true hypergolicity and low toxicity, but was also cost effective. The developed fuel promises to provide a clear advantage not only in the DACS arena, but potentially in the launch vehicle arena as well.

Chemical Studies

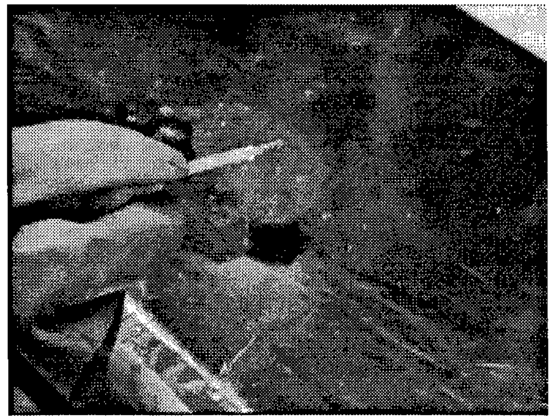
The basis for the NHMF is a fuel that is miscible in all proportions with hydrogen peroxide. This attribute alone would lead to a stable, but detonable solution; thus, a soluble chemical catalyst and a sensitizer were incorporated in the solution. Work conducted during World War II always led to toxic species for all three components. Researchers at NAWCWPNS have come up with a wide series of NHMF species that are environmentally safe, low in toxicity, and low in cost. For the purpose of this paper, composition 17B will be examined as a candidate NHMF.

Candidate components were selected based on kinetic and thermodynamic requirements; then, initial spot-plate testing was accomplished. This was a change in philosophy as thermodynamic optimization was ascertained <u>after</u> true hypergolicity was attained. The spot-plate tests were conducted by loading a container with a minimal amount of candidate fuel, just enough to cover the bottom surface of a 10-ml vial cap. One drop of 90% HTP was added to the fuel, and the effects noted.

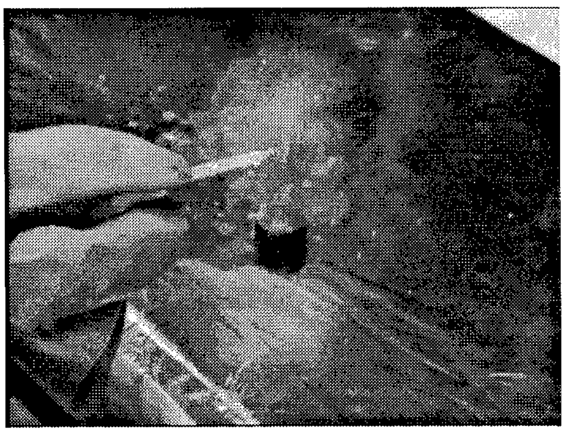
Figure 1 shows a four-frame sequence derived from video footage of a successful hypergolic spot-plate test. The time between frames is 33 ms. Frame one shows the HTP drop on its approach to the cap; frame two shows the initial reaction with gas generation; frame three shows continuing evolution and heating; frame four shows ignition. The total sequence took 100 ms.



Frame One.



Frame Two.



Frame Three.

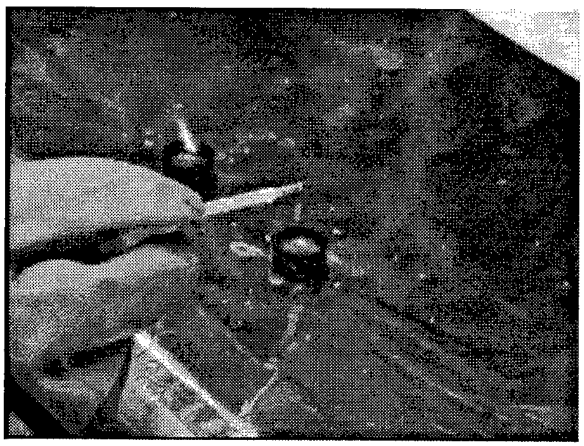
Frame Four.

FIGURE 1. Video Frame Sequence of Moderate Hypergolic Action Using Spot-Plate Method. Frame resolution is 33 ms.

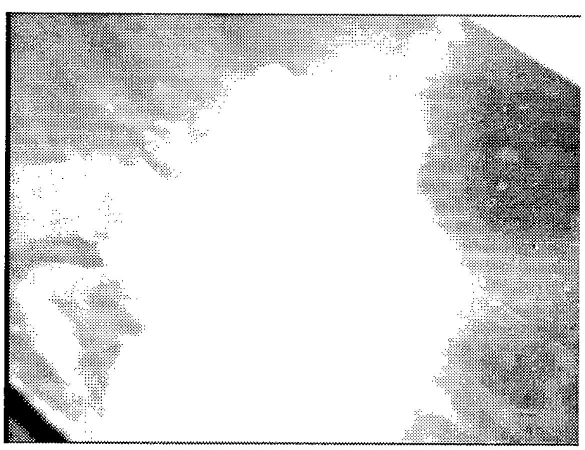
Figure 2 shows a two-frame sequence for NHMF 17B. Frame one shows the 90% HTP drop on the approach; frame two shows rapid burning. Again the estimated ignition time is well below 30 ms. From this simple test, hypergolicity itself can be determined as well as some speed of hypergolicity.

Since NHMF 17B was one of the first compositions to pass the spot-plate test, theoretical specific impulse (Isp) multiplied by specific gravity was calculated as a function of O/F ratio. The reader should note that concentrations within the fuel are fixed in the calculations, not optimized, as normally done. While the energy values are not necessarily the highest, they are assured to be hypergolic due to the previous spot-plate tests. Figures 3 and 4 show density impulse as a function of O/F ratio for the cases of a chamber pressure of 500 psia expanded to vacuum conditions, and a chamber pressure of 1000 psia expanded to sea level conditions, respectively. These cases were chosen to compare DACS, space attitude control system (ACS), and large launch applications. In both cases, NHMF 17B with 90% HTP is compared to hydrazine with nitrogen tetroxide, and monomethyl hydrazine (MMH) with nitrogen tetroxide (NTO). It is seen that NHMF/HTP has the same relatively broad O/F acceptance as MMH/NTO. The peak O/F values are roughly 3.0 and 2.5, respectively. The NHMF is not mixed in a fixed ratio, however. The fuel components can be permuted to deliver a small variance in O/F while maintaining energy and hypergolicity. This is significant because, according to the thermodynamic data and spot-plate information, 17B can be used in the same hardware currently used for MMH/NTO systems.

HTP was produced at NAWCWPNS by a double-run technique using high surface vacuum distillation. The technique uses a single plate still with a rotating batch tank; vacuum is applied to the entire still, including the prime condenser and extract receiver. The hydrogen peroxide charged was 70% w/w technical grade[4] with a high inhibiter loading. Distillation conditions were 50°C and 8.8 mm of Hg vacuum. Typical extract volume was 95% of the initial charge. This first distillation gave uninhibited hydrogen peroxide which was then rerun to yield HTP of defined concentrations. In all cases the hydrogen peroxide concentration was ascertained using a refractive index technique; inhibitor loading was obtained by inductively coupled plasma techniques.[4] The HTP used in these experiments was 91.7% w/w with less than 1.0 mg/l of phosphorus, tin, or sodium ions.



Frame One.



Frame Two.

FIGURE 2. Video Frame Sequence of Fast Hypergolic Action Using Spot-Plate Method. Frame resolution is 33 ms.

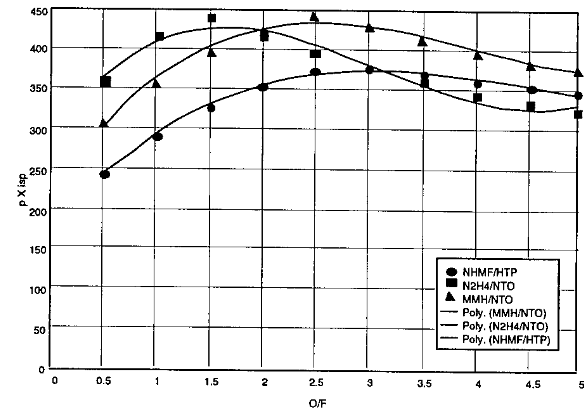


FIGURE 3. Specific Gravity by Specific Impulse as a Function of O/F Mass Ratio for Non-toxic Hypergolic and Conventional Hypergolic Systems. Propellants are combusted at 500 psi and expanded to vacuum conditions.

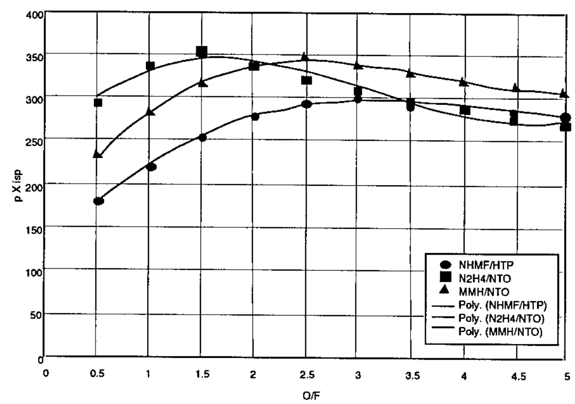


FIGURE 4. Specific Gravity by Specific Impulse as a Function of O/F Mass Ratio Comparing Non-toxic and Conventional Hypergolic Systems. Propellants are combusted at 1000 psi and expanded to sea level conditions.

Rocket Engine Studies

Test Site

The HMX Incorporated test site located at the Mojave California airport was used to support the test firings. The test stand incorporated a vertical firing geometry as depicted in Figures 5, 6, and 7. As can be seen, a spark plug is attached to the thrust chamber; this was used only as a plug and not energized during testing. The instrumentation consisted of MSP 300-series strain gauge pressure transducers which were used to measure chamber pressure, fuel manifold pressure, and oxidizer manifold pressure. Thermocouples measured propellant feed temperature; all data were acquired remotely at a 20-Hz sampling rate.

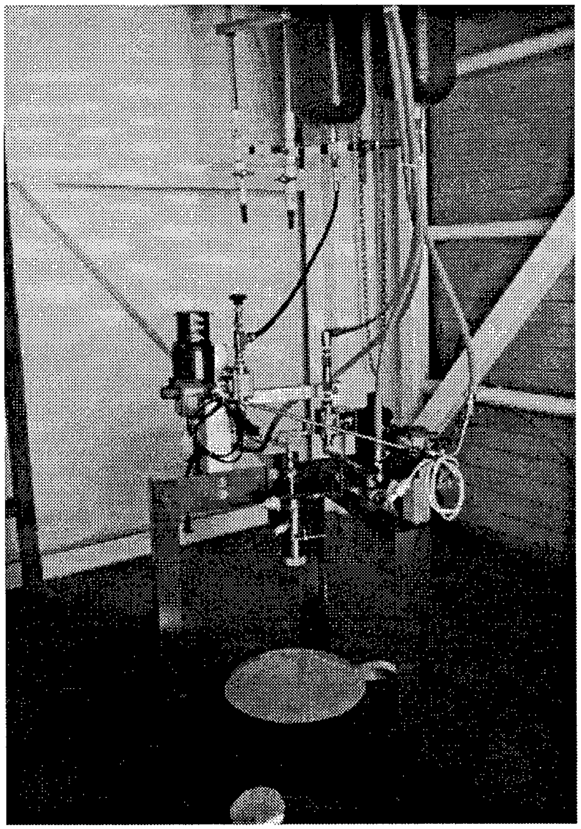


FIGURE 5. Vertical Test Stand.

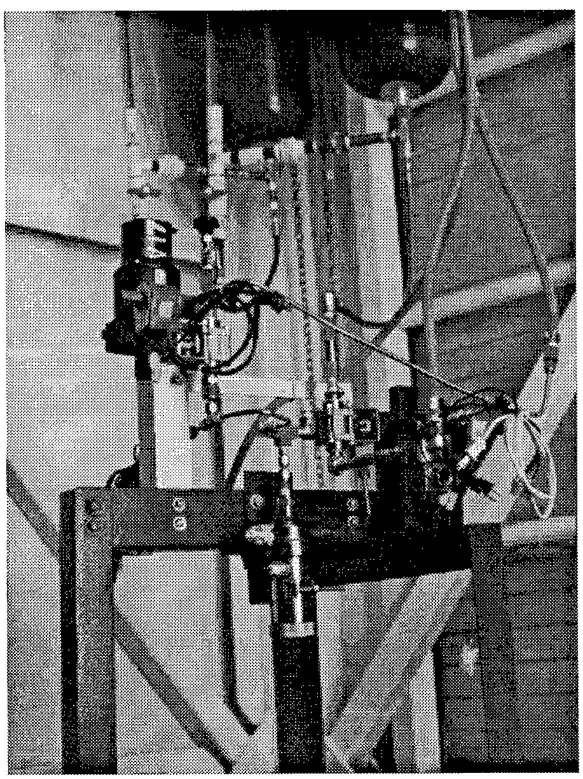


FIGURE 6. Perspective View of Vertical Test Stand.

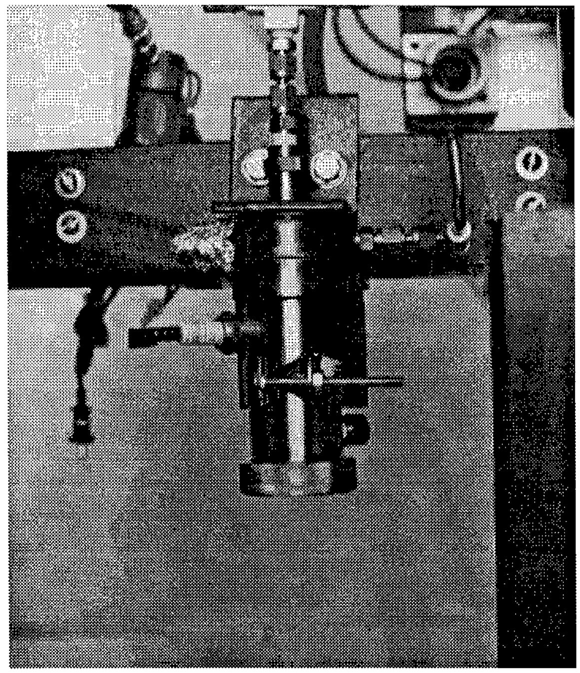


FIGURE 7. Close-up of Test Stand.

Test Hardware

The test hardware was essentially that used in the previous HTP/JP-10 experiments with two significant modifications: it had no ignition point and a modified injector.[3] Figure 8 shows an axial drawing of the rocket engine used in these tests. The spark plug ignition circuit was not used; however, the access hole was still plugged with the spark plug igniter. The O/F ratios were changed by installing threaded inserts into the oxidizer orifices. Figure 9 is a photograph of the injector face plate showing the six oxidizer threaded orifices. The fixed fuel orifice measures 0.028 inch and each of the oxidizer insert orifices measures 0.013 inch.

The use of threaded inserts allowed a measure of tailoring for various fuel and oxidizer combinations, but it had a significant drawback. Initial tests evidenced some leakage around the insert/seat interface. Figure 10 is a photograph of the hardware with the threaded insert modification; the oxidizer circuit is active and no splash plate was used for this photograph. Significant collimation of the fluid streams is evident. The best compromise configuration used the inserts in conjunction with the splash plate. All of the experiments described in this paper used this geometry.

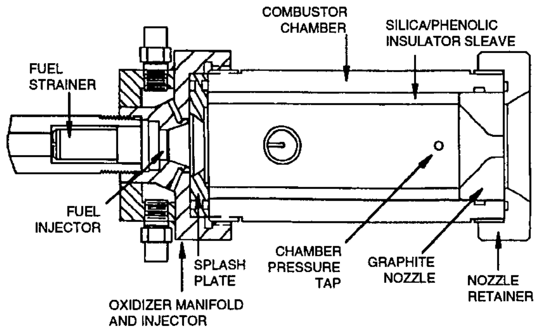


FIGURE 8. Line Drawing of Hypergolic Propellant Evaluation Thruster.

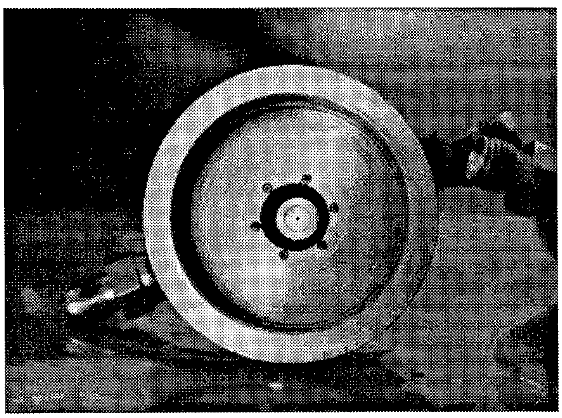


FIGURE 9. Photograph of Hypergolic Thruster Injector Face Showing Threaded Oxidizer Insert Orifices.

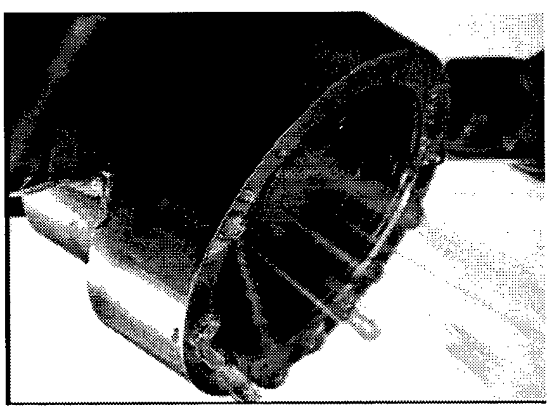
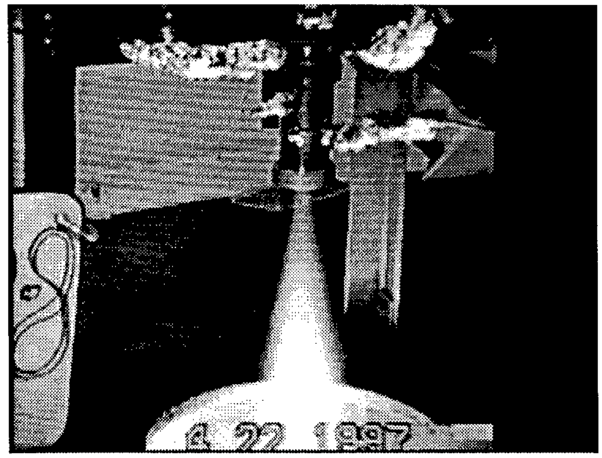


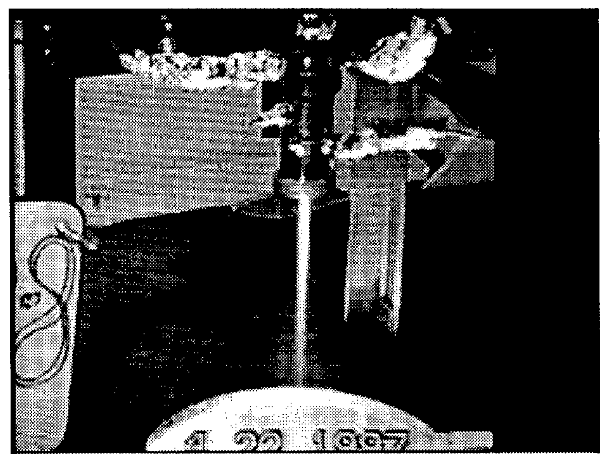
FIGURE 10. Photograph of Modified Injector with Oxidizer Circuit Active. Splash plate removed.

Test Results

Figure 11 shows two frames from video footage of a NHMF/HTP bipropellant firing. The actual time difference between the two frames shown is about 180 ms. This delay was due predominantly to the poor control of the O/F ratio with the original injector configuration and a fuel injection lag. Even with the delay, the combustion appeared stable once initiated.



Frame One.



Frame Two.

FIGURE 11. Video Frame Sequence of High O/F Injector Firing Using 17B Fuel. Ignition delay is ca. 180 ms.

Figure 12 shows a frame from video at the moment of ignition for test M-1 with the proper orifice configuration for a nominal 2.4 O/F ratio and good pressure control. This test had an ignition delay of 23 ms and exhibited stable behavior during firing, as ascertained from the video footage. Two data runs are depicted as Figures 13 and 14. Figure 13 shows a graph of pressure as a function of time for the HTP/NHMF 17B propellants at an O/F ratio of 2.4. The ignition delay was measured as 23 ms. The nominal total propellant flow was 0.05 lbm/s. Figure 14 shows an identical run with a change of the O/F ratio to 3.0. The ignition delay is also low, measured at ca. 24 ms. A summary of the initial experimental results is shown as Table 1. Measured chamber pressures, O/F ratios, and ignition delays are tabulated. It is clear that ignition delays in the tens of milliseconds, and even fractional milliseconds, are in hand. It should be remembered that these data were obtained with a non-optimal injection system due to insert leakage.

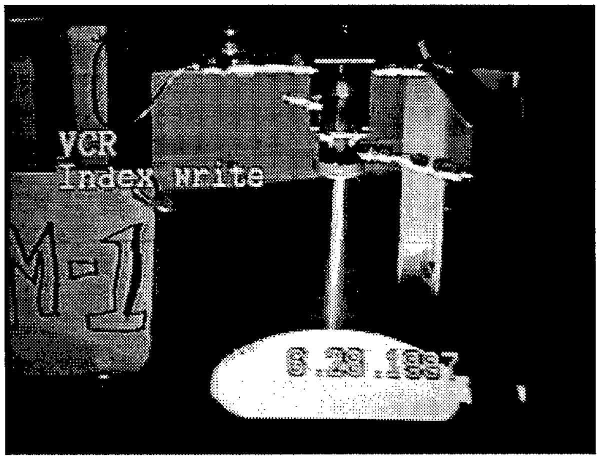


FIGURE 12. Video Frame Sequence of Modified Proper O/F Injector Firing Using 17B Fuel. Ignition delay is 23 ms.

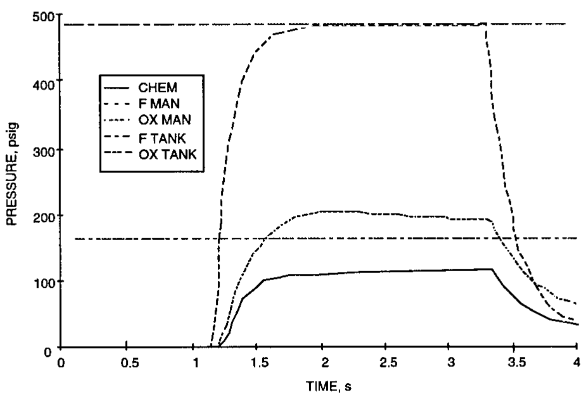


FIGURE 13. Run Pressure Plots of Test Firing M-1. Nominal O/F ratio is 2.4.

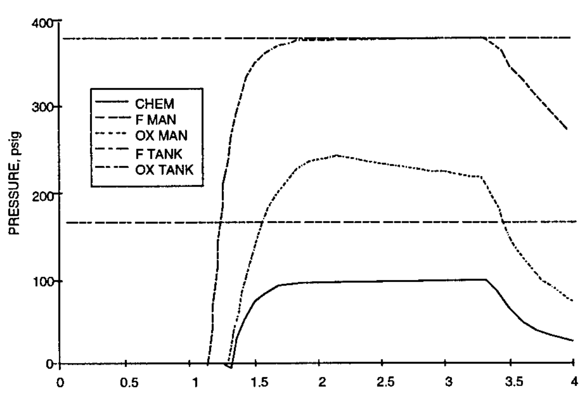


FIGURE 14. Run Pressure Plots of Test Firing M-4. Nominal O/F ratio is 3.0.

TABLE 1. Summary of Experimental Thruster Firings Using Non-toxic Propellants. (All firings listed exhibited hypergolic behavior.)

Test	Chamber Pressure, psig	O/F Ratio, w/w	Ignition Delay by Pressure, ms	Ignition Delay by Video, ms	Comments
M-1	107	2.4	23	125	no lead
M-2	102	2.4	10	66	0.1 s fuel lead
M-3	97	3.0	30	165	no lead
M-4	94	3.0	(24)	130	0.1 s fuel lead
M-5	87	2.0	67	297	no lead
M-6	–	2.4	122	no flame	add mixing cup no lead
M-7	–	2.4	–	no flame	add mixing cup no lead

Economics

A quick examination of the current market production of the raw components was done to ascertain the ultimate costs associated with the HTP/NHMF propellant system. Uninhibited 90% w/w HTP has a current market value of \$0.62 per pound. The NHMF aggregate propellant has a value of \$0.32 per pound. Using measured densities, these values translate to \$7.14 per gallon for HTP and \$2.72 per gallon for NHMF 17B. There is no associated toxic handling costs based on the non-carcinogenic nature of the propellants; these propellants are truly storable (with no smell) at ambient conditions, hence the total costs for use will be remarkably low. A subtle associated cost is that of renewability. The more scarce a chemical commodity, the higher the net cost. All of the components used in the HTP/NHMF propellant system are immediately renewable, and thus will ultimately drive the cost down further.

Summary and Conclusions

Government and industry investigators jointly conducted rocket engine firings to assess the feasibility of a new NHMF/HTP propellant combination. The following conclusions were obtained.

1. A new non-toxic propellant system, NHMF/HTP has been discovered which has performance comparable to that of traditional toxic hypergoles.

2. The optimal O/F ratio for maximum thermodynamic performance of NHMF/HTP lies in the same range as that of MMH/NTO, at about 2.4 to 3.0.

3. The NHMF/HTP system is economical and has a high propellant density. Estimated costs for HTP are \$0.62 per pound or \$7.14 per gallon. Estimated

costs for a candidate NMHF are \$0.32 per pound or \$2.72 per gallon.

4. All of the ingredients in the NHMF/HTP propellant are non-carcinogenic, non-mutagenic, and non-teratogenic.

5. All of the ingredients in NHMF/HTP are immediately renewable within the environment.

6. Tests to date show an exceptionally good ignition delay value of tens of milliseconds down to fractional milliseconds.

This propellant combination should prove to be quite useful to the DACS, orbit transfer, and large launch vehicle user communities. It is advisable that these non-toxic fuels be developed further to acquire larger scale delivered Isp information as well as long term storage data. It would also be useful for DACS mission cycle testing to be completed as soon as possible to prove the worth of these novel propellants.

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