MCR-67-15 (Issue 1)

JPL Contract 951709

STERILIZABLE LIQUID PROPULSION SYSTEM

First Quarterly Progress Report

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January 1967

MARTIN COMPANY
A DIVISION OF MARTIN MARIETTA CORPORATION
Denver, Colorado

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

NOTICE

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FOREWORD

This document is the first issue of the Quarterly Progress Report and is submitted in accordance with Article 1(a)(1)(v)(E) and 2(b)(5) of JPL Contract 951709.

CONTENTS

I. INTRODUCTION

This is the first quarterly progress report to be submitted in accordance with JPL Contract 951709. The report covers the period from 5 October 1966 through 30 December 1966.

The program involves the exposure of an assembled and fueled bipropellant liquid propulsion system to the ethylene oxide (ETO) and heat sterilization environments specified by JPL specification VOL 50503 ETS. After exposure the system will be fired for 300 sec.

The program plan includes a design and component selection phase during which the propulsion system design is evolved. A second phase will involve the procurement of components for both a component test series and for assembly into the complete system. The third phase of the program, which is being carried on in parallel with the design phase, is a materials investigation. During this phase data are being collected and testing is taking place. Where data do not exist testing is being conducted to provide the necessary information. The fourth phase of the program involves the assembly and test of the complete propulsion system. The system will be assembled and propellants loaded and then exposed to ETO and heat sterilization cycles. No attempt will be made to sterilize or to verify sterilization. The intent is to prove the feasibility of exposing a loaded bipropellant propulsion system to both the ETO and heat sterilization environments without system degradation. This will be proved by a 300-sec. hot firing of the system immediately after exposure to the environments. As a final verification the system will be disassembled and the component parts tested and inspected for degradation.

During this report period we were engaged in the system design and materials investiagtion phases. The design and component selection phase is scheduled to last four months. Therefore, total results, conclusions, and final component selections will be presented in the next quarterly report.

Materials compatibility investigations will continue over the total period of the contract. Some of the material screening results obtained to date are presented in this report.

II. CONCLUSIONS

As a result of work completed on the materials investigation portion of the program, a number of conclusions may be drawn:

1) Titanium alloy 6AL-4V and aluminum alloys 6061-T6, 2014-T6, and 2219-T8 are the most promising materials for constructing either oxidizer or fuel propellant tanks and associated hardware;

2) Ferrous based alloys are unacceptable for oxidizer tankage application because of the formation of a contaminant (called "adducts of iron"), rather than as a result of structural degradation;

3) All metals tested are acceptable for use with fuel;

4) Whenever possible, nonmetals should not be used when contact with either propellant at sterilization temperatures is necessary;

5) The effect of Teflon and associated types of compounds on metals, when exposed to propellants at sterilization temperatures, requires further study;

6) A potential hazard exists if fuel or oxidizer should leak into the sterilization chamber during exposure of the module to ethylene oxide;

7) Passivation of the fuel system before loading is required to ensure that no oxidizing substances are remaining.

III. RECOMMENDATIONS

As the result of the materials investigation program, three types of recommendations will be made at this time -- preliminary, firm, and recommendations for future study.

A. PRELIMINARY RECOMMENDATIONS

Preliminary recommendations are based upon preliminary information available at this point from the materials screening program. These recommendations are as follows:

1) Titanium alloy 6AL-4V should be used for construction of oxidizer tankage;

2) Aluminum alloy 6061-T6 should be used for all oxidizer plumbing lines;

3) Valves contacting oxidizer during sterilization cycles should be constructed of aluminum;

4) Titanium alloy 6AL-4V or 6061-T6 aluminum should be used for fuel tank construction;

5) Plumbing lines and valves that contact fuel during sterilization cycles should be of aluminum or stainless steel alloys;

6) Burst discs for either system should be made from 1100-0 aluminum.

B. FIRM RECOMMENDATIONS

Firm recommendations are based on completed testing. They are as follows:

1) Passivation of fuel system should be accomplished in accordance with Materials Engineering Report 67-1R;

2) Oxidizer should meet minimum nitric oxide (NO) content requirement of NASA Specification MSC-PPD-2A, dated 1 June 1966;

3) Modify engine, selected for use in module, as defined in Materials Engineering Report 67-2;

4) Install a purge capability in the ethylene oxide environment chamber that will activate whenever the propellant sensors detect a concentration of 5 ppm of either propellant. This system would act to dilute the atmosphere with either air or nitrogen and would alert operating personnel.

C. RECOMMENDATIONS FOR FUTURE STUDY

Recommendations listed here are presented as an outgrowth of the program and are not considered a necessary activity for meeting the intent of the program. Rather, they are items that could provide valuable information for future design.

1) Investigate effects on metals and propellants when Teflon and related compounds are present during heat sterilization cycle;

2) Determine the precise chemical composition of the adducts of iron when wet with nitrogen tetroxide and when dry;

3) Investigate the possibility of adding inhibitors to nitrogen tetroxide to prevent the formation of iron adducts;

4) Determine feasibility of presterilization of both propulsion system components and propellants before loading to eliminate the many penalties involved in designing tankage for exposure to propellants at 275°F;

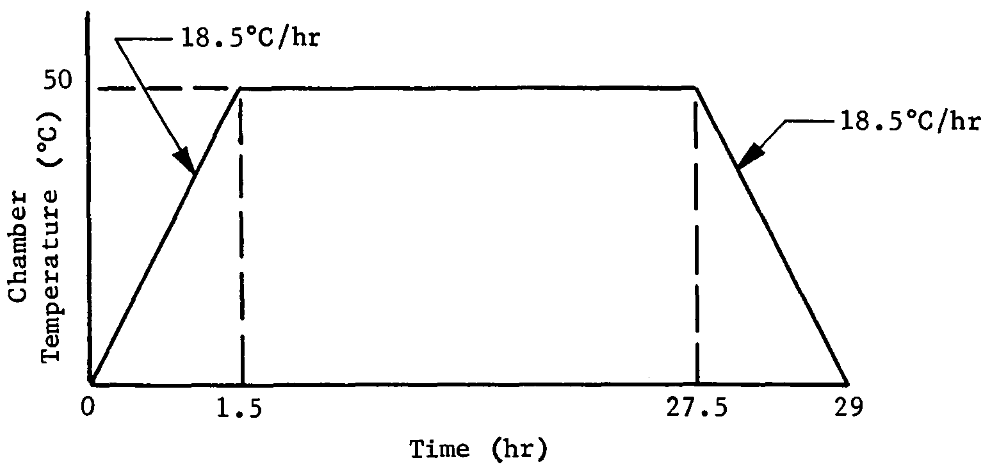
5) Explore possible methods of nonthermal sterilization of propellants during load. Potential methods include ultraviolet radiation, ultrasonic vibration, and filtration.

IV. GENERAL REPORT

A. PROPELLANT SELECTION

During the quarter, effort was initiated and completed on the selection of a propellant combination to be used with the propulsion module. The selection was based upon two significant factors. One factor considered the compatibility of the propellants with the sterilization environments and with the materials of containment during exposure to sterilization. The other factor considered the propellants with respect to performance, engine availability, and test experience.

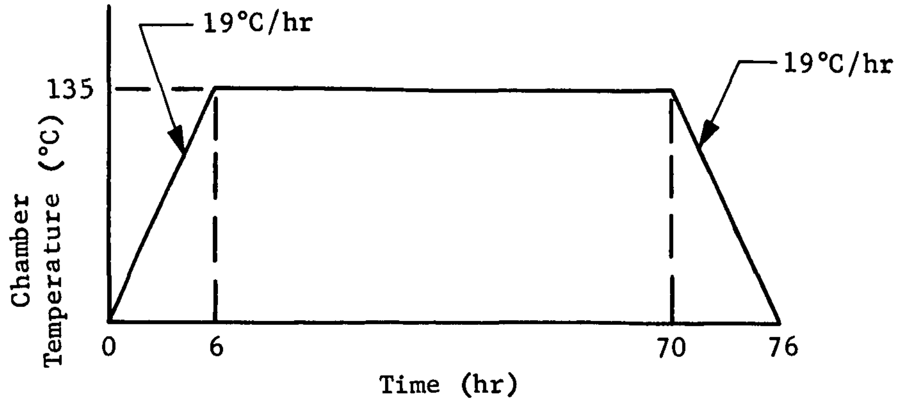
The sterilization environments are defined in detail by JPL Specification VOL-50503-ETS. The requirements include exposure of the propulsion system to both ethylene oxide mixed with freon and to heat. The ethylene oxide/freon decontamination tests consist of six cycles of exposure of the module over the temperature time relationship shown in the following sketch.



ETO Decontamination Cycle

The decontamination test environment is 88 percent Freon 12 and 12 percent ETO at 50 percent relative humidity and a concentration of 600 mg. of ETO per liter of gaseous atmosphere.

The heat sterilization test consists of six cycles of exposure of the assembled module to the following criteria.



Heat Sterilization Cycle

During the heat cycles the test atmosphere is gaseous nitrogen.

Three candidate oxidizers and three candidate fuels were considered. The oxidizers were nitrogen tetroxide (N_2O_4), mixed oxides of nitrogen (MON), and inhibited red fuming nitric acid IRFNA). The fuels were hydrazine (N_2H_4), monomethylhydrazine (MMH) and Aerozine 50 (A-50). The major considerations used for the propellant selection were:

1) Vapor pressure at elevated temperature;
2) Stability at elevated temperature;
3) Material compatibility at elevated temperature;
4) Engine test experience including performance demonstration.

1. Oxidizer Selection

MON mixtures were eliminated early in the selection phase based upon a lack of high temperature compatibility data and the high vapor pressures of these mixtures.

N_2O_4 was favored over IRFNA on the basis of higher performance with the fuels considered, and on the availability of high temperature compatibility data from Bell Aerosystems. A summary of the factors considered is presented in Table 1.

Table 1 Oxidizer Selection Data

Propellant	Vapor Pressure (psia @ 275°F)	Thermal Stability	High Temperature Compatibility	Performance Demonstrated	Production Systems Using This Propellant	Engine Test Experience
N_2O_4	800	Decomposition only slight @ 275°F	Materials available	I_{sp} >290 sec	Many systems	Greatest
IRFNA	125	Equilibrium pressure 300-400 psi @ 275°F	Questionable	I_{sp} <275 sec	Drone system	Minimum
MON	>800	Decomposition only slight @ 275°F	Materials available for ambient temperature use	I_{sp} >290 sec	More than one	Adequate

Based on available data and experience, N_2O_4 was chosen as the oxidizer to be used for the program. The high vapor pressure that will cause a somewhat higher system weight than IRFNA, is more than offset by the material compatibility and engine experience using N_2O_4.

2. Fuel Selection

Since there was little variation in vapor pressures and high temperature compatibility properties for the three candidate fuels considered, the main criteria for the selection were thermal stability of the fuel and performance and system weight advantage with the selected oxidizer. On the basis of specific impulse and system weight, neat hydrazine is clearly superior to either of the other fuel candidates from a pure theoretical standpoint; however, from the standpoint of thermal stability, it is less desirable than either A-50 or MMH. The very limited decomposition rate data available for MMH (at ambient, 160°F and 400°F) are similar to rates observed for pure hydrazine (Ref 1). Certain impurities, particularly oxygen, can increase the sensitivity to thermal decomposition markedly. For example, MMH that has been exposed to air sufficiently to cause a slight yellowish discoloration will show increased thermal instability.

The low sensitivity of UDMH to catalytic decomposition is well documented, and the decreased sensitivity of the mixture with hydrazine/A-50, has been demonstrated in the successful use of this fuel in regeneratively cooled upper stage engines. UDMH was not considered as a candidate even though it exhibits superior thermal properties because of its low performance capability. Stability testing of the candidate fuels is well documented for normal storability limits below 160°F in both open and closed vessels, however, all will decompose rapidly and explosively at elevated temperatures. Bomb test data reported by Rocketdyne (Ref 2) reveal the approximate temperatures at the onset of rapid decomposition for the fuels that are 480°F for N_2H_4, 640°F for MMH, and 720°F for UDMH. Between the normal storage temperature and rapid decomposition temperature of the fuels, very little experimental work indicating decomposition rates has been performed. Consequently, the actual relative stability rating for the hydrazine fuels in the range of interest at 285°F, can only be speculated. A recent attempt to correlate these data at Martin (Ref 3) indicated that the decomposition rates of the candidate fuels are of the same magnitude at ambient temperatures. General opinion of various sources in the industry indicate that the stability rating in declining order is as follows: UDMH, MMH, A-50, and N_2H_4. There is some disagreement as to the comparative stability of MMH and A-50. The most desirable engine operating characteristics favor MMH, which has been chosen as the fuel for this program.

A summary of the factors considered for fuel selection are presented in Table 2.

Table 2 Fuel Selection Data

Propellant	Vapor Pressure (psia @ 275°F)	Thermal Stability	High Temperature Compatibility	Performance Demonstrated	Production Systems Using This Propellant	Engine Test Experience
N_2H_4	25	Good in absence of catalytic materials	Materials available	I_{sp} >290 sec	None	Minimum
MMH	63	Good, some sensitivity to catalysts	Materials available	I_{sp} >290 sec	Many	Maximum
A-50	75	Very good	Materials available	I_{sp} >290 sec	Many	Sufficient

Note: Based on the above data the selected fuel could be either MMH or A-50. Additional considerations are:

1) Less ignition spike occurs with MMH;
2) MMH burns cooler;
3) MMH better film coolant;
4) More engine test experience with MMH on candidate engines;
5) A-50 performance is slightly greater than MMH.

As a final verification of the individual selections of oxidizer and fuel, a check was made of the particular propellant combination. Table 3 compares some of the commonly used combinations with MMH/N_2O_4.

Table 3 Propellant Combination Comparison

Propellant Combination	State-of-Art Rating	Theoretical Vacuum Performance Equilibrium P_c = 150 psia, ϵ = 40		Postshutdown Altitude Ignition (Critical) Operation
		I_{sp} (sec)	Oxidizer/Fuel Ratio	
N_2O_4/N_2H_4	3	340.7	1.35	Poor
$IRFNA/N_2H_4$	3	325.7	1.6	Poor
N_2O_4/MMH	1	337.7	2.2	Good
IRFNA/MMH	2	320.9	2.4	Good
N_2O_4/A-50	1	338.1	2.0	Poor

Here again the selected propellants appear to be the logical choice as a propellant combination.

B. ENGINE SELECTION

The engine and propellant selection activities were carried on simultaneously because of the interdependence of functions. Although a final engine selection has not been made, all engines still under consideration are compatible with the propellant combination selected.

The engine selection is being accomplished in four phases. The factors considered in each phase are as follows:

1) Engine propellant considerations -

   a) Propellant test experience,

   b) Production system experience,

c) Demonstrated performance;

2) Engine program restraints -

a) Engine availability,

b) Engine cost,

c) Engine predelivery characterization;

3) Preliminary engine screening -

a) Selected propellant test experience,

b) Minimum performance capability demonstrated (-3σ),

c) Duration capability,

d) Materials of construction;

4) Final engine screening -

a) 12% ETO - 88% Freon decontamination compatibility,

b) 280°F extended temperature exposure capability,

c) Engine rework required to meet system requirements.

The first phase of the engine selection has been completed and the results of this study are shown in Table 4. The table presents the bipropellant engines in the 50 lb_f to 150 lb_f thrust range, nominal delivered performance demonstrated by developed systems, and general test experience that identifies current small engine state of the art. The original candidate engines proposed for the sterilizable propulsion system are identified by an asterisk.

Table 4 Engine-Propellant Considerations

Propellant Combinations	Production System Usage	Substantial Test Experience	Limited Test Experience	Demonstrated Performance, I_{sp} (sec)
NTO/MMH	1*, 3	4*, 5*, 7*, 8*, 9*, 12*	6*	298
NTO/UDMH			13	260
NTO/N_2H_4			13	--
NTO/A-50	2, 5*	7*, 8*, 9*, 11*	4*	298
IRFNA/UDMH			13	270
MON/MMH		8*	6*	298
MON/MMH Hydrate	6*			287
MON/UDMH	10			260

1. Rocketdyne - Gemini 23 lb_f, 79 lb_f, 94.5 lb_f* - ablative
2. Rocketdyne - Transtage 25 lb_f, 45 lb_f - ablative
3. Rocketdyne - Apollo 91 lb_f - ablative
4. Rocketdyne - Beryllium 100 lb_f* - heat sink
5. Marquardt - Apollo 100 lb_f* - radiation
6. Thiokol (RMD) - Surveyor 104 lb_f* - regenerative
7. Thiokol (RMD) - Apollo, C-1 100 lb_f* - regenerative
8. TRW Systems - Surveyor backup MIRA-150A* - ablative (radiation alternative)
9. TRW Systems - URSA-100R 100 lb_f* - radiation
10. Bell Aerosystems - Agena 2nd propulsion 16 lb_f, 200 lb_f - radiation
11. Bell Aerosystems - NASA Program Model 8414* 100 lb_f - radiation
12. Bell Aerosystems - NASA Program Model 8374 100 lb_f* - adiabatic wall
13. IR&D and/or exploratory testing

As a result of investigations under the first phase of selection, the 100-lb_f engines to be further studied for this program are:

4. Rocketdyne - Beryllium - heat sink
5. Marquardt - Model R-4D - radiation
7. Thiokol, RMD - Model C-1 - regenerative
8. TRW Systems - MIRA-150A - ablative
9. TRW Systems - URSA-100R - radiation
11. Bell Aerosystems - Model 8414 - radiation

Engine 1 was eliminated due to inability to demonstrate required performance and probable inability to meet 300-sec firing duration. Engine 6 was eliminated due to limited test experience with the selected propellants, and Engine 12 was eliminated because no engine is available for this program.

Work was continued under Phases II and III. At this time, engine suppliers have been contacted and specific information requested. In addition, the possibility of using an ablative nozzle has been discarded due to the uncertainity of compatibility with ETO and to the firing duration capability. This type of engine probably will not meet the 300-sec firing duration.

C. SYSTEM DESIGN AND ANALYSIS

Effort was initiated on both system layout and on a design analysis. At the end of the quarter the layout has been completed using the components from the preliminary selection phase described under Section D of this report. In addition, a preliminary system design criteria document has been written and issued. Since the design criteria, system layouts, and component selection are interdependent, all were worked simultaneously and have progressed through initial stages. They will be completed shortly after component final selection.

1. System Schematic

The schematic of the propulsion system evolved during the report period and several changes occurred as requirements became better defined. Figure 1 depicts the system as it now exists. All components inside the interface lines are integral parts of the module and are being selected from available hardware of an airborne, flight qualified configuration. All components outside the interface lines are considered to be facility items and will, therefore, not require qualification status.

The system is a nitrogen gas, pressurized, bipropellant, propulsion system of conventional design. It is separated into five basic sections:

1) Nitrogen gas storage;

2) Pressurant regulation and supply;

3) Oxidizer storage;

4) Fuel storage;

5) Propellant feed and engine.

Three of the basic sections, nitrogen gas storage, oxidizer storage, and fuel storage are considered hermetically sealed areas. That is, they are terminated by normally closed ordnance operated valves or by capped lines. All line or component joints within these systems will be leak checked to a requirement of 1×10^{-8} scc/sec using helium gas at 50 psig. The remaining systems including pressurant regulation and supply, and propellant feed and engine will be required to be bubble tight at operating pressure using nitrogen gas as the pressurant.

2. System Design Layout

The system as initially proposed consisted of spherical gas and propellant tanks arranged in a pyramid configuration as shown in Fig. 2. As the layout of structural members progressed it became apparent that this configuration would require fairly heavy supports for the gaseous nitrogen tank. This was required in order to withstand three-axis, 14-g acceleration loads imposed by the environmental criteria. This criterion, which is defined by JPL Specification 30250B, was used as the basic design guide for the system and its components.

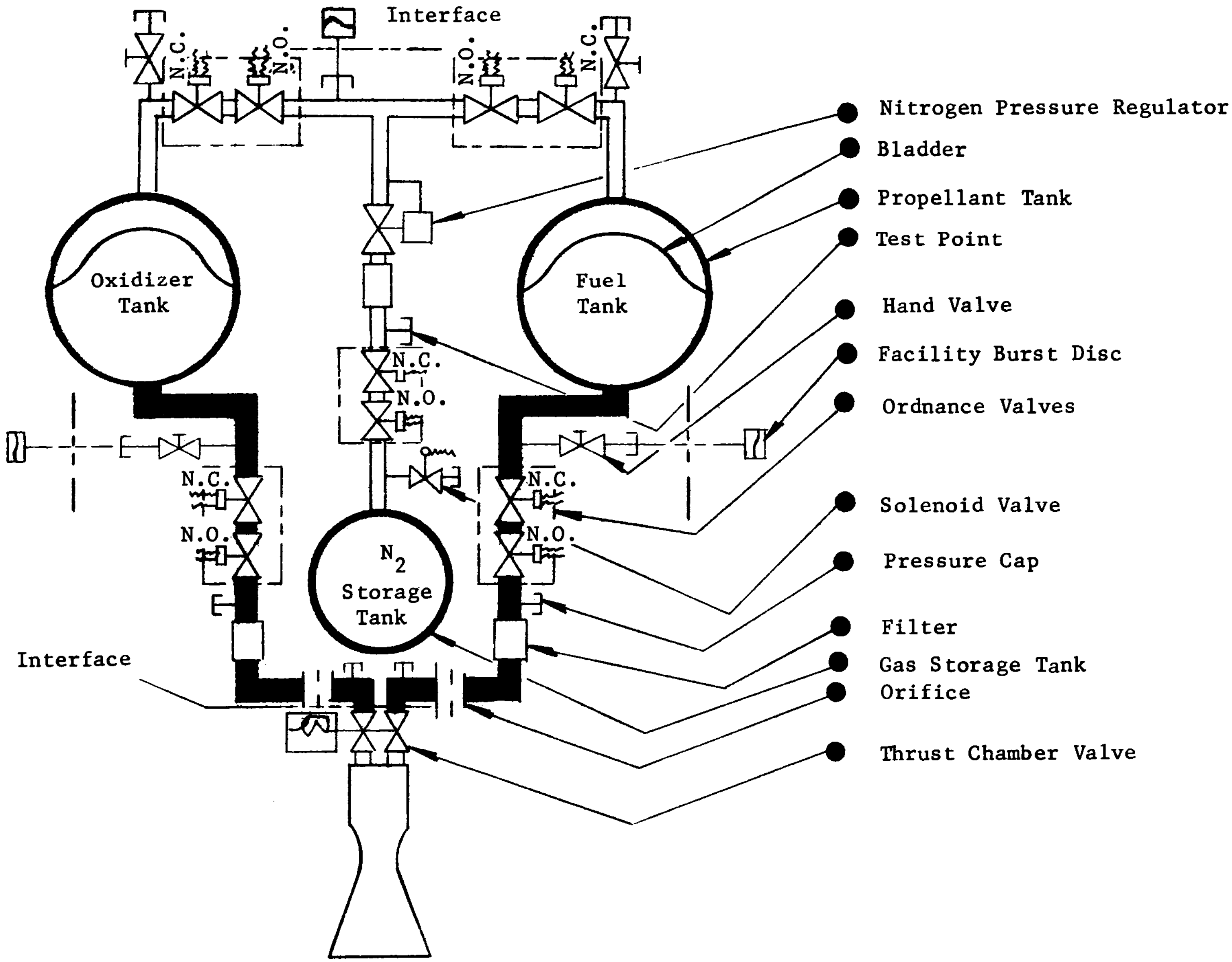


Fig. 1 Sterilizable Liquid Propulsion System

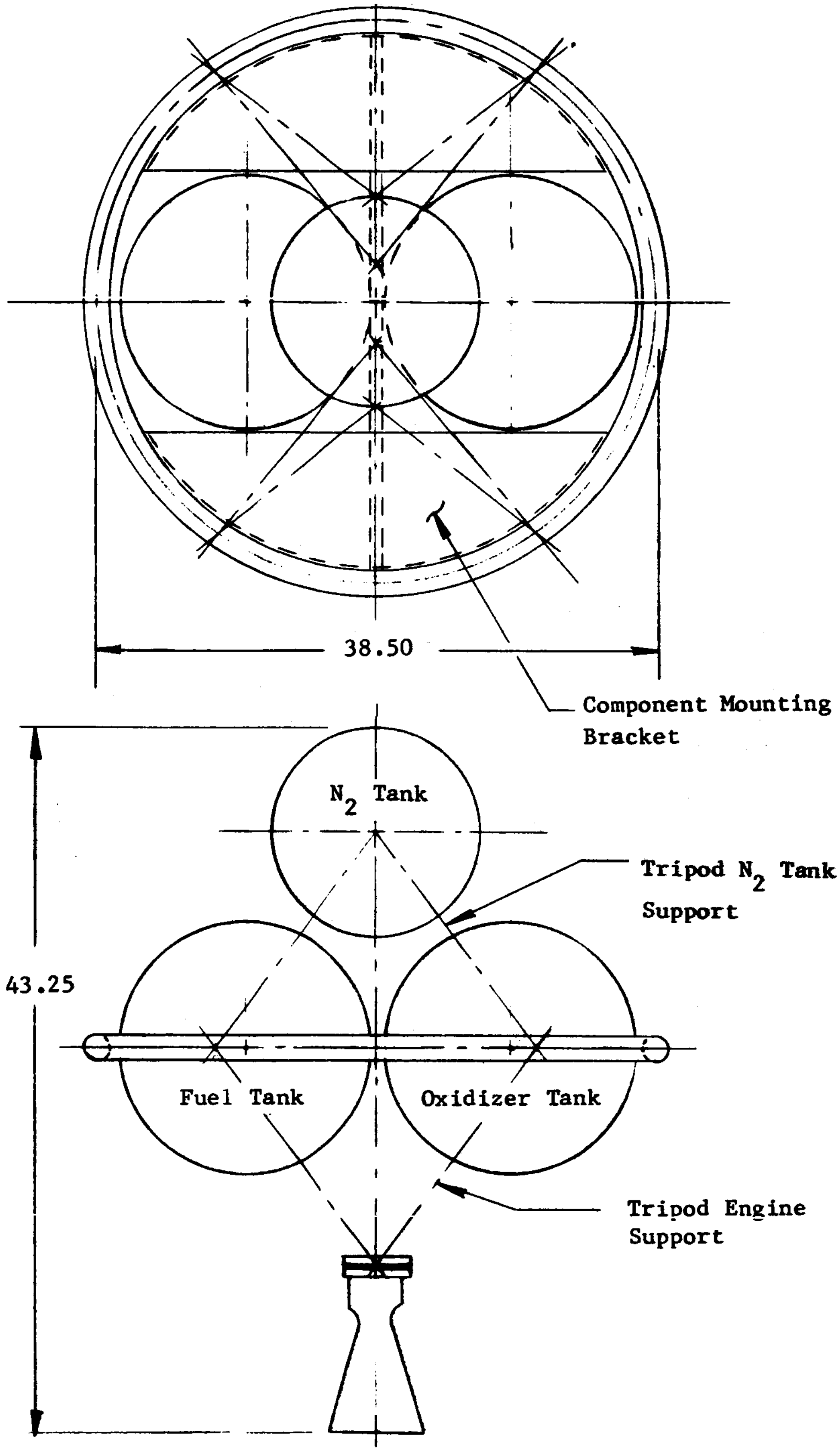


Fig. 2 Pyramid Tank Configuration

An alternative arrangement was, therefore, investigated. This new configuration placed all three tanks in a planar arrangement as shown in Fig. 3. This allowed all tanks to be mounted directly on the major structural support member. Work was continued on this design and it was established as the basic system configuration.

A detailed drawing was made of the triangular support member, which has been stress analyzed. Materials considered included titanium and stainless steel. Since neither material was found to be readily available in the rectangular shape required, it was decided that for this program this member would be fabricated of mild steel and would be coated, if necessary, to protect against corrosion. At this time only the ethylene oxide exposure with 50% relative humidity appears to introduce a corrosion problem. A coating of zinc chromate primer should eliminate the problem.

On the basis of the stress analysis the cross section of the tank support member is 1.5 in. by 2.5 in. rectangular with a wall thickness of 0.125 in.

The design layout was completed and was submitted to JPL for review and approval. Detail design work will progress using this configuration as component final selections are made. An artist's concept of the completed module is shown in Fig. 4.

3. System Analysis and Design Criteria

During the report period considerable system analysis was conducted in support of system layout and design and component selection. Analysis that was conducted included propellant tank sizing and gas storage container size verification. Investigations were made into two potential problem areas, propellant decomposition and oxidizer (NTO) freezing.

The propellant tank sizing analysis was conducted to determine the minimum allowable volumes and proof and burst pressures for each tank. The tank volume calculations considered the following:

1) Propellant mass loaded, 75.95 lb_m of oxidizer and 48.48 lb_m of fuel;

2) Approximate volume of the expulsion device, 5%;

3) 5% ullage volume at sterilization temperature;

4) Propellant expansion from room temperature (70°F) to sterilization temperature (285°F), 41% for oxidizer and 14% for fuel.

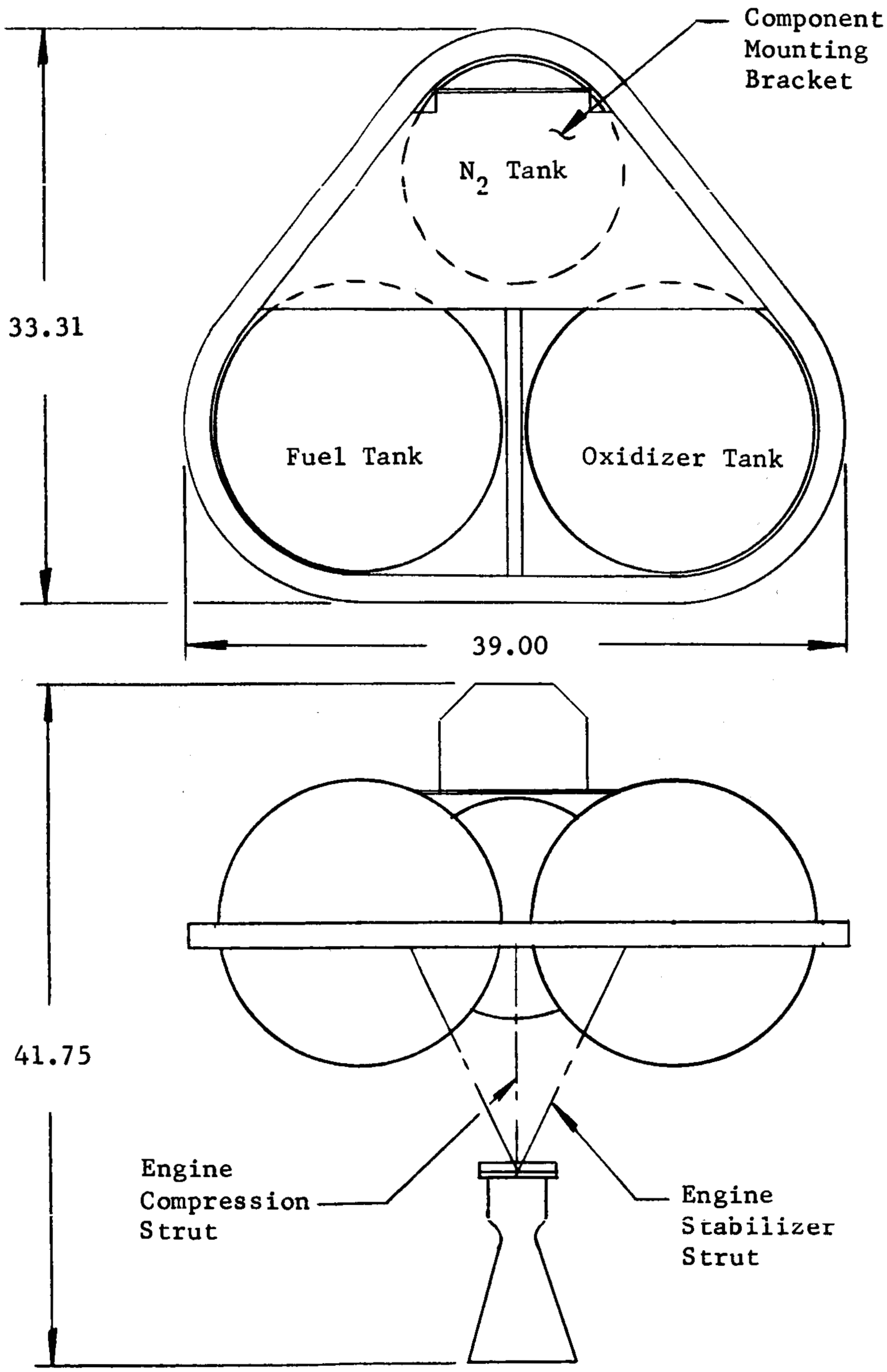


Fig. 3 Planar Tank Configuration

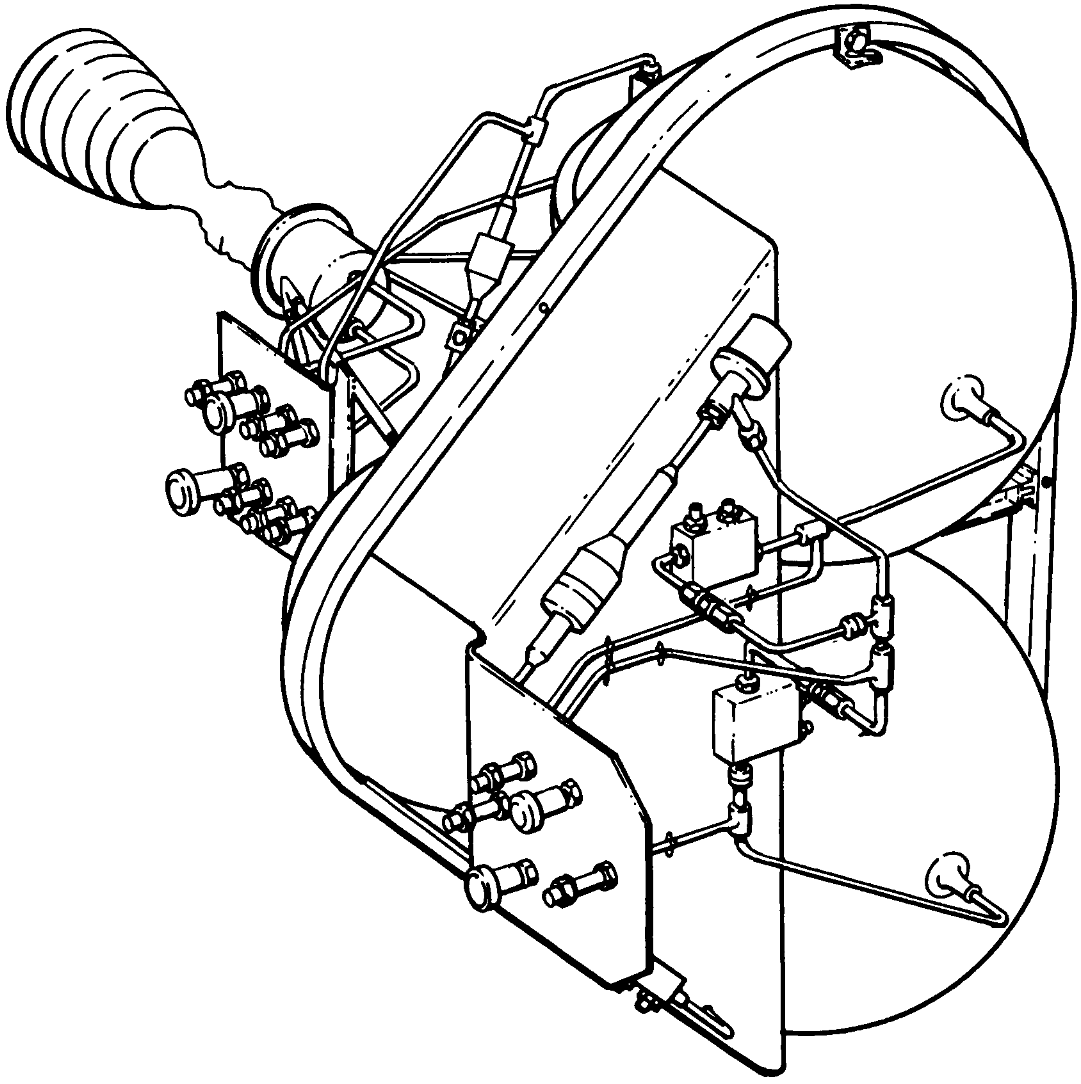


Fig. 4 Artist's Concept of Planar Configuration

The results of these calculations are shown in Table 5. The minimum proof and burst pressures for the tanks considered the worst conditions of tank pressure and temperature and safety factors of 2 and 4 for yield and ultimate, respectively. The worst condition in the oxidizer tank was a pressure of 945 psia at the selected sterilization design temperature of 285°F. A 400 psia tank pressure at room temperature resulting from the burst disc setting was considered as the worst condition for the fuel tank. The minimum proof and burst pressures at room temperature for the oxidizer and fuel tanks are also presented in Table 5. Since these values are given at room temperature, the oxidizer tank proof and burst pressure include a margin for verification up to 285°F.

Table 5 Results of Propellant Sizing Analysis

Sizing Parameters	Oxidizer Tank	Fuel Tank
Tank Volumes (cu in.)	2294.27	1938.82
Worst Operating Condition	945 psia @ 285°F	400 psia @ 70°F
Test Conditions @ 70°F (psia)		
Operating	1027*	400
Proof	2054	800
Burst	4108	1600

*Material strength at 285°F is 92% of the strength @ 70°F.

The pressurant storage analysis was conducted after preliminary selection of the pressurant storage container and pressurant isolation (ordnance) valve. This analysis was conducted to determine the amount of nitrogen required for pressurization and to determine if the size of the selected container at the selected loaded conditions was adequate for the pressurization of the propellant tanks. For a 1728-cu-in. sphere, the loaded condition was selected to be ambient temperature (70°F) and a pressure of 1850 ± 50 psia. The primary factors considered in selecting the loaded sphere pressure were:

1) Sphere design pressures at 70°F for existing sphere;

2) Required ordnance valve safety factors of 1.5 and 2.5 and an ordnance valve proof pressure of 5400 psia and burst pressure of 8000 psia at 70°F;

3) A margin to verify the proof and burst pressures up to a temperature of 285°F was considered.

A propellant tank pressurization and thermodynamics computer program (Martin Program OD041) was used to perform the pressurant storage analysis. This computer program was used to simulate the expected test firing. The simulated test firing consisted of a 100-sec prepressurization period followed by a 300-sec burn (propellant outflow) period. The prepressurization time of a 100 sec was approximately the time required for prepressurization at the maximum nitrogen flow rate. The burn time of 300-sec is a design requirement. Because of a computer program limitation, the pressurization and propellant storage system was simulated by a nitrogen sphere supplying nitrogen to one propellant tank instead of two tanks. The volume of the single tank was equal to the total volume of both fuel and oxidizer tanks. Two runs were made; one run using oxidizer (NTO) and the other run using fuel (MMH). The computer program calculated the pressure and temperature in both the nitrogen container and the propellant tank. It also calculated the nitrogen mass in the storage container and the nitrogen and propellant masses in the propellant tank as a function of time.

The results of the pressurant storage analysis, presented in Table 6, verified that the selected nitrogen sphere size and loaded conditions were adequate for pressurizing the largest of the candidate propellant tanks.

Table 6 Results of Pressurant Storage Analysis

Storage Container Parameters	Oxidizer Run	Fuel Run
Initial Pressure (psia)	1800.0	1800.0
Final Pressure (psia)	760.0	731.0
Total Mass GN_2 Loaded (lb_m)	6.53	6.53
Total Mass GN_2 Used (lb_m)	3.44	3.56
Residual Mass GN_2 (lb_m)	3.09	2.97

The final storage container pressures in both runs were well above the minumum allowable nitrogen sphere pressure of 400 psia. The fuel run gave slightly lower final nitrogen sphere pressure and slightly higher nitrogen usage values than did the oxidizer run. These results were due primarily to the way the propellant expulsion was simulated. The fuel run simulated propellant expulsion using a diaphragm in the tank and the oxidizer run used a screen. After obtaining nitrogen and propellant mass flow rates, line sizing was completed with the selection of 1/4-in. gas lines and 1/2-in. propellant lines.

As a part of the pressurant storage analysis, the possibility of freezing oxidizer (NTO) during module propellant expulsion was investigated. During pressurant sphere blowdown, the temperature of the nitrogen entering the tank could possibly drop below the oxidizer freezing temperature, and therefore, could result in some NTO freezing.

The pressurization and propellant expulsion of the oxidizer tank was simulated using the same computer program that was used for the pressurant storage analysis. The results of this investigation indicated that while the nitrogen entering temperature dropped approximately to the freezing temperature of the oxidizer (472°R), the oxidizer temperature only dropped 2°R from its initial temperature of 530°R. The main reason for this small drop in liquid temperature was due to the high heat capacity of not only the liquid but the propellant tank. Another, but less significant, factor that attributed to the small liquid temperature drop was the increase in ullage temperature during prepressurization. During prepressurization the ullage gases were compressed and the temperature increased. This warmed instead of cooled the liquid. This factor is less significant because even if the ullage temperature was allowed to cool down, the high heat capacities of both the liquid and tank are sufficient to keep the liquid from freezing.

Another potential problem involves the amount of noncondensible gas that might be produced from MMH during the heat sterilization tests. It is also anticipated that the analytical determination of the rate and total quantity produced is not possible withing reasonable accuracy limits. The best solution to the problem would be to take gas samples after a component level heat sterilization test, and analyzing these gas samples to provide the necessary answers.

A system design criterion was initiated and a preliminary draft was completed during this reporting period. This document will take the form of a model specification; and along with the system design layout and detail designs, will completely define the propulsion system. The type of data provided by the design criteria document includes:

1) Propulsion system description;

2) Engine description;

3) Component description;

4) System performance requirements;

5) Interface requirements;

6) Design safety factors.

The preliminary draft contains only a general description of the propulsion system and specifies environmental, safety factors, and system performance requirements. This document does not yet give a complete description of engine and components. The final draft of the system design criteria document will be completed after engine and component selection is completed.

D. COMPONENT DESIGN AND ANALYSIS

As the system schematic became firm and the design layout progressed, investigations were started to locate qualified components for the system. Requests for supplier proposals were issued on all components of the system except for the expulsion devices. In the case of expulsion devices, it was certain that hardware to meet the system requirements did not exist and would have to be manufactured to meet a specific requirement. Component specifications were written to describe the devices that were initially considered as a screen for the oxidizer tank and a diaphragm or bladder for the fuel tank.

Considering the screen for the oxidizer tank, the initial concept consisted of a stainless-steel screen of spherical shape, mounted inside the propellant tank. The diameter of the screen would be such that when mounted in the tank, an annular space of from 1/8 to 1/4 in. would be provided between the screen and the tank wall. This particular configuration, if the proper screen mesh size is used, will allow positive expulsion under -1 g conditions. All propellant except that contained in the annulus can be expelled with the outlet at the top of the tank.

As the materials compatibility testing progressed, it became evident that stainless steel was not compatible with N_2O_4 at 275°F. A sample of pure nickle screen was obtained and it too was not compatible. At this time, no other screen material of the proper mesh size was known to exist so a diaphragm or bladder expulsion device was considered.

During this same period, investigations were being made into bladder materials for the fuel (MMH) tank. Samples of butyl and ethylene propylene rubber (EPR) were obtained and tested with the fuel at elevated temperatures. Results indicated that neither material should be used with fuel. Teflon, however, had been tested and did show promise. Both propellant tanks were at this time anticipated to be of titanium with Teflon-laminate hemispherical diaphragms.

A critical review by an equipment selection committee set up within the Martin Company revealed several facts:

1) Hemispherical diaphragms of Teflon laminate are not state of the art;

2) Spherical bladders of Teflon are developed and are flight qualified for N_2O_4 and A-50 propellants; however, they are a high-cost item with a short cycle life;

3) Since spherical bladders are costly, it will follow then that hemispherical bladders could both be a development problem and could be costly.

In order to overcome the above problems, the incorporation of a screen trap device is being considered for both propellant tanks. No compromise of expulsion device checkout would be required. Using a trap device with aluminum screen of 200x200 mesh, a liquid head of approximately 5 in. can be supported. With a trap height of less than 5 in. (Fig. 5), a significant and repeatable quantity of propellant can be expelled under -1 g conditions.

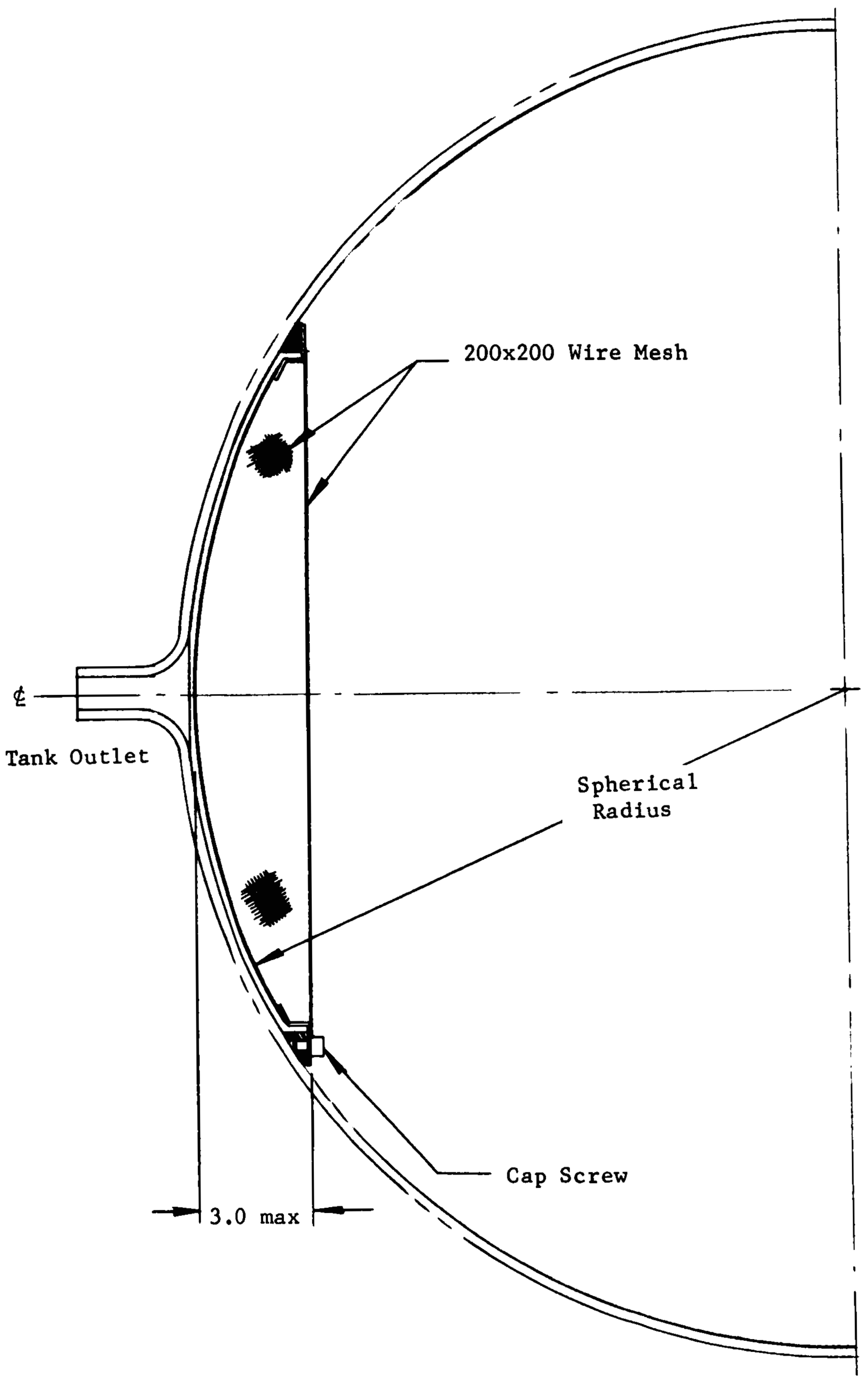


Fig. 5 Zero-g Propellant Expulsion Screen Assembly

1. Component Availability Investigation

During the period, proposals were received from component suppliers and selection of system components is in progress. Component selection guidelines were established listing technical, cost, and delivery requirements and tentative first, second, and third choice selections are being made. Table 7 is a sample selection sheet.

Ordnance Valves - This valve, used in five places in the system, is being supplied by JPL as GFE. Analysis has indicated that the structural design of the valve is compatible with system operating pressure requirements. Since the valve and squib have been exposed to the sterilization environment without degradation, it will be used in the system and no further search for a valve will be made. It is a combination of normally open and normally closed valves in one housing and has been used on the Mariner program.

Solenoid Valve - A single valve is to be used in the system as a gaseous nitrogen fill and drain valve. Five suppliers proposed valve configurations (one did not supply enough data for a preliminary evaluation). In all cases, only assembly drawings were submitted. This prevented a rigorous analysis of tolerances and thermal effects on operation. None of the designs proposed will meet the system requirements without some modification. Modification will be detailed in the test plan.

Gaseous Nitrogen Regulator - Five suppliers proposed valve configurations to meet this requirement. All proposals were evaluated and suppliers were contacted concerning required changes. In all cases, verbal agreement was reached that the changes would be made if the component were selected for the program. Again, detail drawings were not submitted by the vendors. This prevented an in-depth analysis of effects of the sterilization environment.

Filter - A total of five proposals were received in response to the RFP request. Evaluation is being made using the component selection guidelines. An attempt was made to obtain an all-welded assembly of stainless-steel construction. When it became apparent that stainless steel and N_2O_4 were not compatible at elevated temperatures, the filters were removed from the propellant fill and drain systems. In this position, they would be exposed to the propellants during the sterilization environment. This particular filter was intended to filter the incoming propellants during loading. Its function will be accomplished by a filter in the loading system outside the interface.

Table 7 Component Selection Sheet

Component Selection Criteria Gas Pressure Regulator						
1. Basic Design Analysis						
a) Insensitivity to thermal changes (-10 → +10)						
b) Protection of small orifices (-10 → +10)						
c) Complexity (0 → 5)						
d) Seat design (0 → 5)						
e) Structural capability (0 → 10)						
2. Materials of Construction - compatibility (0 → 10)						
3. Leakage						
a) Internal (0 → 5)						
b) External (0 → 5)						
4. Performance						
a) Regulation pressure bandwidth (0 → 10)						
b) Overshoot on lockup (0 → 5)						
c) Overshoot on inlet "squib valve" initiation (0 → 5)						
d) Pressure band drift due to environmental changes (0 → 5)						
e) Allowable inlet pressure variation (0 → 10)						
5. Vendor						
a) Previous experience requiring minimum development (0 → 10)						
b) Delivery (one negative for each week past target date)						
6. Envelope and weight (0 → 5)						
7. Qualification Status						
a) Degree of testing in compliance with JPL 30250B (0 → 20)						
b) Changes required (0 → 20)						
Total						

Hand Shutoff Valve - A total of four hand valves will be used in the system. All will be exposed to either propellant liquid or vapor. Proposals for this component were received from four suppliers. All proposed components were of stainless-steel construction. Again, when the stainless-steel incompatibility with oxidizer became known, all proposals were rejected. The original request for proposals was revised to require valves constructed of aluminum or titanium and was resubmitted to the suppliers. At this time, only one proposal acceptable for evaluation has been received. This particular design is of all aluminum construction, including an aluminum-bellows stem seal. It has not been previously manufactured by the supplier, and is an exact duplicate of an existing stainless-steel design.

Martin is making additional efforts to find an acceptable design that can be available at the time of final component selection.

Propellant and Gaseous Nitrogen Tanks - Proposals for both propellant and gaseous nitrogen storage vessels have been received from three suppliers. At this time, titanium tanks are favored in all positions due to the compatibility and high strength-to-weight ratio. Tanks are available also in stainless steel and aluminum. Aluminum tanks, while they are compatible, are heavy and are not currently in production by any supplier, although suppliers will build to order.

2. Component Final Selection

During the next reporting period, a final selection will be made for each system component. In general, only a single configuration of each type of component will be selected, despite more than one usage location in the system. The component-level test phase requires individual components of each type found in the final system to be exposed to the sterilization environment for twice the time required of the system. During this test, each component will be also exposed to the fluid it will normally contact in the system assembly. Table 8 lists the component requirements for both component-level and system-level testing.

Table 8 Program Component Requirements

Component	Component Test	System Test	Total Required
Ordnance Valve	1	5	6
Solenoid Valve	1	1	2
GN_2 Regulator	1	1	2
Filter	1	3	4
Hand Valve	1	4	5
Propellant Tanks with Expulsion Devices	2	2	4
GN_2 Tanks	0	1	1
Engine	0	1	1
Throttling Valve (Engine)	1	0	1

E. MATERIAL INVESTIGATION

Six principal areas of attention were considered during this report period. They included:

1) A literature search to prevent redundant testing and to assist in establishing test procedures;
2) Prescreening tests to yield short term data that would eliminate materials from further consideration;
3) Isolation prescreening tests consisting of unplanned tests to obtain additional details regarding the adduct formation in N_2O_4 when in contact with steels;
4) Screening tests (300 hr) for early materials design information;
5) Reactivity tests of ethylene oxide atmosphere with propellants to establish design criteria for the leak detectors;
6) Vapor pressure determination of propellants.

Each of the above will be discussed further.

1. Literature Search

The initial study was confined to determining which materials would be the most promising candidates for construction of the propulsion module. Exposure to the propellants and the atmosphere at elevated temperatures was considered.

a. Propellant Compatibility

Initial review of the potential materials of construction was conducted using information developed during the Titan II program. Materials that were previously not compatible with N_2O_4 or the UDMH/hydrazine blend were not considered further.

The most promising candidate materials were then researched further for additional data. These materials are:

304L Stainless Steel	Hastelloy C
321 Stainless Steel	Carpenter 20 Cb
17-4PH (H1075) Stainless Steel	Maraging Steel
6AL-4V Titanium Alloy	Teflon (TFE)

Important or unusual facets of compatibility data concerning each of the candidate materials is listed below, first for MMH, then for NTO.

1) Monomethylhydrazine (MMH)

Only a limited amount of data is available on the propellant at either room or elevated temperatures. Because of this lack of information, a survey of materials compatibility with hydrazine was conducted to predict MMH materials compatibility. Since the chemical properties of MMH and hydrazine are quite similar and hydrazine presents the more critical condition due to its greater reactivity, it was assumed for this program that their compatibility characteristics are interchangeable. In addition, a review of the compatibility of these materials with UDMH revealed no discrepancies in the data.

<u>304 and 321 Stainless Steel (MMH)</u> - These alloys were selected because they exhibit good weldability characteristics and are less susceptible to intergranular attack or stress corrosion than most other 300 series stainless steels. In general, hydrazine solutions alone exhibit little or no corrosive effect on stainless steels. However, stainless steels containing more than 0.5 percent molybdenum are not recommended.

An Aerojet report (Ref 4) points to incompatibility due to apparent decomposition, which was indicated by higher vapor pressures. However, we noted a considerable difference in pressures between two identical test runs. Catalytic decomposition was probably involved because of the presence of contamination. Therefore, these data are questionable.

The Defense Metals Information Center (DMIC) (Ref 5) lists 304 and 321 stainless steel as Class 1 in both liquid and gaseous hydrazine at 140°F. MMH was described as compatible with 304 and 321 stainless steel.

Rocketdyne (Ref 6) lists 304 and 321 stainless steel as a compatible material with hydrazine if the metal has been properly cleaned.

<u>17-4PH Stainless Steel (MMH)</u> - This material was selected because it possesses good weldability properties, is easily fabricated, and exhibits good corrosion and heat resistance. Its strength-to-weight ratio is superior to the 300 and 400 series stainless steels. Aerojet (Ref 4) shows a pressure increase from 9 psi to 17 psi after storage in a 17-4 tank after 17 days storage at 160°F. DMIC (Ref 5) lists this alloy as Class 1 when exposed to hydrazine at 140°F.

<u>A-286 (MMH)</u> - This alloy possesses many characteristics that enhance its value as a tankage or structural material for MMH at elevated and ambient temperatures. The weldability, response to heat treatment, and other manufacturing processes are excellent. The most significant characteristic of this material is its resistance to stress corrosion. This property may be of importance in this program. Rocketdyne (Ref 6) lists the material as compatible with hydrazine if it is cleaned properly.

<u>Titanium 6AL-4V (MMH)</u> - This alloy of titanium possesses excellent mechanical properties and good elevated temperature characteristics. Its high strength-to-weight ratio and weldability are partial reasons for its use in such applications as the Titan IIIC transtage. In addition to many Martin Company reports, its suitability at 160°F is also attested to by DMIC (Ref 5) and Rocketdyne (Ref 6).

<u>Hastelloy C (MMH)</u> - Hastelloy C combines high temperature properties and excellent corrosion resistance to become a potentially valuable material for aerospace applications. It is available in both wrought and and cast forms. DMIC (Ref 9) lists Hastelloy C as a Class 1 material in liquid hydrazine at 125°F; however, Rocketdyne (Ref 6 and 7) contradicts the DMIC rating and lists it as unsuitable for hydrazine exposure.

Carpenter 20Cb (MMH) - The chief value of Carpenter 20Cb is its high corrosion resistance. It has been used widely in the chemical, petroleum, and pharmaceutical industries. As a weldment, the addition of columbium minimizes carbide precipitation so that assemblies may be used in the as-welded condition.

Response to fabrication and manufacturing processes is similar to the 18-8 stainless steels. Its chief disadvantage in aerospace application is its low (85,000 psi tensile strength) mechanical properties.

There were no available references to specific compatibility in either MMH or NTO. Due to its low strength-to-weight ratio it is considered a back-up alloy for severe corrosion application.

Maraging Steel - 18% Ni (MMH) - Although this excellent new structural material will find its place in many aerospace applications, it is not recommended for tankage or long storage in contact with MMH.

The maraging steel family is not corrosion resistant and as such will form iron oxide unless protected. MMH reacts catalytically with iron oxide and may result in violent decomposition and catastrophic failure of the storage vessel.

Teflon, TFE (MMH) - Teflon possesses excellent thermal and chemical resistance properties. It has been widely used in the aerospace industry for both propellant and high temperature applications.

Mechanical properties vary considerably with the type of molding powder used and the degree of crystallinity achieved during sintering. Application of this material to a particular design should be carefully considered because of its inherent cold flow characteristics.

DMIC (Ref 5) lists this material as Class 1 with hydrazine at 140°F. Rocketdyne (Ref 6) lists Teflon as compatible with hydrazine, with only a small decrease in physical properties after seven weeks exposure. Aerojet (Ref 4) indicates no apparent change after exposure to MMH at 160°F for one week.

Compatibility and Decomposition of MMH - Additional information of value to the program was noted in the Olin Chemical Division (Ref 8) product data on MMH handling and storage.

The Olin report states:

"There has been very little work done on the compatibility of various materials with MMH. The acceptability of materials in contact with MMH depends upon the specific application for which they are intended. The requirements for long-term storage differ considerably from those pertaining to a piece of equipment used one time. An occasional peculiar usage may make it desirable to utilize a material which is not generally recommended.

"Catalytic decomposition can be caused by contact with rust, molybdenum, copper and its alloys, and spontaneous fire will result. When a film of MMH comes in contact with certain metallic oxides, particularly those of iron, copper, lead, and manganese, it may cause the MMH to decompose due to a chemical heat of decomposition. This heat may be sufficient to raise the temperature high enough to cause spontaneous ignition."

2) Nitrogen Tetroxide (NTO)

Numerous aerospace and research organizations have been active in testing compatibility of NTO with various structural and nonstructural material. Paramount among these efforts was the work by Aerojet and Martin supporting the development of the Titan II and III family propulsion and tankage systems. The knowledge gained from the seven years of testing, evaluation, and field experience has greatly restricted the list of materials to be tested for this program. The literature search confirmed that in addition to the Martin Propellant Compatibility Report (Ref 9), there was much data available covering the temperature range of 60 to 180°F, but very little data in the range of the dry heat sterilization cycle temperature. It has been shown by tests at Martin that the degradation rate on materials at elevated temperatures is not linear and that significant side-effects, which are not typical, may be experienced.

The information presented in the following discussion indicates that the candidate materials have a high potential for satisfying the program's environmental requirements. The data were obtained from many different tests, in different laboratories for unlike applications. Therefore, uniform confirmation testing for this application must be accomplished to assure that the design and performance goals will be met.

304 and 321 Stainless Steel (N_2O_4) - These alloys were selected because they exhibit good weldability characteristics and are less susceptible to intergranular attack or stress corrosion than most other 300 series stainless steels. These materials are listed as Class 1 at 140°F and 160°F, respectively, in Ref 9. Alley, Hayford and Scott (Ref 10) report zero attack on 304L after one year exposure at 165°F. Bell Aerosystem (Ref 11) lists these alloys as Class A in contact with N_2O_4 at 160°F for a period of 14 days.

Aerojet (Ref 4) reports that corrosion rates for aluminum and stainless steel alloys shown for the 3-day and 90-day exposure periods indicate an initial high corrosion rate occurred. After building up a protective film, the corrosion rates for the 3-day period were of the order of 0.1 Mpy (mils/year), and less than 0.01 Mpy for the 90-day period.

17-4PH Stainless Steel (NTO) - This material was selected because it possessed good weldability properties, is easily fabricated, and exhibits good corrosion and heat resistance. Its strength-to-weight ratio is superior to the 300 and 400 series stainless steels.

Bell Aerosystems (Ref 12) lists this alloy as Class A in liquid N_2O_4 at 100°F after 90 days of exposure.

Bell Aerosystems (Ref 11) shows a weight change of less than 0.0007% after 90 days of exposure to N_2O_4 at 65°F.

A-286-Aged (NTO) - This alloy possesses good mechanical properties in both cryogenic and elevated temperature environments. It is weldable and responds to normal fabrication methods. Its chief attribute in this program may be its excellent stress corrosion resistance. DMIC (Ref 5) lists A-286 as Class 1 in NTO at 60°F.

Titanium - 6AL-4V (NTO) - As mentioned in the section on compatibility with MMH, this widely used titanium alloy is generally considered throughout the aerospace industry as compatible with NTO. It is used as NTO tankage extensively in Gemini, Surveyor, LEM, and the Titan III transtage.

Many test reports and papers such as "Effect of Nitrogen Tetroxide on Metals and Plastics" (Ref 10) verify its apparent suitability in various room temperature and the 100 to 200°F range. Recently, however, several failures have occurred in elevated temperature storage of NTO in 6AL-4V. These failures, which have been stress corrosion in nature, appear to be associated with the amount of nitric oxide present in the oxidizer. Bell Aerosystems (Ref 12) lists this material as Class A at 70 to 165°F after 27 days exposure.

Hastelloy C (NTO) - Hastelloy C combines high-temperature properties and excellent corrosion resistance to become a potentially valuable material for aerospace applications. It is available in both wrought and cast forms. It is listed by DMIC (Ref 5) as a Class 1 material in liquid hydrazine at 125°F.

Maraging Steel - 18% Ni (NTO) - Search of applicable documents revealed no information on the maraging steel family compatibility with NTO. It was selected for evaluation due to its excellent mechanical properties and fabrication characteristics.

It is difficult to make a direct comparison with other steel families because the maraging steel group becomes a family within itself. Comparison does reveal that the maraging steels include the same alloying constituents as many other ferrous alloys which are considered compatible. Long-term storage of NTO in vessels made from carbon steels, low alloys, 18-8 type, and 400 series stainless steels has been satisfactory. Certainly all indications point to the value of including this promising new material in the evaluation.

Teflon, TFE (NTO) - Teflon possesses excellent thermal and chemical resistance properties. It has been widely used in the aerospace industry for both propellant and high temperature applications. Mechanical properties vary considerably with the type of molding powder used and the degree of crystallinity achieved during sintering. Application of this material to a particular design should be carefully considered because of its inherent cold flow characteristics. DMIC (Ref 5) lists Teflon as Class 1 when exposed to N_2O_4 liquid at 160°F for an unlimited exposure time.

Particulate Formation (NTO) - Particulate formation is also of great concern. If the ferrous alloys exhibit corrosion rates in the presence of N_2O_4 at 275°F, existing information suggests the probability of the formation of significant quantities of $Fe(NO_3)_3 \cdot N_2O_4$. This substance is an insoluble nitrate formed in N_2O_4, contaminated with nitrosyl chloride (NOCl), in the presence of metallic iron. Development of a means of tying up the nitrosyl chloride must be considered if appreciable quantities of the iron adducts are formed.

b. Thermal Properties of Materials

A study of the effects of the thermal property variation in the range 70 to 285°F was conducted. The effects of the thermal environment on the chemical and physical properties of the candidate materials are compiled in Tables 9 and 10.

In the metallic area, members of the ferrous, titanium, and other heat resisting groups exhibit little change in the temperature range. Aluminum alloys may experience a slight loss in properties at the maximum temperature and those affected by long-term overaging will experience some degradation in elongation and tensile strengths and an increase in its susceptibility to intergranular and stress corrosion.

Table 9 Ethylene Oxide and Thermal Compatibility of Metals during Decontamination and Sterilization Cycles

Material	Coefficient of thermal expansion at 70 to 280°F in/in/ft	YTS at 70°F	YTS at 280°F	UTS at 70°F	UTS at 280°F	Ethylene Oxide Compatible	Remarks
304 st. stl, plate	9.0 to 9.4 x 10^{-6}	28 ksi	25 ksi	75 ksi	70 ksi	C	(1), (2)
321 st. stl., sht, plt, strip	8.4 x 10^{-6}	30-35 ksi	*	85-90 ksi	*	C	
347 st., stl., sht, plt, strip	9.2 x 10^{-6}	40 ksi max.	*	100 ksi max	*	C	
446 st. stl.	5.6 x 10^{-6}	45 ksi	*	75 ksi	*	C	
17-4 ph st. stl.	6.1 x 10^{-6}	170 ksi min	160 ksi min	190 ksi min	180 ksi min	C	
17-7 ph (th1050) sht. and plt.	5.9 x 10^{-6} approx	140 ksi min	130 ksi min	170 ksi min	165 ksi min	C	
Waspalloy	6.7 x 10^{-6} approx	56 ksi	55 ksi	80 ksi	76 ksi	C	
A-286, Sheet and plate	8.9 to 9.3 x 10^{-6}	95 ksi min	92 ksi min	140 ksi min	139 ksi min	C	1
L-605, bar and forgings	6.8 x 10^{-6} approx	45 ksi min	36 ksi min	125 ksi min	110 ksi min	C	Hot worked and stretched
AM-355, bar and forgings	6.5 x 10^{-6} approx	155 ksi min	*	170 ksi min	*	C	
Rene' 41	6.5 x 10^{-6} approx	100 to 130 ksi	*	170 ksi max	*	C	
Inconel X-750	7.1 to 7.6 x 10^{-6}	100 ksi min	99 ksi min	160 ksi min	159 ksi min	C	
Molybdenum, comm. pure	2.8 x 10^{-6} approx	79 ksi min	*	91.3 ksi min	*		Stress relieved
Molybdenum, comm. pure	2.8 x 10^{-6} approx	43.7 ksi min	*	58.2 ksi min	*		Recrystallized
Alnico IV	11.3 x 10^{-6}	-	-	2.3 ksi	2.2 ksi	C	No yield strength listed
6061-T6 aluminum	13.4 x 10^{-6}	35 ksi min	32 ksi min	42 ksi min	35 ksi min	C	Sheet and plate
Titanium, 6AL-4V	5.3 x 10^{-6}	120 ksi min	*	130 ksi min	*	C	Annealed Sheet, plate, bar
Titanium, 6Al-4V	5.3 x 10^{-6}	120 to 150 ksi	106 to 132 ksi	130 to 160 ksi	107 to 132 ksi	C	Heat treated bar & forging
Beryllium 12% Beo	6.5 x 10^{-6}	50 ksi min	45 ksi min	70 ksi min	60 ksi min		Pressed block
Tantalum/10%w, sheet	3.7 x 10^{-6}	82 ksi min	*	96 ksi min	*		
Columbium sheet	4.0 x 10^{-6} approx	-	-	80 to 100 ksi	65 to 80 ksi		Cold worked
Maraging steel	5.6 x 10^{-6}	245 ksi min	*	255 ksi min	*	C	For N_2O_4 use only
Hastelloy C, sheet	6.5 x 10^{-6}	68 ksi	62 ksi	120 ksi	120 ksi	C	
Carpenter 20, sheet	9.4 x 10^{-6} **	50 ksi	*	90 ksi	*	C	Group "C"

* Less than 5% reduction in tensile strength between 70°F and 280°F

** Coefficient of expansion is between 68°F and 1200 °F

Table 10 Summary of Typical Nonmetals Compatible with Decontamination and Sterilization Cycles

Material Use	Trade Name	Basic Material	Applications
Adhesives	PD-454	Epoxy	General applications
	PD-458	Epoxy	General applications
	RTV-102	Silicone	One Component -100° to 320°F
	RTV-511	Silicone	General applications
	RTV-560	Silicone	General applications
	Eccobond 57c	Epoxy	Electrically conductive -70° to 350°F
	RTV-60	Silicone	General applications
	Eccobond 601	Epoxy	Thermally conductive
Coatings and Finishes	• D-4D paint	Silicone-alkyd	Thermal control coating
	• Vitavar PV-100	Silicone-alkyd	Thermal control coating
	• Wash primer	Penetrant primer	Penetrant primer
	• Zinc chromate primer	Zinc-chromate	Corrosion protection
	Silicone primer SS1101	Silicone	Primer for adhesive bonding
	• Lowe Brothers 17865	Glyceryl-pthalete	Heat resistant paint
	MSD-105	Zinc oxide-silicate	Thermo conductive coating
Tapes	• 3M-850	Metallized polyester	Sealing and joining mylar sheet
	Schjeldahl GT	Polyester	Heat sealable adhesive tape
	• 3M-56	Polyester	Harness bundle wrap
	• 3M-EE-3990	Copper foil tape	Electromagnetic harness shielding
	Silicone tapes DC-269	Silicone	Seal component against corrosive environment
	AM-FAB TV-20-60	Fluorocarbon	Insulation tape
Encapsulants	RTV-60	Silicone	Encapsulating
	LTV-602	Silicone	Potting and encapsulating
Insulating Material	Tissue Glass - 200a	Glass fiber-Cellulose	Thermal insulation
	Amfab 20-60	Fluorocarbon-glass	Thermal insulation
	•Epoxy glass S-30205, P-2	Epoxy-fiberglass	Circuit boards
	Thermofit RNF-100	Polyolefin	Thermal insulation
	Mylar (pre-shrunk 300°F)	Polyester	Electrical and moisture insulation
Lubricants and Greases	Grease G-300	Silicone	Bearing lubricant
	• Dry film	Molybdenum-disulfide	Lock assemblies
	Fabroid	Glassfibers-fluorocarbon	Bearing surfaces
	Grease MSD-104	Silver filled silicone	Joint filler

• Sterilizable in an inert atmosphere

Source - General Electric Document No. 65SD4518, Design Criteria for Typical Planetary Spacecraft to be Sterilized by Heating.

NOTE: Decontamination refers to the surface exposure of materials to the 12% ethylene oxide/88% Freon 12 fluid.

Sterilization refers to the six 96 hour day heat cycles at 275°F.

In the nonmetals area, data presented in reports from earlier studies were reviewed. When using information of this type for some of the plastics, the formulation and cure cycle must be known unless that specific material was tested. Compatibility properties can be significantly changed by variation in these items.

Data presented in Table 10 lists compatibility of a cross section of the materials studied.

Candidate Materials Compatibility with 12% Ethylene Oxide/ 88% Freon - Results of the survey on compatibility of the candidate materials with the ethylene oxide decontamination fluid indicates that data are available on most material families. Those data were compiled in Tables 9 and 10. Those materials on which information was not available will be tested and evaluated so that conclusive data will be obtained.

2. Prescreening Tests

This series of short-term tests was performed to verify literature data and to assist in development of procedures for conducting the screening tests. The tests consisted of exposing small material samples to the propellants in combination with the dry heat sterilization temperatures for periods up to 120 hr. Sample containers were fabricated from 304 stainless steel Hoke cylinders or 1-in. tubing sections of appropriate materials. The materials tested included:

- 6061-T6 aluminum
- 1100-0 aluminum
- 6AL-4V titanium
- 321 stainless steel
- Nickel
- Lead
- FEP and TFE Teflon
- B-591-8 Butyl Rubber, Parker
- E-515-8 Ethylene Propylene Rubber, Parker
- AF-E-110 Carboxy Nitroso Rubber
- S-9711 Silastic Compound

A number of important items of information were developed during this series of subscale tests. The formation of adducts of iron was found to be a major problem. With only one exception, the phenomenon was found in all tests conducted on ferrous-based alloys in the presence of NTO. In that instance a sample of 321 stainless steel was placed in an open glass vial containing NTO and inserted into a 304 stainless steel Hoke cylinder, which also contained NTO that did not, however, cover the vial. At completion of exposure of the system to 275°F for 120 hr, a light residue was found on the walls of the Hoke cylinder but none on the specimen. This phenomenon led to the conception of additional isolation prescreening tests. These tests were conducted to ascertain whether the ferrous-based alloys would form the adducts in the absence of any other metal and any nonmetal.

No nonmetals were tested that proved to be completely compatible with N_2O_4 at 275°F. TFE and FEP Teflon specimens were slightly affected in tests up to 70 hr. Results were not clear since the first series of specimens were exposed in stainless steel Hoke cylinders, which resulted in oxidizer contamination. A second test of 69 hr at 275°F in a 6061-T6 aluminum container revealed similar effects on the Teflon materials, and a thin, white precipitate remained on the container walls and the Teflon specimen after the propellant was drained.

Elastomers including silastics, butyl rubber, ethylene propylene rubber, and nitroso rubber lost significant mechanical properties, blistered, ignited, or went into solution after short-term exposure to N_2O_4 at 275°F.

Both nickel and lead sustained attack. This resulted in formation of nickel nitrate and lead nitrate, respectively. Sufficient attack occurred to eliminate either material from further consideration.

All metals exposed to MMH demonstrated compatibility. All nonmetals exposed to the fuel caused it to discolor. The exact significance regarding effect on the fuel is not known at this time. Ethylene proplyene rubber was least affected of the elastomers when tested for 24 hr at 275°F. TFE and FEP Teflon specimens lost little in mechanical properties after 80 hr of exposure to MMH at 275°F; however, fuel decomposition occurred.

3. Isolation Prescreening Tests

This series of tests was generated to determine the effect of propellant on materials when no other metal or nonmetal was present. Special containers were fabricated with appropriate welded end plates to assure a single constituent system rather than introducing unknowns from commercially available tube fittings. Both propellants were considered.

The results of these tests proved adducts of iron will be formed by any ferrous-based alloy when in contact with N_2O_4 at 275°F. Rate of formation appears to be approximately linear and increases as the amount of alloying agents decreases. Conversely no residual contamination is formed when aluminum alloys or titanium alloys are exposed to the same environment.

Fuel was not found to react with any metal alloy except 316 stainless steel. This alloy was not considered for systems use but did form a part of the container used for screening tests. No attack was observed on the metal, however, decomposition of the fuel did occur. This is attributed to the presence of molybdenum in the alloy.

4. 300-hr Screening Test

This test was performed in the same manner as the full-scale 600-hr test except for duration. It was intended to provide advance information for materials selection and to indicate any basic error in the conception of the 600-hr test. Since this test is a forerunner of the more extensive 600-hr test, the following photographs are included showing various views of the apparatus.

Figure 6 shows the specimen rack and test vials without propellant being lowered into the fuel bomb. Following proper loading, the bomb will be closed and lowered into an ethylene glycol bath that is heated to 275°F by immersion heaters. The heated bath is shown at the technician's left.

The fuel test cell is shown in Fig. 7. The test bomb, rack, and barrel to be loaded for the 600-hr test is shown in the background. The bomb on the hoist is about to be lowered into the 300-hr test container in the foreground.

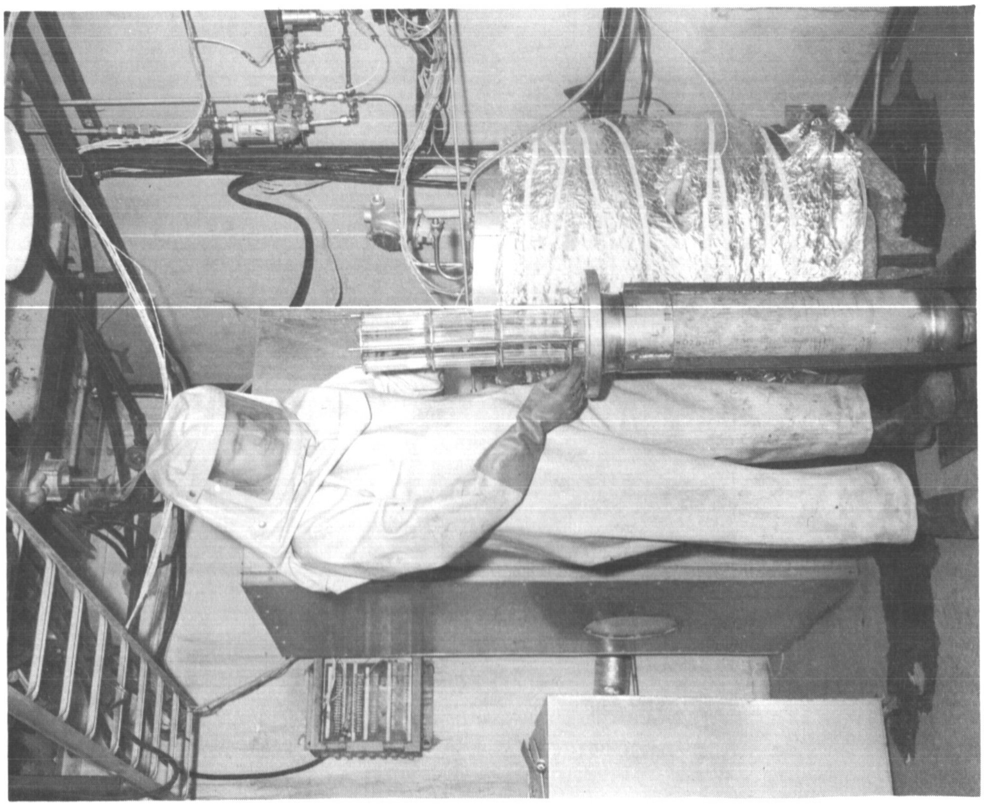


Fig. 6 Assembly of Materials Test Bombs

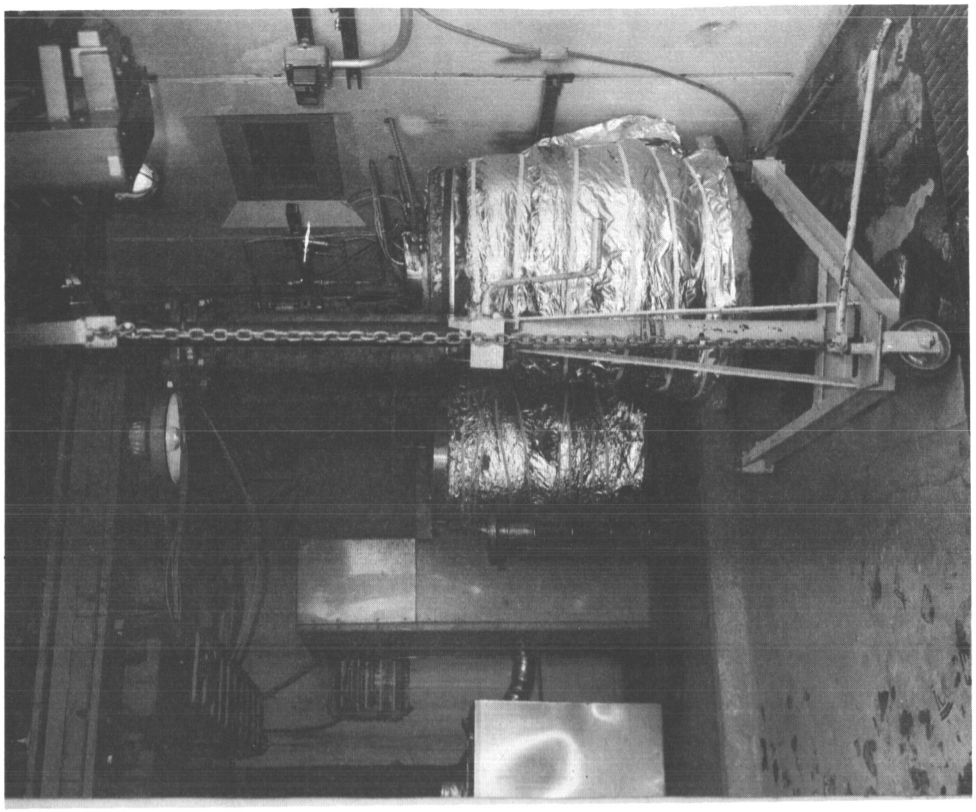


Fig. 7 Fuel Test Cell

Figure 8, the interior of a test bomb, shows the position of test tubes and rack. Propellant and test tube covers have not been installed. This arrangement is typical for both the fuel and oxidizer tests.

Figure 9 shows the interior of the oxidizer cell with bombs (600-hr on left, 300-hr on right) before final connections and loading. The plumbing on the wall is the pressurization and vent relief system. The 300-hr bomb is on a dolly to facilitate removal from the test cell when the test is completed. Oxidizer bombs were directly heated with an electric blanket (under insulation).

In Fig. 10 the 300-hr fuel bomb is shown after test exposure was completed. The bomb will be lowered into a holding rack for flange removal. The barrel at the left is the same as in Fig. 7, but the insulation has been removed.

The results of the 300-hr test showed no attack on any materials exposed to the fuel. The following materials were all found to be compatible:

304 stainless steel	Carpenter 20 Cb
321 stainless steel	Hastelloy C
347 stainless steel	6AL-4V titanium alloy
17-7 stainless steel	1100-0 aluminum
17-4 stainless steel	2014-T6 aluminum
A-286 aged	2219-T8 aluminum

Figure 11 shows the fuel specimens after the 300-hr exposure. The specimens were unaffected and the propellant was a clear light straw color, unchanged from its original condition. Each specimen was isolated from the other by the stopper shown in each test tube. Alloys found compatible with N_2O_4 were:

1100-0 aluminum	Commercially pure titanium
2014-T6 aluminum	6AL-4V titanium
2219-T8 aluminum	Hastelloy C
6061-T6 aluminum	

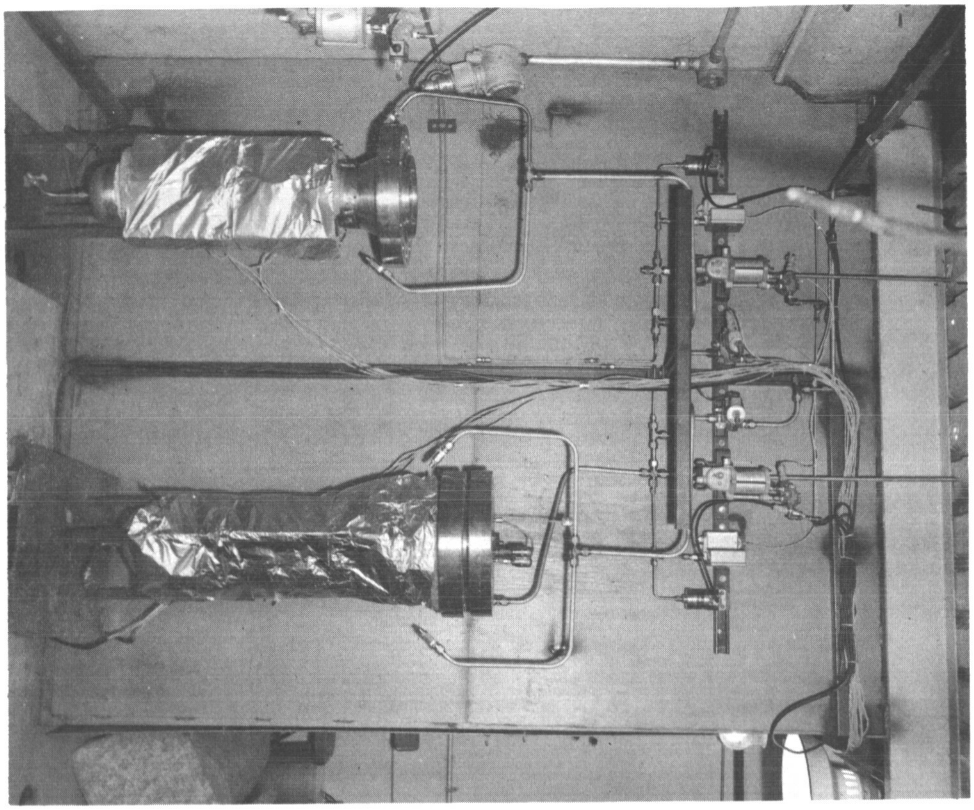


Fig. 9 Oxidizer Test Cell

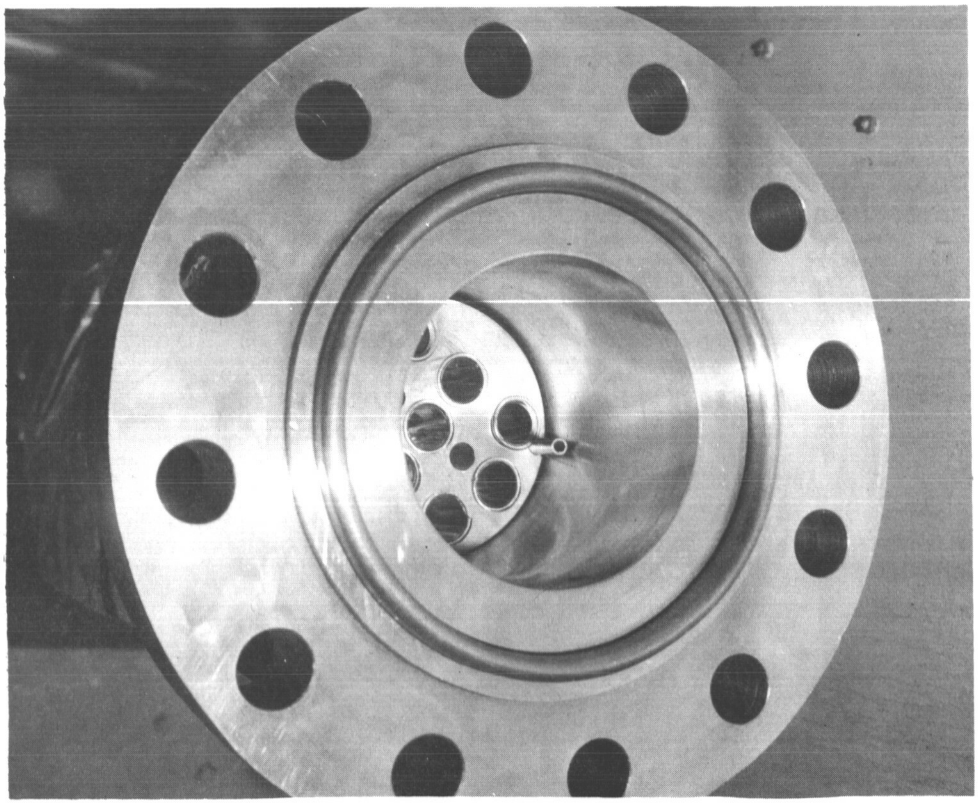


Fig. 8 Interior of Materials Test Bomb

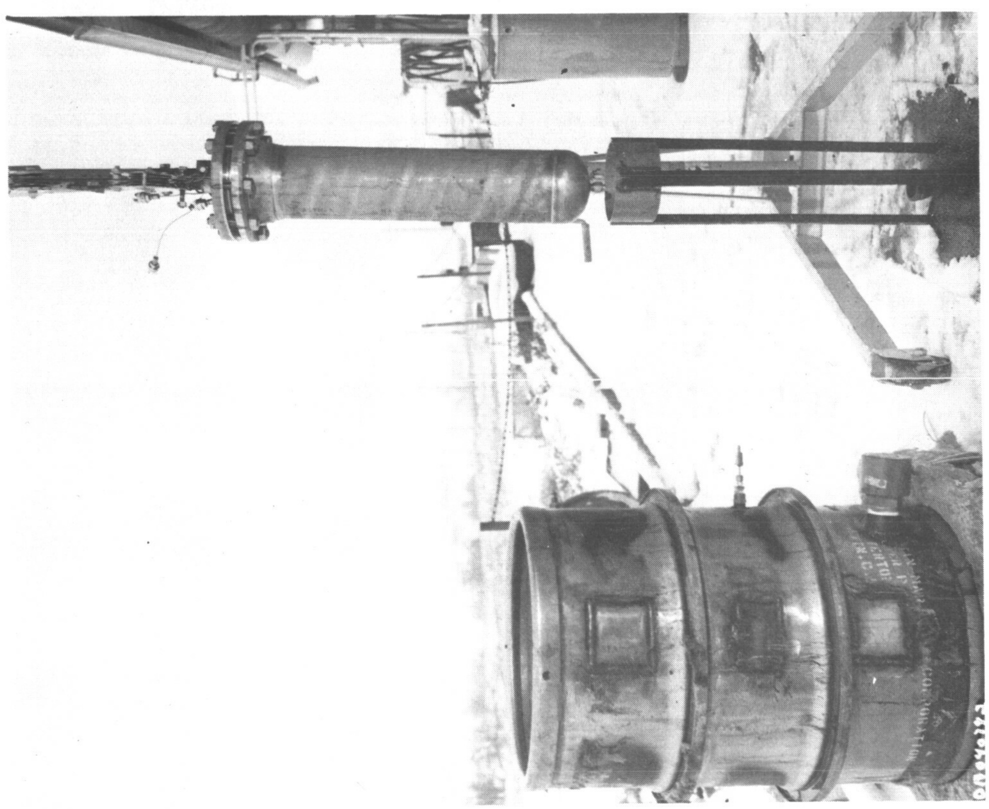


Fig. 10 300-hr Fuel Bomb

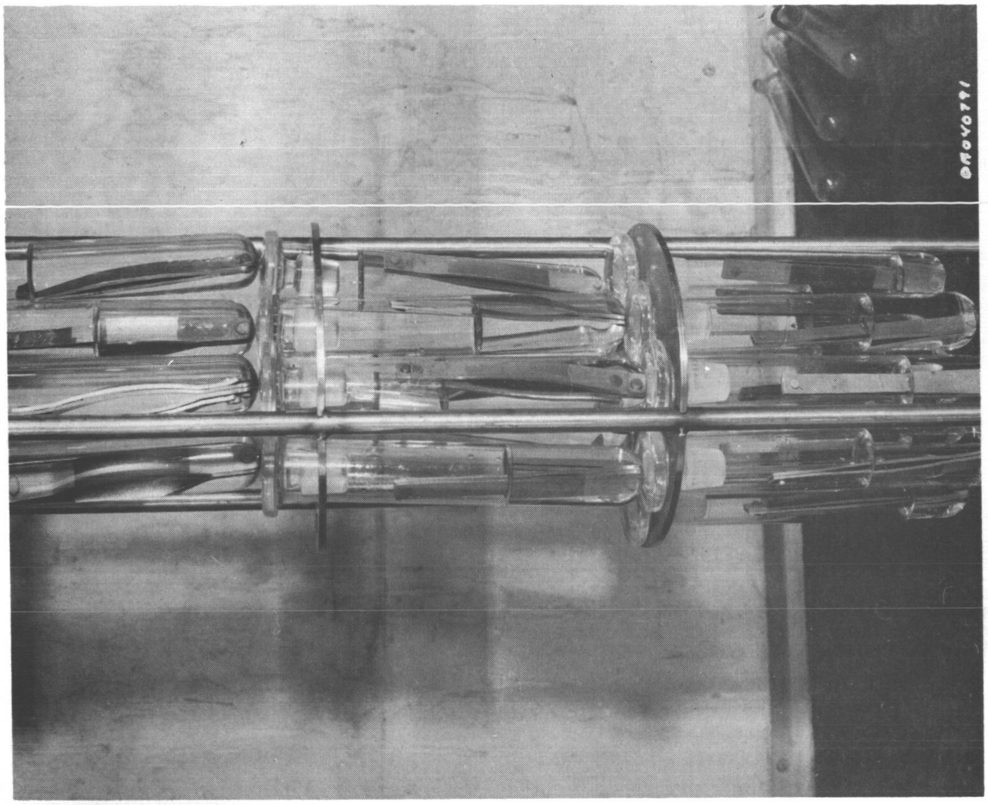


Fig. 11 300-hr Fuel Specimens

Alloys found to be incompatible with N_2O_4 were:

304 stainless steel	Nickel
321 stainless steel	A-286
347 stainless steel	Carpenter 20 Cb
17-4 stainless steel	Maraging steel
17-7 stainless steel	Lead

The formation of adducts of iron was found in all instances of exposure of ferrous-based alloys to the oxidizer. The ferrous materials were incompatible because of the formation of a material in the oxidizer that would be detrimental to the system operation. The adduct is identified because it:

1) Precipitates from the liquid propellant;
2) Does not transfer in the vapor phase;
3) Has a large volume when wet but shrinks to less than 10% of original volume when dry;
4) Has the apparent viscosity of cold molasses with a high adhesive strength;
5) Is amorphous when dried of oxidizer.

The maraging steel was the only ferrous alloy which demonstrated structural failure. It was prestressed to 75% of yield. The specimen fractured in both the tested stressed area and in areas around the rivet. Significantly, this alloy contained the least amount of corrosion resistant metals, was the highest strength alloy tested, and formed the greatest amount of adduct (Fig. 12).

Figures 13, 14, and 15 show the specimens after exposure to N_2O_4 for 300-hr at 275°F. The small amounts of propellant remaining are due to distillation which occurred during rapid cooling of the bomb from 275°F to 40°F. Unaffected bright specimens are aluminum alloys. The titanium specimen (not shown) had a similar appearance, but the test tube was broken during removal from the test bomb. Rivet staining may be seen in several specimens. Ferrous-based alloys show a blackened effect (iron adduct). Iron adduct formation is most clearly seen on the bimetal specimen in Fig. 15 (aluminum interior specimen and 321 stainless outer specimen). Note fractured maraging steel specimen at extreme right.

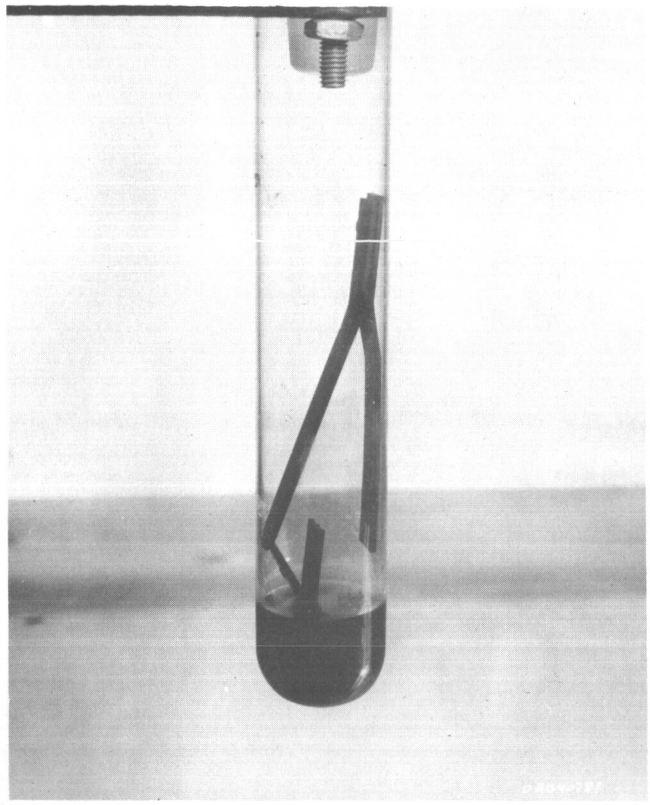


Fig. 12 Oxidizer Test Maraging Steel Specimen

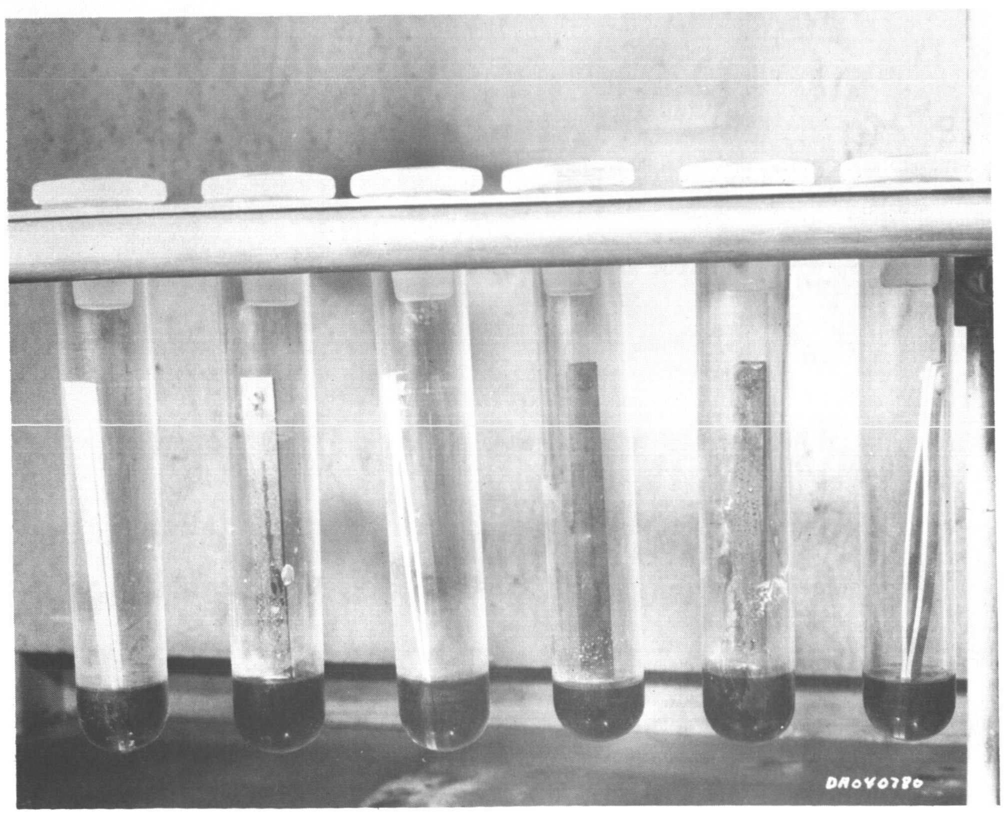


Fig. 13 Oxidizer Test Specimens

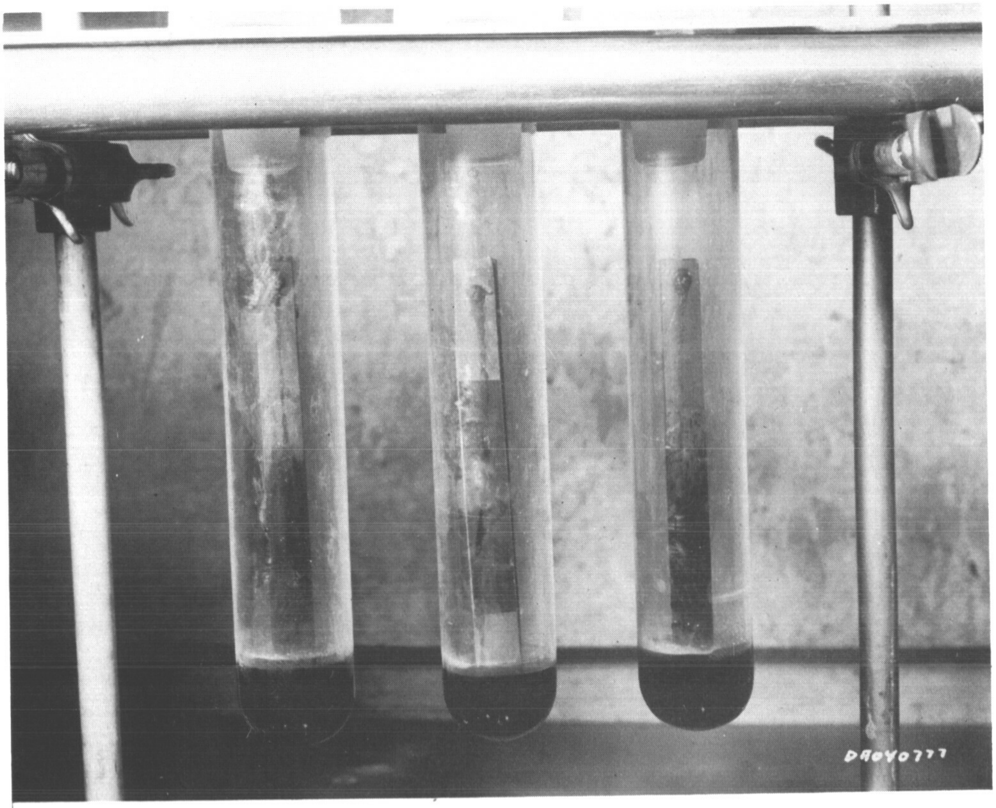


Fig. 14 Oxidizer Test Specimens

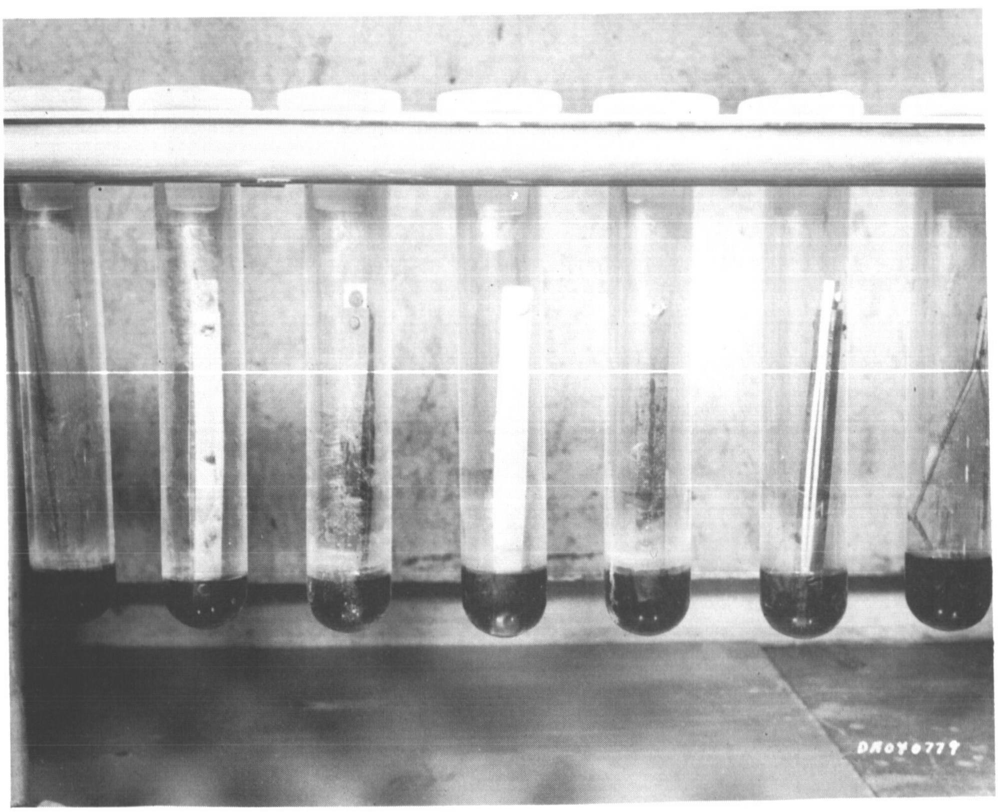


Fig. 15 Oxidizer Test Specimens

Figure 16 shows the 304 stainless steel specimen rack after 300 hours in N_2O_4 at 275°F. The rack was clean and bright before exposure. Deposits are iron adduct. The rack was made from stainless steel rather than aluminum alloy as specified in the test plan to provide uniformity of test bomb materials.

5. Reactivity of Ethylene Oxide Atmosphere with Propellants

This test was performed to determine whether a safety hazard would exist if a leak occurred in either the fuel or oxidizer system during exposure to the ethylene oxide atmosphere. Results of tests indicated that a minimum pressure rise of 4 psi could be expected in the event of a fuel leak and 26 psi if an oxidizer leak providing propellant fume concentration was at least 5×10^3 ppm. This problem will be considered further.

6. Determination of the Vapor Pressure of MMH at Elevated Temperatures

A test program was conducted to verify the vapor pressure and stability characteristics of MMH fuel at the temperature levels associated with the decontamination and sterilization processes.

The schematic of the test fixture is shown in Fig. 17. The glass test vessel has a capacity of 185 ml, and contains an integral thermometer well. The glass outlet tube of the test vessel was connected to the stainless steel fixture piping by a Swagelok connector with a Teflon seal. A relief valve and appropriate hand valves were provided in the system.

The test vessel was supported in an ethylene glycol bath. The bath container was equipped with wall heaters and an agitator to control the heating of the bath.

A vacuum pump was provided to evacuate the test vessel and connecting piping prior to filling with MMH. A 300-series stainless steel Hoke bottle (300 ml capacity) was provided to hold the fuel sample for introduction into the test vessel.

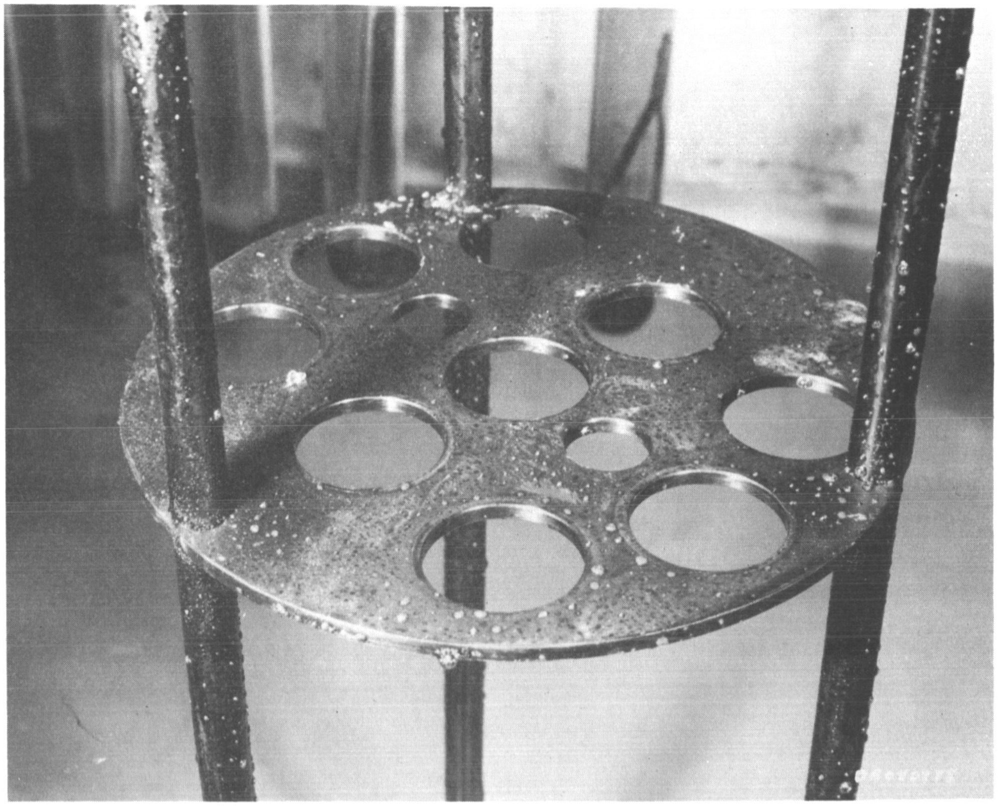


Fig. 16 Oxidizer Test Specimen Rack

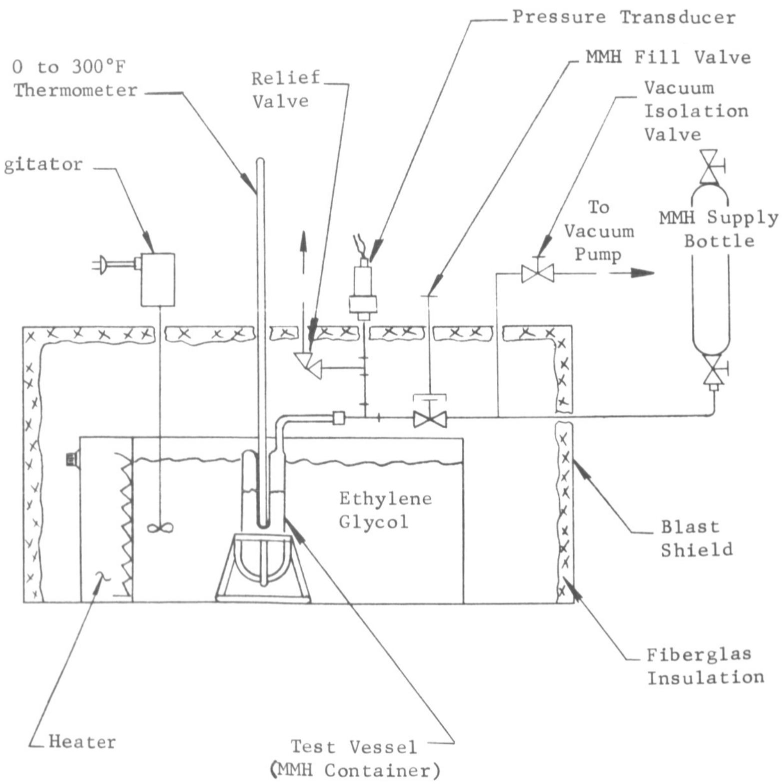


Fig. 17 Test Fixture Schematic, MMH Vapor Pressure Determination

The instrumentation locations are shown in the schematic of the test fixture (Fig. 17). Vapor pressure was measured with a strain gage-type transducer and a potentiometric voltmeter. Accuracy of this system was ±0.1 psia for pressures up to 50 psia and ±0.5 psia for pressures above 50 psia. Temperature of the MMH was determined with a mercury-in-glass thermometer having a range of 0°F to 300°F and an accuracy of ±1°F. Bath temperature was read with a copper-constantan pyrometer having an accuracy of ±3°F in the range of interest.

The test system was thoroughly cleaned prior to assembly, and proof-pressure tested after assembly. The system was then leak-checked at 285°F with helium, using a mass spectormeter leak detector.

The 300-ml supply bottle was filled from the storage drum by GN_2 pressure transfer and then connected to the test fixture fill port with the bottle stop valves closed. The test system up to the bottle stop valve was then evacuated to approximately 150-microns Hg. The vacuum system was then isolated and the stop valves on the supply bottle opened to admit approximately 120 ml of MMH into the test vessel (MMH level about 2 in. above the bottom of the thermometer well). The fill valve was then closed and the supply bottle was disconnected.

The test runs were made by heating the bath to obtain MMH temperatures of 150°F, 200°F, 250°F, 275°F and 285°F. In some cases, the temperature was first brought to 285°F and the set-points were run in descending order. One test run included a hold period of 30 minutes at 285°F as a stability test.

A total of six test runs were made. The last two runs were considered to be of unquestioned validity. The results of the first four runs were considered to be of dubious validity due to the fact that the MMH was boiling during the test, presumably due to leakage of vapor from the system at the higher temperatures. No boiling was evident on the two final runs.

The vapor pressure data from the final runs are shown in Fig. 18, which shows a vapor pressure of 67 psia at 285°F. The data at 150°F and above show agreement (±5%) with published information (Ref 13) from the Johns Hopkins Liquid Propellant Information Agency. The data below 150°F show a difference of 1.5 psi between the test data and published values. The relatively low temperature regime was considered to be of incidental importance to the overall program; therefore, the acquisition of valid data in the high temperature regime was considered a satisfactory fulfillment of the test objectives.

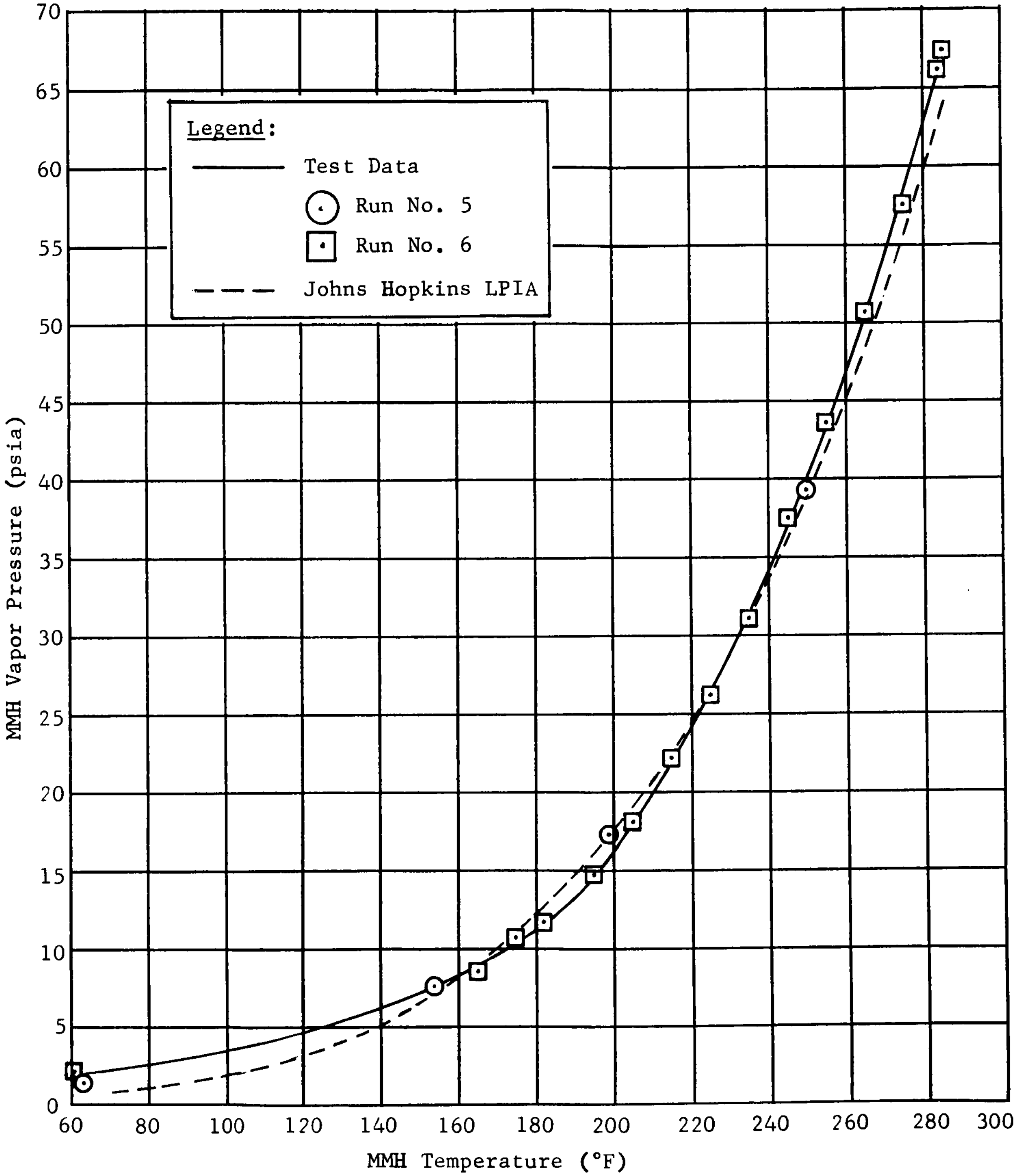


Fig. 18 Vapor Pressure of MMH

Stability of the MMH was demonstrated by the repeatability of vapor pressure characteristics during two successive runs on the same fuel sample, and also by the constancy of vapor pressure exhibited during a 30-minute hold period at 285°F.

Propellant Sensitivity - The heating of MMH to 275°F has been some cause for concern because of recent reports of violent decomposition.

All specimens to be tested in fuel have been thoroughly cleaned to a lox-clean level and then passivated. In general, the passivation procedure includes exposure to a 25% MMH solution at 275°F for 24 hr.

There have been no incidents of violent decomposition of the fuel resulting in rupture of any test apparatus. Some decomposition occurred during the material testing. This was attributed to the materials being tested and not to contamination. Detailed passivation procedures have been published and are now in use by the testing organizations.

F. TEST PLAN

Work was started during the period on a detailed test plan for the component and system test phase of the program. An initial rough draft was completed with the exception of the component descriptions. A final draft and issue of the plan will not be completed until after component final selection which will occur during the next reporting period. In addition to component descriptions, the plan will include test equipment descriptions, test sequences, flow charts, and a schedule which will include milestones.

The completed plan will be submitted to JPL for review and approval.

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