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INVESTIGATION OF BINDERLESS REVERSE
HYBRID PROPELLANT SYSTEMS

(u)

by

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China Lake, California

March 1965

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FOREWORD

The work described in this report was accomplished under Task Assignments RMMP 21-001/216-1/F009-01-016 and RMMP 24-112/216-1/F009-06-09.

The report was reviewed for technical accuracy by M. K. Kaufman and D. H. Williams.

Released by   Under authority of
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Propellants Division   Propulsion Development Dept.
1 August 1964

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ABSTRACT

Several binderless reverse hybrid propellant systems were investigated theoretically and experimentally for their suitability as high performance systems. The systems were compared theoretically to a propellant with a measured density of 1.92 g/cm^3 and a measured specific impulse of 260 lb-sec/lb. A binderless system comprised of a solid phase of ammonium perchlorate-lithium perchlorate eutectic, reinforced with aluminum metal, was selected for scale-up and development. The liquid phase of the system was hydrazine or a slurry of added fuel in hydrazine. The results of investigations in the areas of combustion research, safety and compatibility studies, process development, ignition, motor firings, and fuel slurry development are reported. (CONFIDENTIAL)

ACKNOWLEDGEMENT

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INTRODUCTION

The Naval Ordnance Test Station, China Lake, California, decided to devise a hybrid (combination solid-liquid) propellant system with performance characteristics equal to or better than existing solid or liquid systems. For definitive purposes, a mythical propellant system with a measured specific impulse (I_{sp}) of 260 lb-sec/lb and a measured density (ρ) of 1.92 grams/cm^3 was set as a goal. Assumptions of an I_{sp} efficiency of 95-96% and a density achievement of 98% resulted in a reference propellant with a theoretical I_{sp} of 272 and a density of 1.96. A hybrid task team devised propellant systems which might meet this goal. For evaluation purposes the burnout velocities (V_{BO}) at a mass-to-volume ratio (M/V) of 88 of the new theoretical systems were compared to that of the 272/1.96 theoretical goal propellant.

Three of the devised systems met or exceeded the performance goal on a theoretical basis and all three were subjected to laboratory evaluation for basic feasibility studies. Of the three systems, the one which showed the most potential gain was the binderless reverse hybrid. This system was selected for research and development work to determine its practicality and adaptability for scale-up. Details of the considerations in the selection of this high risk/high gain system are given in Ref. 1. This report describes the research and development work and its results.

BINDERLESS REVERSE HYBRIDS

A brief description of binderless reverse hybrid systems and some of the basic concepts involved will aid in understanding the work performed in the research and development areas.

System Description

A reverse hybrid system is one in which the solid phase is the primary oxidizer source while the liquid phase provides fuel and working fluid. The binderless reverse hybrid concept is illustrated in Fig. 1. The original concept involved using metal in the form of sponge-like or corrugated material to provide structural integrity for the system. Void spaces in the metal skeleton would then be filled with a fusible oxidizer material and, upon solidification, a solid grain would result with the usual type of polymeric binder eliminated. The obvious advantages are those of increased system energy and increased system density.

BINDERLESS
SOLID GRAIN

HYBRID

FUSIBLE OXIDIZER OR
OXIDIZER EUTECTIC

LIQUID INJECTANT
(FUEL + WORKING
FLUID)

POROUS METAL
SKELETON

SOLID GRAIN
(OXIDIZER + LIMITED
FUEL)
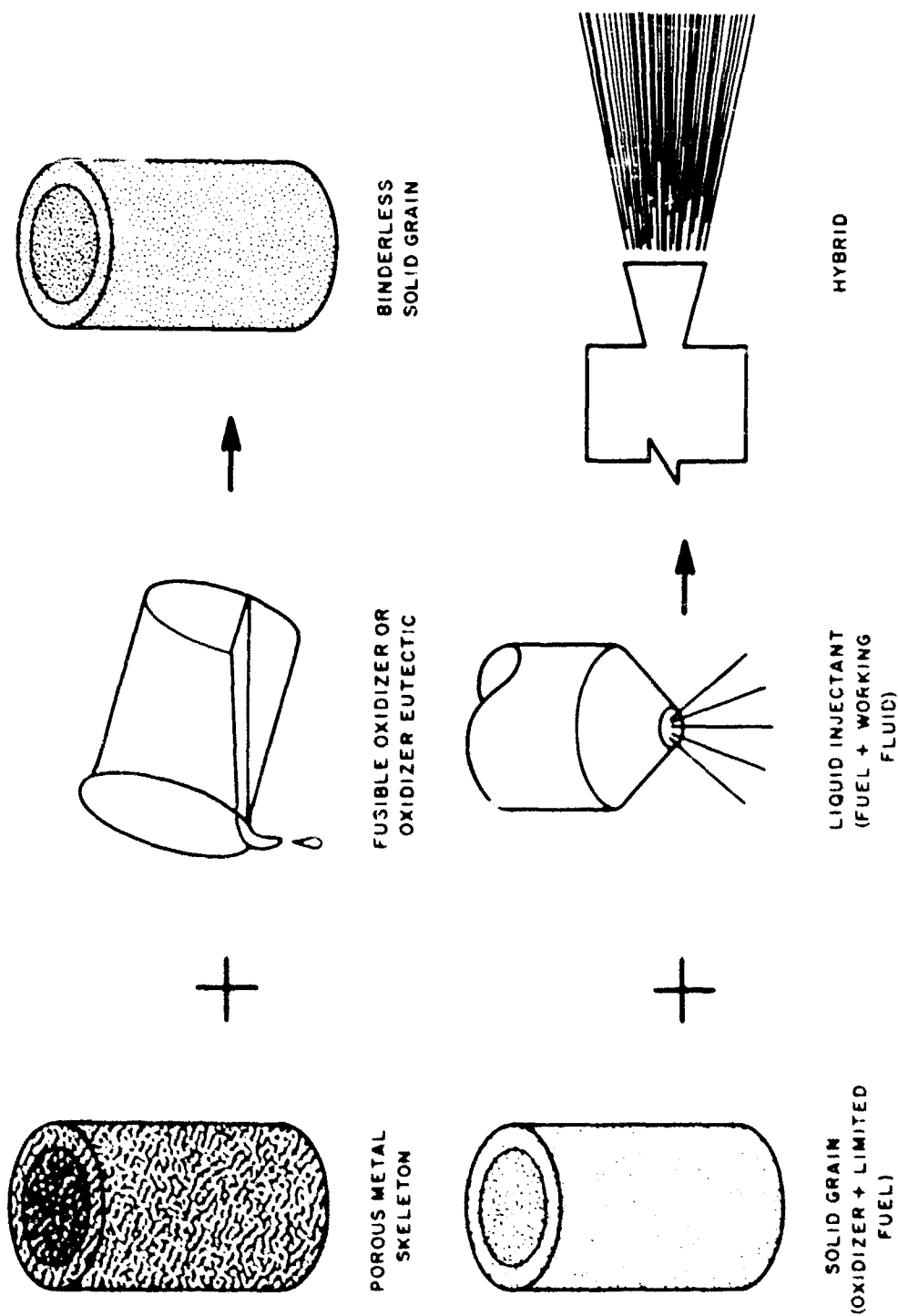
FIG. 1. Binderless Reverse Hybrid Concept.

Theoretical Calculations

Calculations were made using the IBM computational program of Ref. 2. Many oxidizer-metal/liquid-fuel combinations were examined and the calculations showed that a wide range of I_{sp} and/or ρI_{sp} was possible through variation of components. A condensation of these calculations is given in Table 1. For comparison purposes two high performance mythical propellants are included in the table. A complete list of calculations made is given in Ref. 3.

Work Areas and Phases

Most of the NOTS work on binderless systems was directed toward the nitronium perchlorate-lithium perchlorate/aluminum reinforced/hydrazine (NP-LP/Al/N_2H_4) and the ammonium perchlorate-lithium perchlorate/aluminum reinforced/hydrazine systems (AP-LP/Al/N_2H_4). Although many of the work areas and phases overlapped, for reporting convenience, the following systems comprised the major phases of the work.

     I.   NP-LP/Al screen
    II. AP-LP/Al screen + N_2H_4
   III. AP-LP/Al powder + N_2H_4
   IV. Class 1 modified AP-LP/Al powder
    V. Class 2 modified AP-LP/Al powder
   VI. Class 2 modified AP-LP/Al powder/Al screen

The areas of investigation (again with considerable overlap) included the following:

       combustion research
       fuel slurry development
       safety and compatibility studies
       process development
       ignition
       motor firings

PHASE I: NP-LP/Al SCREEN

Loading Equipment

A remotely controlled 2.5-inch mechanical loading device was designed and installed. Figure 2 is a cutaway view of the loader, and Fig. 3, a photograph of the loader in an open position. The basic design was patterned after a small research-scale loader with which the Dow Chemical Co. had investigated the use of various filler materials in a binderless solid-propellant system. The loader was enclosed in a dry box to make use of inert and extremely dry atmospheric conditions.

Details of the design and loading technique development are reported in Ref. 4.

TABLE 1. Binderless Propellant Systems

Ingredients	I_{sp}, lb-sec/lb	Density, g/cc	Flame temp, °F	Mol wt exhaust gas	V_{BO}, ft/sec at M/V = 88	Approx % of goal
LP +AP +N$_2$H$_4$ +Al	269	1.86	6,806	35.77	7,269	96
LP +AP +N$_2$H$_4$ +Be	276	1.82	7,413	36.94	7,378	97
LP +AP +N$_2$H$_4$ +Zr	231	2.51	6,856	47.44	7,584	100
LP +AP +TAG +N$_2$H$_4$ +Al	272	1.95	6,951	35.01	7,603	100
LP +AP +TAG +N$_2$H$_4$ +Be	289	1.78	6,603	29.0	7,591	100
LP +AP +TAG +N$_2$H$_4$ +Zr	235	2.61	6,709	44.44	7,901	104
NP +LP +TAG +N$_2$H$_4$ +Al	286	1.91	7,031	31.57	7,898	104
NP +LP +TAG +N$_2$H$_4$ +Zr	246	2.51	6,995	41.71	8,096	100
Hypothetical No. 1	310	1.50	----	----	7,608	100
Hypothetical No. 2	320	1.50	----	----	7,868	103

FIG. 2. Motor Loader.

OUTER CHAMBER
LOADING PISTON
METAL FOAM
COOLANT OUT
MOTOR & OXIDIZER HOLDER
JACKET FOR HEATING & COOLING
CARTRIDGE HEATER
MOTOR TUBE
COOLANT IN
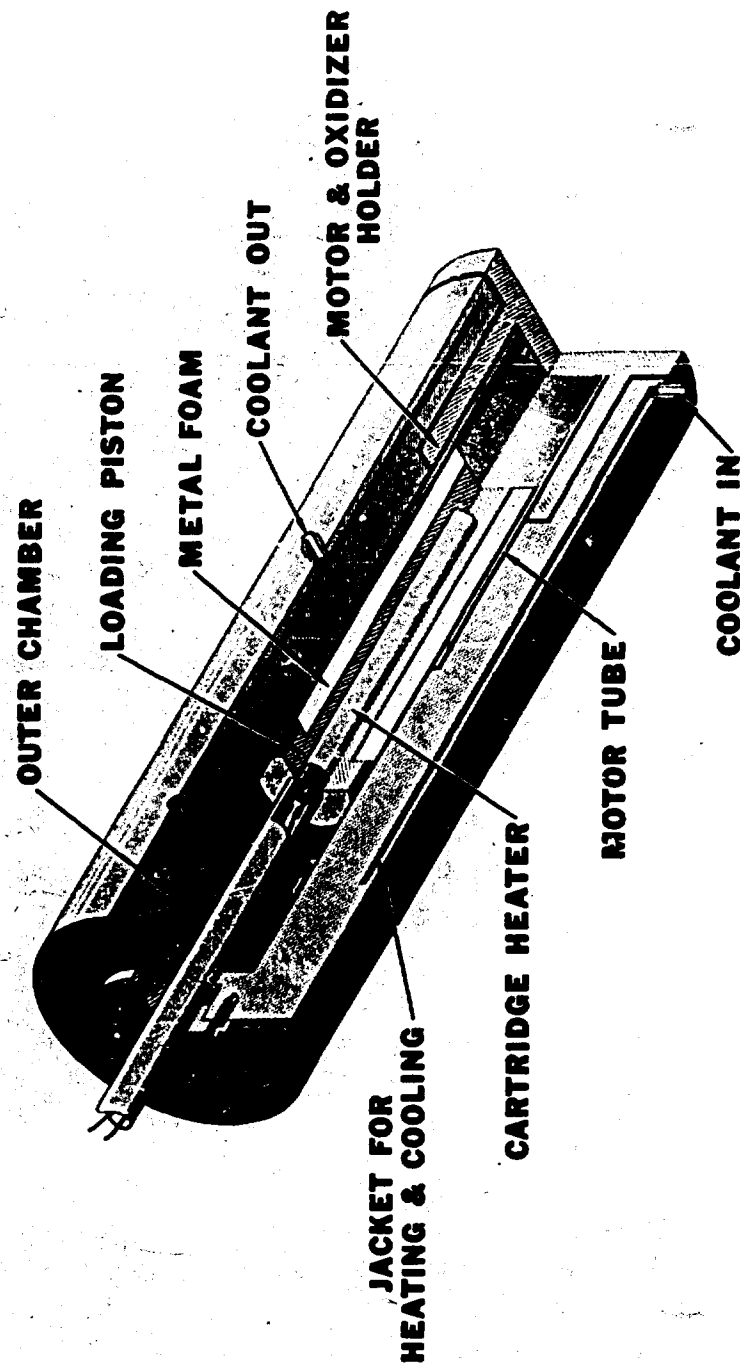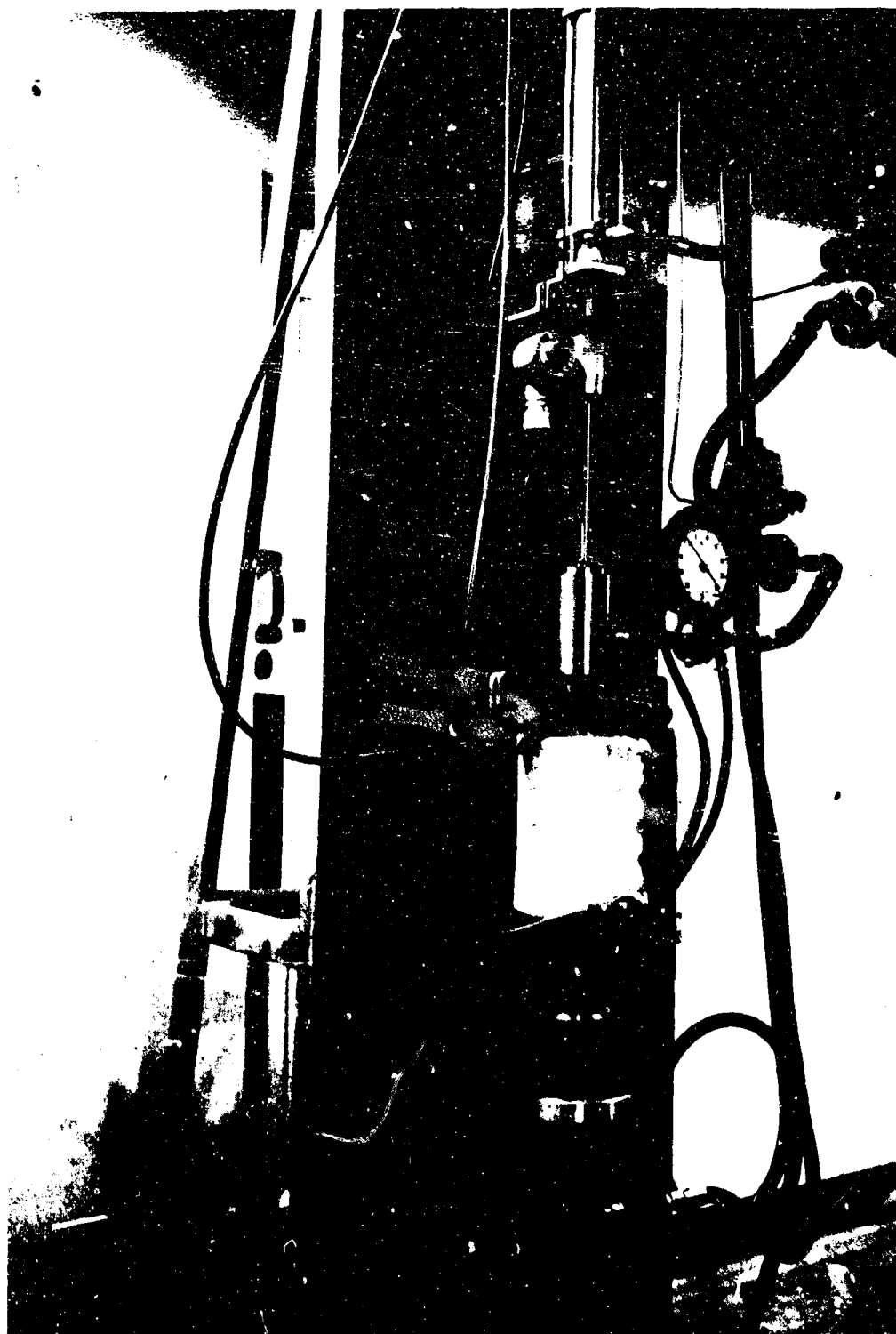
FIG. 3.   The 2.5-inch Mechanical Loader in Open Position.

NP-LP Eutectic Properties

A differential thermal analysis was made of mixtures of NP and LP to check for the eutectic melting point and rate of thermal decomposition. The eutectic formed at temperatures of 115-120°C over the composition range tested (20-70% NP). The weight loss of 70% NP-30% LP mixtures when held at 120°C for a period of one hour averaged about 1%.

Samples of aluminum, zirconium, and Teflon powders were immersed in molten NP-LP eutectic for periods of up to an hour. There was no visible reaction nor apparent change in the rate of thermal decomposition during the time the powders were immersed. The conclusion reached was that the mixtures with immersed powders could be used safely in the loading process.

Propellant Loadings

Two live propellant loadings were accomplished with NP-LP eutectic. A carpet-rolled aluminum screen was used for reinforcement. The screen used was type 1100 with a wire diameter of 0.005 inches and a screen mesh weave of 40 by 40 wires per inch.

For the first loading, an intimate mixture of NP and LP was placed in a 2.5-inch motor tube, the aluminum screen was placed via a friction fit around the loading piston, and the entire assembly heated slightly above the eutectic melting point. For complete eutectic melting, a heating period of approximately two hours was required. Vacuum was used to remove decomposition products, the loading piston was actuated, and the grain was pressed. An excellent, well formed grain resulted. The grain was allowed to cool and during the solidification process shrank so tightly around the loading piston that the piston could not be removed.

The motor was subjected to a 20-foot drop test with the loading piston (which weighed about two pounds) in place. Upon impact the motor ignited with a bright flash, copious quantities of smoke, and a sharp report. It did not continue burning. Examination of the residue showed that only a partial burn had occurred and that approximately one-sixth of the grain was consumed. The remainder was intact. The motor tube was not ruptured to any extent but was deformed by the developed pressure.

For the second loading, the same techniques were used. Again, no difficulty was encountered in the eutectic formation or grain pressing operations. However, at the beginning of the cooling cycle, a fire and pressure blow occurred in the loading equipment. Damage to the equipment was relatively minor and no personnel were involved. Investigations showed that the most probable cause of the incident was a reaction between the molten eutectic and a small amount of epoxy adhesive used in the

hardware assembly. Small pieces of cured epoxy adhesive dropped into a small beaker of molten eutectic reacted vigorously and burst into flame. The pressure blow was probably initiated by this reaction in a pressurized atmosphere of NP decomposition and sublimation products.

Further work with this system was discontinued pending results of work with the more easily processed AP-LP eutectic.

PHASE II: AP-LP/Al SCREEN + N_2H_4

The switch to the AP-LP eutectic involved three major advantages of this system over the NP-LP:

1. It is less reactive chemically.

2. It is less viscous and no pressure is required for loading.

3. No dry box operation is required during loading.

Loading Equipment

A non-pressurized grain loading technique was developed for the AP-LP/Al screen combination. The basic scheme is illustrated in Fig. 4. The assembly consists of two aluminum liners which fit into the 2.5-inch hybrid test motor. The grain skeleton and a mandrel are placed in the bottom or casting liner and the bottom is sealed. Small pieces of the pre-made eutectic (excess) are placed in the upper or hopper liner.

The entire assembly is then placed in a hot air oven (with provision made for vacuum operation and thermocouple temperature readings at crucial spots). The entire assembly heats up, vacuum is applied, and the eutectic melts and flows down into the pores of the aluminum skeleton. Upon cooling, the eutectic solidifies and the solid grain is formed. The casting mandrel is pushed out of the assembly by use of a remotely controlled hydraulic cylinder.

Propellant Loadings

Approximately 25 grains were loaded with the AP-LP eutectic via the technique described above. As the technique developed, loading efficiency increased. Grains containing up to 98% of the theoretical oxidizer weight were produced. The most serious difficulty encountered was ammonium perchlorate decomposition caused by the extremely long (4-5 hours) heating period required for heat transfer through a vacuum. No further loadings used this technique, because of development of superior techniques in other phases of the work.

EUTECTIC PIECES

UPPER LINER
(HOPPER SECTION)

ASSEMBLY SEAL

MANDREL

BOTTOM LINER
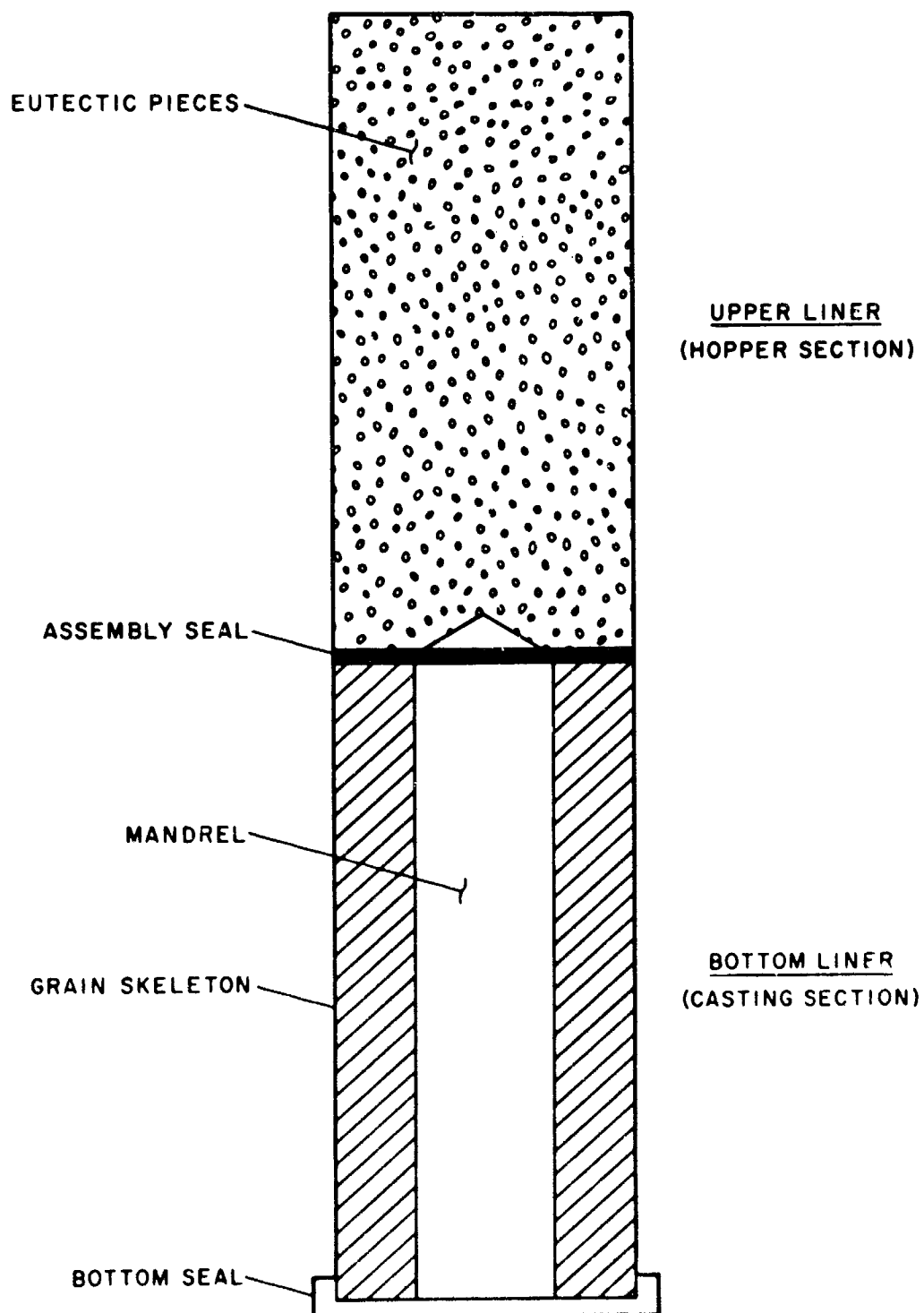(CASTING SECTION)

GRAIN SKELETON

BOTTOM SEAL

FIG. 4. Non-pressurized Grain Loading Technique.

Motor Firings

     Three attempts to fire eutectic LP-AP grains were made in 2.5-inch motors using liquid propellant ignition. The motor is shown in Fig. 5. A mixture of 75 wt % N_2H_4 and 25 wt % unsymmetrical di-methyl hydrazine (UDMH) was injected through a conical spray injector and inhibited red fuming nitric acid (IRFNA) was injected as a coherent stream to one side of the center. The firings resulted in two ignition failures and one motor failure from over-pressurization. Previous data from other companies indicated an approximate burn rate of 1.0 in/sec. It was concluded that too small a nozzle had been used and a second series was attempted with a larger nozzle. This series resulted in three ignition failures.

     A third series of motors used conical spray injectors on both the fuel and oxidizer with the axis of the fuel injector on the axis of the motor and the oxidizer injector located to one side with its axis 45 degrees off the motor axis. Strand data had indicated a burn rate of approximately 0.5 in/sec; therefore, the flow rates and nozzle size were calculated for this burn rate. The first motor ignited and apparently burned at approximately 200 psi. The nozzle area was decreased approximately 50% and the second motor apparently burned at 400 psi. The third attempt was without IRFNA injection and used a catalyst coating on the grain surface. This test resulted in ignition failure, presumably because of flooding of the propellant grain. A summary of the tests appears in Table 2.

     Firing numbers 7 and 8 were later determined to also be unsuccessful firings; i.e., no eutectic ignition occurred. The burning and observed pressure probably resulted from the N_2H_4–IRFNA reaction followed by a short period of either monopropellant operation or monopropellant plus a slight amount of oxidizer action. The eutectic and pieces of screen were evidently eroded away by the force of the injection stream. No further work was done in this phase because of developments from other phases of the work.

<div align="center">

PHASE III: AP-LP/Al POWDER + N_2H_4

</div>

     The poor results observed in Phase II resulted in a significant effort to remove or reduce the amount of metal present in massive form. Most of the effort was devoted to substitution of aluminum powder for all or part of the aluminum screen.
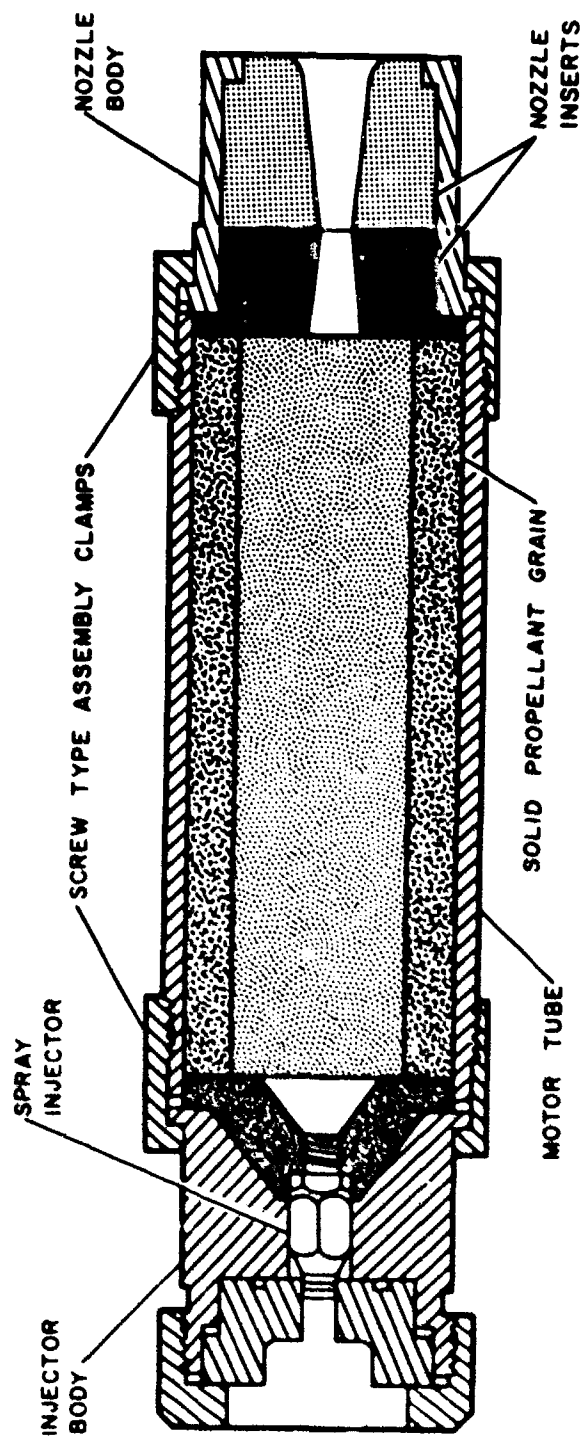
FIG. 5. The 2.5-inch Diameter Static Test Motor.

TABLE 2.   Summary of Early Static Firing Attempts

Test	Ignition system	Nozzle dia	Fuel inj time	Oxygen inj time	Remarks
1	Bi-propellant	0.75	0.5	0.25	Ignition failure. No oxidizer flow.
2	Bi-propellant	0.75	0.5	0.5	Ignition failure. Bi-propellant operated at 400 psi.
3	Bi-propellant	0.60	1.2	1.2	Pressure failure. Bi-propellant was operating at 800 psi and very rough.
4	Bi-propellant	1.0	3.0	3.0	Ignition failure.
5	Bi-propellant	0.9	3.0	3.0	Ignition failure.
6	Pyrogen + bi-propellant	0.9	3.0	3.0	Ignition failure.
7	Bi-propellant intersecting conical spray	0.7	6.1	1.3	Grain apparently burned. No indication of time at which solid ignited on pressure trace. Pressure dropped from 400 to 200 psi when liquid injection stopped.
8	Bi-propellant	0.5	4.8	1.0	Approx 2/3 of grain apparently burned. One spot burned to wall near head end. Pressure dropped from 800 to 400 psi when liquid injection stopped.
9	Catalytic on grain surface	0.4	3.1	---	Ignition failure. Catalyst washed out. ·

Strand and Slab Burning Tests

In an initial effort to examine the ignition and combustion charac-
teristics of the combination of AP-LP and aluminum powder, hereafter
referred to as aluminized eutectic, strands and slabs of the material
were burned in window burners.

In the first slab burning experiments, the sample configuration con-
sisted of a slab of the eutectic material approximately 1/4- by 1/4-
by 1/8-inch thick, sandwiched between two pieces of JPN (a Jet Pro-
pulsion Laboratory designation) propellant approximately 1/4- by 1/4-
by 1/32-inch thick. The JPN was ignited on one edge of the sandwich
by an electrically-heated wire; the JPN flame in turn melted and in some
cases ignited the eutectic.

The results of these first tests using the eutectic with 20μ aluminum
powder were as follows:

> Two attempts at 400 psi; neither were self-sustaining
> Four self-sustaining burns at 600 psi
> Six self-sustaining burns at 800 psi
> Two self-sustaining burns at 1,200 psi

Motion pictures taken on some of the 800 psi tests showed that the eutectic
sample melted before any visible indication of ignition of the eutectic;
during combustion, the sample was surrounded by a considerable amount
of smoke, making it extremely difficult to determine the location of the
flame zone with respect to the surface of the eutectic. The luminosity
during eutectic combustion was an order of magnitude brighter than during
JPN combustion alone. When attempts were made to burn the eutectic
with aluminum screen (no Al powder) in the JPN sandwich arrangement
at 1,000 psi, the samples were not self-sustaining.

In the initial strand burning experiments the following results were
obtained:

Pressure, psi	Burning rate, in/sec
1,000	0.26
1,100	0.34
1,200	0.39 and 0.40
1,300	0.46

An igniter mixture of Al, potassium perchlorate ($KClO_4$), and polymethyl-
vinyltetrazole (PMVT) was used. The strands would not ignite in tests
at 800 and 900 psi.

On the basis of these experiments, it was concluded that the combination of eutectic and screen would not burn in a self-sustaining manner but that the combination of eutectic and powder would. Ignition was observed to be difficult in these experiments and some effort would have to be devoted to investigation of ignition methods or aids.

Additional strand and slab burning tests were made with the aluminized eutectic using a finer grade (5μ mean particle size) of aluminum powder.

The slab tests employed an N-5 propellant "donut" with a hot wire through the hole as the igniter system.

Six tests were made using the eutectic with 5μ Al powder, two at 1,200 psi, two at 600 psi, and two at 300 psi; the four at the higher pressures ignited and were self-sustaining; the two at 300 psi showed signs of melting on the outer surface, but were not self-sustaining.

Four tests were made using 70% eutectic, 30% 5μ Al, and one sheet of Al screen. Two samples at 1,200 psi and one at 600 psi ignited and were self-sustaining; a fourth test at 600 psi did not ignite, probably due to faulty igniter placement. No trace of the screen was found after that test, indicating that the screen burned when Al powder was present.

Four tests were made using eutectic, 5μ Al powder and rolled Al screen, mounted in a fuzed quartz tube. One sample at 1,200 psi was self-sustaining. Two samples at 800 psi were self-sustaining and the sample at 600 psi was not self-sustaining. Motion pictures of one of the samples showed the liquid nature of the combusting eutectic. No evidence of unburned Al screen was found in the combustion bomb from the samples which contained screen and were self-sustaining.

The strand tests indicated a change in combustion behavior at higher pressures (1,500-2,000 psi) as a result of the finer size of aluminum. Movies showed a steadier, more regular flame above the strand with less violent scattering or eruption of metal particles from the surface and a thinner layer of liquid eutectic than in the previous tests at lower pressures. The burning rate increased significantly to about 0.6 in/sec at 1,000 psi.

Ignition Experiments

A number of materials were tested as coating materials for eutectic charges in attempts to bring about spontaneous ignition of 98% hydrazine. Materials tested included chromium trioxide, ferric oxide, copper oxide, "copper chromite" (85% CuO, 15% Cr_2O_3), nitrocellulose, phosphorus

pentoxide, Norite A (activated charcoal) potassium ferricyanide, potassium persulfate, and mercuric oxide. All of these substances, except potassium ferricyanide and potassium persulfate, ignited hydrazine at room temperature on contact (in air) at varying rates. The finely divided "copper chromite", which is sold as a burning rate catalyst, was the most rapid and active material.

In attempts to find a carrier material for some of the more active oxides, they were incorporated in a lacquer made from nitrocellulose and acetone (or ethyl acetate). In this state they no longer ignited hydrazine. An ignitable coating could be made, however, by dusting the finely divided oxides onto the lacquer mixture while it was still wet. Difficulty was experienced in making such a coating adhere to LP-A^D surfaces.

Another mixture containing copper and cobalt oxides on an alumina carrier was prepared according to directions given by Jet Propulsion Laboratory (Ref. 5). This material had been developed for use in a gas generator. The preparation as made here gave rapid decomposition (fizzing and gas with some sparking) of the hydrazine but no flame.

The action of the metal oxides tested in these experiments was found to be chemical and not catalytic. Variations in reactivity of a given material probably were related in particle size. Chunks of eutectic, covered with the nitrocellulose (NC) lacquer and copper chromite preparation, burned vigorously in the presence of hydrazine in atmospheric pressure. This technique for hypergolic ignition was used in one static firing attempt but apparently the force of the hydrazine injection was sufficient to "wash-out" the coating material prior to ignition.

Safety Investigations

The necessity for introduction of finely divided metal powders to molten oxidizers led to detailed safety and processing investigations.

A Techno-Products drop weight tester was modified in order to obtain rough values of the sensitivity of components and formulations of the LP-AP/Al and the LP-AP/Zr systems at elevated temperatures and in the molten stage. In addition, samples were submitted for friction and electrostatic initiation tests. No fires were obtained to the limits of the testing machines for the friction and electrostatic tests. For the impact sensitivity tests, the information which follows was obtained.

TABLE 3. Techniques Evaluated for Production of 2.5-Inch
Aluminized Eutectic Grains

Techniques	Results
1. Direct casting: Molten material poured into cold mold and mandrel	Many severe cracks in grain
2. Direct casting: Molten material poured into heated mold and mandrel	Many severe cracks plus additional voids from eutectic decomposition at hot surfaces
3. Increment casting: Approximately 1/8 of complete grain cast and allowed to solidify. . . . repeated	Many small cracks randomly oriented and spaced—some separation between increments noticed
4. Layer dipping: Mandrel dipped into molten bath of eutectic, then removed and coating allowed to solidify. . . . repeated	Small hairline cracks along the length of grain
5. Controlled cooling: Grains formed by techniques 2, 3, and 4 placed in a holding oven and cooled very slowly to allow maximum fusion of cracks	Small hairline cracks both longitudinally and radially oriented
6. Direct casting of solid billet: Heated mold with no mandrel	Good, void-free, crack-free grains

For subsequent machining operations the same principle was used (forming a pilot hole and then enlarging) but the drill was modified so that a stream of air could be directed on its point for cooling and dust removal. No further incidents occurred and several acceptable grains were formed in this manner.

Further technique development resulted in the production of grains requiring no subsequent machining. Foundry casting techniques were directly applicable to the eutectic system because the problems are the same (although of greater magnitude for the eutectic). Some of the problems considered included:

1. Residual stress

2. Dissolved gases

3. Decomposition gases

4. Injection during pouring and/or entrapped air

5. Shrinkage

Techniques evaluated for solution of these problems included:

1. Annealing techniques

2. Use of flexible mold parts

3. Use of vacuum

4. Use of pressure

5. Controlled pouring conditions

6. Controlled cooling conditions

7. Use of riser techniques

8. Use of differential (directional) solidification methods.

The major problems proved to be residual stress and grain porosity, both caused by the great amount of volumetric shrinkage accompanying the solidification of the molten eutectic. It was determined that this shrinkage was on the order of 20% for the eutectic alone (14% for the aluminized eutectic).

Annealing techniques, controlled cooling methods, and the use of flexible mold parts were evaluated as means of relieving residual stresses. Annealing consisted of periods of slow heating of finished grains to a temperature slightly below the eutectic melting point. There was no real evidence of significant stress relief. Severe cracks occurred if grains were machined. Controlled cooling techniques involved placing the hot, just solidified grain in a temperature controlled oven and gradually

reducing the temperature to ambient. Cracks were fewer and smaller but still present when grains were subjected to machining processes. The best method of stress relief proved to be the use of a flexible mandrel which could contract with the eutectic as if solidified. Mandrels were prepared from RTV silicone rubber, placed in the mold, and the molten mix cast directly. Machining operations performed on the resultant grains showed evidence of greatly reduced residual stress and resulted in acceptable grains without cracks or fissures.

Most of the attempts to eliminate shrinkage porosity were direct adaptations of techniques used in foundry practice. The use of (1) careful pouring techniques to eliminate injection of air, (2) an extra reservoir (riser) of molten oxidizer to aid in directional solidification, and (3) the use of different temperatures for different parts of the mold, resulted in grains with good, solid matrices.

The objective in directional solidification is simply to control the freezing of the casting in such a manner that hot molten material is always available to fill in shrinkage voids. For the typical cast propellant grain this would mean freezing from the bottom up, the last part to freeze being the top of the grain. This was accomplished by insulating the top part of the mold (to retain heat) and introducing chills to the bottom part of the mold (to remove heat). An expansion chamber was placed on top of the mold to act as a riser or reservoir of molten material available to fill in the shrinkage voids.

The use of vacuum and/or pressure complicated porosity problems rather than reduced them. This was probably because of additional decomposition under vacuum conditions or additional entrapped or dissolved gas under pressure conditions. Because acceptable grains were produced without vacuum or pressure, very little work was done along this line.

Although a substantial amount of effort was directed towards the attainment of void and crack-free grains, there is evidence that the presence of voids or cracks in the solid would not result in unsatisfactory motor performance. United Technology Center, in a presentation given at the Hybrid Contractor's Symposium, Huntsville, Alabama, February 1964, reported on hybrid firings in which solid fuel grains with deliberately introduced porosity and/or cracks performed without incident. In addition, the high speed movies of strand and slab burnings indicate that the rather substantial layer of liquid eutectic on the grain surface would eliminate the presence of porosity or cracks in the combustion region and would, in addition, act as a barrier to flame propagation through voids or cracks. The importance attached to porosity and crack-free grains, therefore, was based primarily upon considerations of loading density and mechanical properties rather than ballistic behavior.

Ignition and Motor Firing Tests

Several test firings were conducted to evaluate the effect of powdered aluminum in the LP-AP/Al/hydrazine system. A four-arm cruciform auxiliary grain (of Mg-Teflon or double base composition) was used to ignite the eutectic grain. A schematic diagram of the ignition arrangement is shown in Fig. 6. The auxiliary grain was initiated by a Mk 1 squib in a bag of pyrotechnic mix.

A series of fire tests was made using a cruciform grain of high energy X-12 double base propellant. The first motor overpressurized and ruptured apparently upon initiation of the firing sequence and definitely prior to hydrazine injection. The second motor was designed for a lower ignition pressure and failed to ignite during the ignition sequence. However, after a delay of a few seconds and the initiation of a nitrogen flush, ignition did occur and a rather steady burn was observed. There was no indication as to whether the observed burning was residual hydrazine, dry eutectic, or a combination of both. Motor no. 3 burned during the igniter action time but chamber pressure dropped to zero shortly after the N_2H_4 entered the chamber. In the fourth motor, the pressure rose to 2,000 psi upon ignition but dropped immediately to 300 psi when hydrazine was injected. The igniter on motor no. 5 failed to function and approximately 5.5 seconds after the squib pulse, the motor ruptured due to an overpressure. The chamber at this instant contained double-base (X-12), Mg-Teflon pyrotechnic mix, eutectic, and hydrazine. The probable cause of ignition was a hypergolic reaction between the X-12 propellant and the hydrazine. As a result of this series of tests, there was much concern about the possibility of the liquid hydrazine quenching the combustion of the solid and it was decided to fire some eutectic/aluminum powder grains without hydrazine injection.

Table 4 summarizes the test conditions and results of the next firing series, conducted without hydrazine injection and using Mg-Teflon igniter grains.

Test no. 1 and 6 resulted in early pressure failures. Tests 2, 3, 4, and 5 burned at a very low pressure for some 3 minutes. This burning appeared to be very low efficiency combustion of the eutectic. There was a very large amount of white smoke and sporatic spurts of flame during the firings. Examination of the motor showed deposition of aluminum oxide on the nozzle indicating that there was some pyrotechnic burning of the eutectic. A puddle of eutectic was observed below the motor after runs 2, 3, 4, and 5, which apparently had melted and was blown out during the test. The high speed movie coverage of firing no. 6 showed pieces of flaming eutectic in flight away from the vicinity after the pressure rupture.
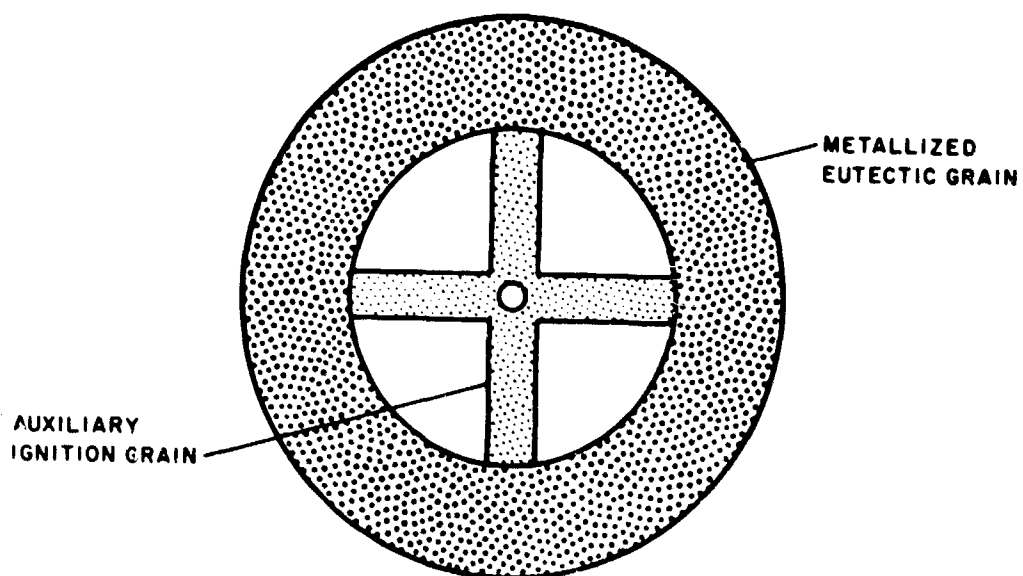
AUXILIARY GRAIN DESCRIPTION

1. DOUBLE BASE COMPOSITION

2. MAGNESIUM – TEFLON COMPOSITION

3. DOUBLE BASE – NITROCELLULOSE LACQUER –
   COPPER CHROMITE

4. MAGNESIUM – TEFLON, OTHER SHAPES

F.G. 6.   Auxiliary Grain Ignition Method.

TABLE 4.   Static Firings of LP-AP/Al Powder Grains

Test number	Igniter grain length, in.	Nozzle dia, in.	Results
1	4	0.6	Pressure ruptured. A blow-off plate was used to increase pressure during ignition
2	2	0.6	Smolder (chuffing-slow, inefficient combustion)
3	2	0.5	Smolder
4	3	0.5	Smolder
5	4	0.5	Smolder
6	4	0.4	Pressure rupture

The overall conclusions from these tests were that the aluminized eutectic can burn as a pyrotechnic, but burns very poorly and inefficiently and that the presence of hydrazine apparently contributes negatively to the combustion, acting as a quenching agent in the system.

In a separate series of tests the use of hydrazine decomposition was investigated as an initiator for the ignition grain.   Copper chromite was used as the catalyst and was applied to one side of each wing of the ignition grain.   Laboratory tests had shown that there might be some difficulty in igniting the magnesium-Teflon so the first two runs used a high energy X-12 cruciform.   In the lab tests the ignition of X-12 by hydrazine decomposition appeared to be instantaneous.   The two motor environment tests using X-12 had ignition delays of 2 and 3 seconds.   Two tests using Mg-Teflon grains resulted in "washout" of the copper chromite catalyst and no ignition of the cruciform grains indicated that the ignition of the X-12 grains probably resulted from the double-base and hydrazine reaction itself rather than decomposition of the hydrazine by the copper chromite catalyst.

PHASE IV: CLASS 1 MODIFIED AP-LP/Al POWDER

Search for Additives

The static firings of previous phases of the work emphasized the need for improvement in the ignition and combustion characteristics of the aluminized eutectic. In an effort to improve these properties, a study of the effect of additives in small amounts was started. Samples were prepared for differential thermal analysis (DTA) studies containing 5% of additives representative of several classes of compounds which, it was thought, might have a beneficial effect on the combustion process.

Organic materials, added for the purpose of supplying additional heat, included graphite, decolorizing carbon, polystyrene, Teflon 7, melamine, and hexane diamine. Exotherms at comparatively low temperatures indicated a potential hazard in adding organic compounds to the molten LP-AP/Al mixture. The best stability was shown by Teflon and melamine. Because oxides were known to promote smooth deflagration and increase burning rates of ammonium perchlorate-containing solid propellants, mixtures were made containing such inorganic compounds as copper chromite, molybdenum trioxide (M_oO_3), molybdenum disulfide, and barium dioxide. A third approach to the problem consisted in the addition of materials which might act as "fluxing" agents on the oxide coating on the aluminum particles. Several of the compounds tested showed pronounced exothermic reactions near the melting point of aluminum.

DTA Studies

DTA runs were made for the various ingredients and combinations of ingredients of the AP-LP/Al system. Although minor differences could be detected, for example, in the curves for physical blends of AP-LP and fused eutectic of AP-LP, a typical summary curve for the overall system was obtained (see Fig. 7). The runs were conducted under air and under nitrogen atmospheres and were continued to temperatures of 1100°C.

This curve proved to be of value in attempts to evaluate the possible effects of additives to the system and in postulation of a combustion mechanism theory. The principal reactions of the basic system as seen in the curve are the following:

1, 2, 3   loss of water from the lithium perchlorate tri-, di-, and mono- , hydrates
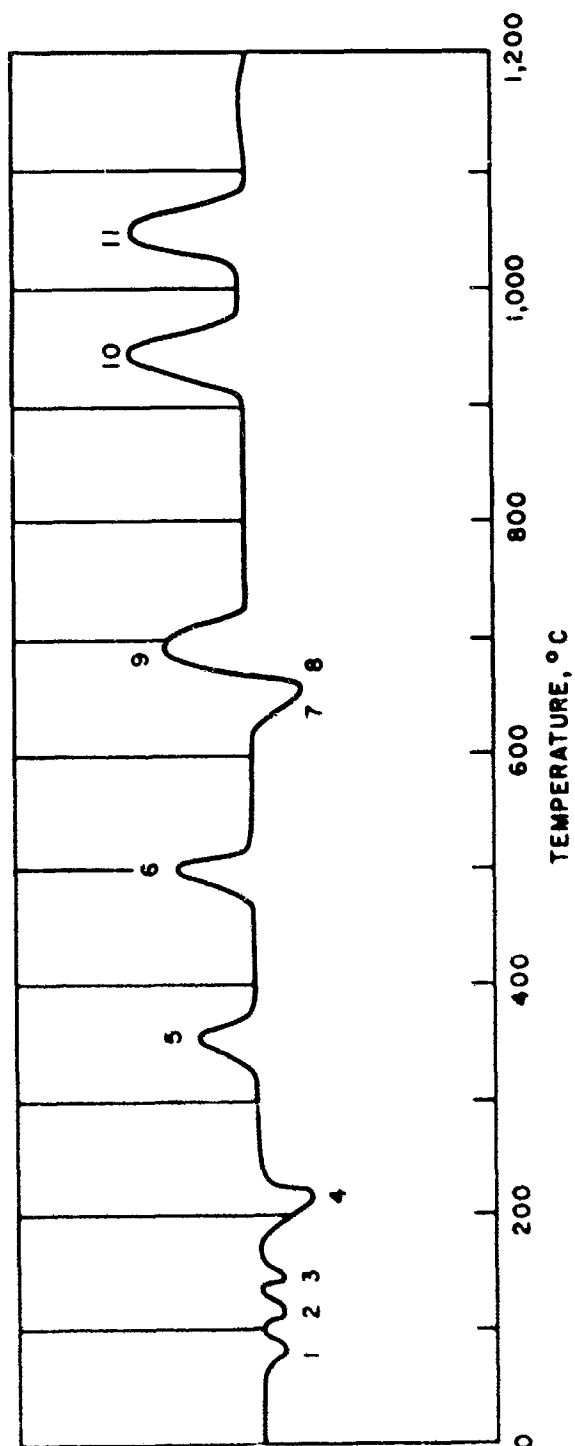
4   fusion of AP-LP eutectic

5   decomposition of AP

FIG. 7. DTA Summary Curve.

6   decomposition of LP

7   fusion of lithium chloride (LiCl)

8   fusion of aluminum

9   partial oxidation of aluminum

10   additional oxidation of aluminum

11   additional oxidation, or possibly nitridation of
aluminum.

Under the DTA experimental conditions (heating rate 6°C/minute),
the gaseous decomposition products from the perchlorates would have
diffused away before the melting point of aluminum is reached, and thus
the last three exotherms are probably due to reaction between the metal
and air present in the apparatus. This hypothesis is supported by the
work of Markowitz and Boryta (Ref. 6), who ran thermogravimetric and
differential thermal analysis of aluminum under air, oxygen, and nitrogen,
separately. They found that the aluminum reacted in all three cases
between 900-1000°C, and that the reaction with nitrogen was considerably
more rapid than with oxygen. In our DTA studies, exotherms 10 and 11
were observed with aluminum in an air atmosphere, but only exotherm 11
was observed with aluminum in a nitrogen atmosphere. This may be an
indication that the last exotherm is a nitridation rather than oxidation
reaction.

Comparison of the data curves of LP-AP to those of LP alone and
AP alone showed closely related behavior. Most of the major endotherms
and exotherms observed with AP or LP alone were also observed with
the eutectic at about the same temperatures (corresponding to phase tran-
sition, melting points, and/or decomposition). Two major differences
were noted: (1) a major endotherm appeared with the LP-AP in the 190°C
temperature range (melting point of the eutectic); and (2) the 270-280°C
exotherm observed with AP alone disappeared on the eutectic curve. The
indication of this second effect is that the normal low-temperature decom-
position of solid AP does not take place in the liquid eutectic and hence,
that major decomposition of the eutectic does not occur until much higher
temperatures (360 and 470°C) are reached.

Another interesting result was that the exotherm around the melting
point of the aluminum was smaller in the case of Al alone then in the case
of Al plus eutectic. Since LiCl would be present as a decomposition prod-
uct of LP in the eutectic mixture, it was suspected that this effect might
be caused by the presence of LiCl. DTA runs were made of Al plus LiCl
and a significant increase in the magnitude of the exotherm around 660°C
was observed over that of the Al alone. The conclusion was that LiCl
apparently acts as a temporary fluxing agent for the aluminum oxide, and
thus permits an increase in the extent of attack by the surrounding air.

DTA runs were also made with the aluminized eutectic and the additives being tested for effect on ignition or combustion. Changes in the onset temperature or the magnitude of the reactions noted above were considered quite important.

Large effects were noticed in runs made on samples containing fluxing agents. These compounds appeared to contribute significantly to the probable condensed phase oxidation of aluminum. In later tests, additives like potassium borofluoride (KBF) and sodium aluminum fluoride (Na_3AlF_6) appeared to be even better than calcium fluoride (CaF_2) or LiCl, displacing the aluminum oxidation exotherm towards lower temperatures and increasing its magnitude.

Strand and Slab Burning Studies

Samples containing several of the additives were prepared for strand and slab burning tests.

A summary of the results of the slab burning tests is presented in Table 5.

TABLE 5. Slab Burning of Aluminized Eutectic with
Additives at Various Pressures

Sample Composition	Pressure			
	1000 psi	800	600	400
95% LP/AP-20 μ Al, 5% "Copper Chromite"	Ignition and consumption	~30% residue	No go twice	No go
95% LP/AP-20 μ Al, 5% CaF_2	Ignition and consumption	No go	No go	No go
95% LP/AP-20 μAl, 5% MoO_3	Ignition and consumption	No go	No go	No go
70% LP/AP, 15% 20 μ Al, 15% "Pyrofuse"	Ignition and only 1/2 of sample consumed	No go	No go	No go
"Control" (5 μ Al powder)	Ignition and consumption	-- --	~20% residue	No go

The results were only slightly encouraging from the standpoint of any apparent changes in the case of ignition or combustion. However, in crude laboratory tests, samples of aluminized eutectic containing CaF_2 could be ignited with a gas flame and would burn in a self-sustaining manner at atmospheric pressure. The conclusion was that the ignition process in the slab burner had been inadequate.

Burning of strands containing additives resulted in more noticeable effects. For samples of standard aluminized eutectic composition containing 5% of CaF_2, the data showed a steep line from 600 to 1,650 psi with a pressure exponent of 4.0, then from that point a slope of essentially zero up to pressures of 3,500 psi. At 1,000 psi, burning rate (r_b) = 0.7 in/sec; at 1,650 psi, r_b = 5.5 in/sec. The values of r_b above the 1,650 psi readings showed large standard deviations, but were still considered significant because they indicated a tendency for the eutectic towards "run away" combustion at high pressures.

Ignition and deflagration of these strands at low pressure levels differed from the results obtained earlier from slab burning studies where attempted ignition of the same formulation produced "no go's" at 600 and 800 psi, respectively. These differences were probably due to dissimilar experimental conditions such as the use of inhibitors on strands and none on slabs, or differences in the energy level of ignition techniques for the two methods.

A comparison of this strand data with that obtained from a standard eutectic formulation with 5 μ aluminum, but containing no fluxing additive, showed that at 1,000 psi there was no significant difference in burning rate: 0.6 in/sec without CaF_2; 0.7 in/sec with CaF_2.

At 1,600 psi, however, a big change was noted: 2.5 in/sec without CaF_2; 4.6 in/sec with CaF_2. In both instances, the pressure exponents were extremely high:

n = 3.68 at 800-1,400 psi (without CaF_2)

n = 4.04 at 600-1,650 psi (with CaF_2).

In several other strand burning test series, the same types of results were noted: relatively easy ignition (even at low pressures), apparent improved combustion (self-sustaining and less residue in the burner), but high pressure exponents (3.8 to 4.1 dependent upon test conditions, sample preparation, etc.). With pressure exponents this high and on the basis of motor firings with the standard aluminized eutectic, no grains containing CaF_2 were processed for motor firings.

PHASE V:　CLASS 2 MODIFIED AP-LP/Al POWDER

The high pressure exponents observed in strand burning tests and apparently verified in motor firings led to a study of modifications to the system which might result in exponents of less than unity.

Use of Metal Additives

The following powdered metals were incorporated, at the 5% level, in the standard aluminized eutectic composition:

1.　Magnesium,　-325 mesh

2.　Zirconium,　22 micron

3.　Zirconium,　5 micron

4.　Boron, crystalline, -100 mesh

Strand burning rate data were obtained from each lot.　Strands were burned at several pressures between 300 and 2,000 psi.　No significant reduction in the previously obtained slope (5% CaF_2, n = 4.04 at 600-1,650 psi) was attained with the first three metals listed.　The burning rate-pressure curves all fell within a narrow band.　The slopes obtained were 2.7, 2.6, and 2.1 for 22μ Zr, Mg and 5μ Zr, respectively.　Boron additive, however, reduced the slope to 0.86 at pressures below 1,000 psi. Above that pressure, the slope increased rapidly to 3.4.　An identical lot was prepared and the relatively low slope of approximately 0.84 was again confirmed.　Thus an indication was obtained that the slope could be lowered for the pressure range below 1,000 psi.

Other Investigations

As an extension of this work and in order to test other potential methods of pressure exponent reduction, the series of experiments described in Table 6 was conducted.　In this experiment the effects of such variables as changing heat transfer characteristics, utilization of additional fuel, use of metal additives at higher levels, utilization of fluxing agents, and removal of aluminum from the system was investigated.

Several of these techniques were eliminated on a processing basis as a result of problems noted in preparation of strands for burning rate and pressure exponent determination.　For those samples which were successfully processed and burned, the greatest changes in slope (and the only slopes of less than 1) were noted in formulations containing no aluminum powder.

TABLE 6. Experimental Investigation of Pressure Exponent
Reduction for the LP-AP System

Exp no.	Parts LP	Parts AP	Parts Al	Additive	Purpose
SS 1	46	24	30	C	Change heat transfer characteristics; provide additional fuel.
SS 2	46	24	30	Copper chromite	Change heat transfer characteristics, use r_b additive
SS 3	46	24	20	Zr	Test effect of Zr at higher content level.
SS 4	46	24	20	B	Test effect of B at higher content level.
SS 5	46	24	30	Na_3AlF_6	Test effect of cryolite (new fluxing agent).
SS 6	30	40	30	--	Higher AP content - lower LP content.
SS 7	30	40	30	CaF_2	Use of fluxing agent with higher AP content.
SS 8	30	24	30	HAP	Replacement of diluent LP with HAP (more fuel, energy).
SS 9	67	33	--	C	Removal of aluminum - change heat transfer.
SS 10	67	33	--	Teflon wool	Removal of aluminum - substitute reinforcement.
SS 11	67	33	--	Nylon chopped strands	Removal of aluminum - substitute reinforcement.
SS 12	67	33	--	Zr	Removal of aluminum - use of Zr.
SS 13	50	50	--	C	Removal of aluminum - higher AP content - heat transfer.
SS 14	40	50	10	C	Low Al content - added fuel - heat transfer.
SS 15	46	24	20	C Glass wool	Substitute reinforcement - added fuel - heat transfer.

Because removal of aluminum was the only method which gave an exponent substantially less than unity, a short additional series of tests was used to determine the maximum level of aluminum which could be tolerated. The consideration behind this effort was the requirement for about 30% aluminum in the overall formulation for optimum performance. As a possible compromise solution, the maximum amount of aluminum which still gives a useable pressure exponent would be retained in the solid phase and additional aluminum would be incorporated into the liquid phase which could then be injected as a slurry.

The new tests incorporated aluminum at the 0, 10, and 20% levels and also included carbon and/or calcium fluoride as combustion aids. Samples were prepared and burned as strands. Compositions and results were as follows:

Sample no.	LP	AP	Grams			r_b, in/sec 500 psi	r_b, in/sec 1,000 psi	Apparent pressure exponent
			Al	C	CaF_2			
SS 16	67	33	--	5.0	--	0.126	0.175	0.46
SS 17	67	33	--	2.5	--	0.115	0.154	0.42
SS 18	67	33	--	1.0	--	0.093	0.128	0.44
SS 19	60	30	10	5.0	--	0.130	0.234	0.82
SS 20	60	30	10	2.5	--	0.108	0.218	0.75
SS 21	60	30	10	1.0	--	0.109	0.178	0.71
SS 22	60	30	10	5.0	1.0	0.113	0.230	1.20
SS 23	60	30	10	2.5	1.0	0.103	0.220	1.10
SS 24	60	30	10	1.0	1.0	0.098	0.230	1.20

Consideration of the data from the complete series of experiments (SS 1-24) indicated the following trends. The powdered aluminum has a detrimental effect on the pressure exponent and can be utilized at a maximum level of about 10%. The addition of graphite to the system aids its combustion (burns faster and/or sustains burning better) and variation of weight level up to 5% does not influence the pressure exponent greatly. The use of calcium fluoride even at levels somewhat below 1% results in pressure exponents greater than unity.

As a result of this series of experiments and the previously described tests with metal additives, several potential formulations were now available with pressure exponents less than unity. No additional formulations or reduction techniques were investigated.

Process Development

A summary of the process development problems encountered with the various experimental investigations is given in Table 7.

TABLE 7. Processing Observations of Experimental
Investigations for Lowering Pressure Exponents

Sample no.	Observations
SS 1	Easily processed, strands darker than unmodified material
SS 2	Sparking observed at one point in process, otherwise easily made
SS 3	Severe settling problems with this much zirconium - impractical
SS 4	Mix too viscous to process - impractical
SS 5	Easily processed
SS 6	"Fume-off" - decomposition of AP evident
SS 7	Some AP decomposition evident - no knowledge of resultant formulation
SS 8	Not attempted - considered too hazardous for local operation
SS 9	Easily processed, some segregation of carbon noted
SS 10	Eutectic would not bond to Teflon wool - impractical
SS 11	Uniformity of reinforcement a severe problem
SS 12	Zirconium settling a severe problem
SS 13	Decomposition of AP
SS 14	Decomposition of AP
SS 15	Uniformity of reinforcement a severe problem
SS 16-24	Easily processed

In most cases, processing was attempted by local addition of the additives in the correct proportion to the nonmelted eutectic. For those formulations presenting processing problems, the attempt was also made to add the additive to the molten eutectic. No fires or accidental ignitions were observed except as noted in experiment SS 2.

PHASE VI: CLASS 2 MODIFIED AP-LP/Al POWDER/Al SCREEN

System Requirements and Properties

The solid propellant formulations discussed in Phase V which contained little or no aluminum powder presented these three major problems:

1. Inadequate physical properties because of the lack of aluminum reinforcement.

2. Slow burning rates probably because of the decreased heat transference.

3. Nonoptimized metal content of 0-10% as compared to the desired 30%.

A potential method of solving these three problems was the incorporation of aluminum screen in the grain. Since the matrix material was self-sustaining the grain would burn even with aluminum present in massive form (5 mil wire diameter). The screen therefore could serve as (1) a structural property reinforcement, (2) an agent to increase burning rate, and (3) additional aluminum fuel. Some support for the screen aiding in functions (1) and (2) had been derived from mechanical property tests involving eutectic containing aluminum screen, and from strand burning tests involving eutectic containing a combination of aluminum powder and screen.

The preliminary measure of mechanical properties of the aluminum screen eutectic system was obtained in a crude pull test with an Instron tester. In this test a sample consisting of a flat slab of 5 mil aluminum screen filled with the LP-AP eutectic was used. When the sample was gripped, some of the eutectic crumbled out and, during the test, failure occurred right at the end of the grip where the sample was deficient in eutectic. The value of maximum tensile strength obtained was >1,560 psi. This value was considered minimum.

Strands containing 5μ aluminum powder + 5 mil screen were burned in both regular and inverted fashion (ignition from below). The regular position burning rates of strands containing both screen and powder were two to three times faster than those for strands containing powder alone and burned in the regular position (see p. 27). The inverted position burning rates were approximately twice as fast as those of strands ignited from the top. The most probable explanation in each case was increased heat conduction caused by the presence of Al screen, and by the upward flow of hot gases over the unburned portion of the sample.

The following table gives the strand burning rate data as discussed in the preceding paragraph.

Strand Burning Rate Data - Oxidizer Eutectic
(LP/AP, 5 μ Al) containing 5 mil Al screen, 70°F

Normal		Inverted	
r_b, in/sec	Av pressure, psi	r_b, in/sec	Av pressure, psi
0.97	910	2.88	955
1.22	1,145	2.50	1,150
1.52	1,345	2.33	1,395
1.60	1,700	4.00	1,710
3.36	2,235	5.29	2,235

On the basis of these factors, two formulations were derived which could be processed for static firings to determine motor performance of the reduced pressure exponent propellants.

The new formulations were as follows:

Ingredient	Special formulation 1, % by weight	Special formulation 2, % by weight
Lithium perchlorate	45.9	46.8
Ammonium perchlorate	22.6	23.4
Carbon	3.5	2.0
Aluminum powder	----	10.0
Aluminum screen	28.0	20.0

Process Development

Processing of motors for these formulations was accomplished by using carpet-rolled aluminum screen as a structural skeleton. The screen used was 5 mil wire diameter (60 x 45 mesh size) type 1100.

The first technique attempted was a high temperature gravity casting. A casting assembly consisting of a motor liner, rolled screen, a flexible silicone room temperature vulcanizing (RTV) mandrel, a bottom capping plate, and a reservoir chamber (or riser), was heated in an oven at 415°F.

During the heating period, the matrix material formulation was prepared and melted. The grains were cast and the entire assembly returned to the hot oven for a 15 minute period to allow thorough seepage of the eutectic into the skeleton pores. The oven was then turned off and the grains allowed to solidify and cool slowly. This technique resulted in a small amount of decomposition of the eutectic. Because the solidification was not directional, void spaces were observed at several locations.

In subsequent series, the techniques were changed slightly in accordance with previous experience obtained while processing eutectic-aluminum powder grains. In the later series, the use of insulation around the reservoir, rapid cooling of the lower half of the mold, and the use of vibration during the period while the eutectic was still molten, resulted in greatly improved grains with good surfaces and a minimum of voids.

The grains were X-rayed and the loading fractions calculated. Sixteen of the best grains were selected for use in static test firings.

The X-ray examination showed the presence of fine voids in many of the grains but this was not considered a serious problem because of the combination of their small size and the apparent combustion mechanism for the eutectic-aluminum solid (combustion proceeds from a molten liquid layer of eutectic which coats the grain surface). The voids were apparently formed at points where individual ires from separate layers of screen came into contact closely enough to prevent thorough seepage of the molten eutectic into the screen pores.

Loading fractions were obtained for the grains by calculation of the theoretical weight of propellant which could be loaded into the grain volume and division of this number into the actual propellant weight. For most of the grains selected for firings, the loading fractions were in the 0.96-1.00 range.

Motor Firings

Prior to firing the grains as hybrid motors, it was decided to fire a few as solids in order to obtain preliminary information on ignition characteristics, approximate burning rates, and pressure exponent effect in the motor situation.

The first solid firing used a grain composed of special formulation 1 (strand burning pressure exponent = 0.46). The nozzle throat diameter used was 0.350 inch to give a calculated pressure of approximately 750 psi (strand burning rate ~0.150). The igniter used was 2.5 grams of magnesium-Teflon composition PL 6085 with a Mk 1 squib. As auxiliary ignition material, four 3/32-inch strands of magnesium-Teflon composition PL 6239 were cemented inside the grain perforation. Upon firing, the igniter material burned quickly and smoothly with a moderate pressure rise (peak pressure ~325 psi in 0.100 seconds). The pressure then dropped to a low level as the eutectic grain sputtered and burned slowly for a period of about 30 seconds.

The second firing used a grain composed of formulation 2 (strand burning pressure exponent = 0.75). The ignition system was the same as in the previous firing and the nozzle throat diameter was calculated to give approximately 500 psi. The firing results were much the same as in the first firing with a moderate pressure rise from the burning of igniter material followed by a long period of slow burning and sputtering of the eutectic grain. Near the end of burnout, a flame was visible at the nozzle exit and definite chuffing sounds were heard—indications that some burning was occurring in addition to the decomposition.

The third firing also utilized a grain of formulation 2. The nozzle was sized for a 750 psi chamber pressure and the ignition heat and pressure were increased by using a large auxiliary ignition grain cemented in the perforation. This grain was magnesium-Teflon in the shape of a cruciform and provided about 60 grams of material as compared to less than 10 grams in the previous two firings. This firing resulted in overpressurization and indicated that possibly over-ignition had occurred.

A number of additional test firings were made using a variety of ignition techniques. The results varied widely and are given in summary form in Table 8.

TABLE 8. Summary of Motor Firings of Solid Phase
Modified Eutectic Compositions

Test motor no.	Formu-lation	Nozzle size	Ignition technique	Results
1	1	0.350	Squib and 4 - 3/32 in. strands	Sputtered and burned slowly and inefficiently
2	2	0.400	Squib and 4 - 3/32 in. strands	Sputtered and burned slowly and inefficiently
3	2	0.350	Squib and 3 in. cruciform	Overpressurization
4	2	0.350	Squib and 8 - 3/32 in. strands	No ignition
5	2	0.350	Squib and 8 - 3/32 in. strands	No ignition
6	2	0.400	Squib and 3 in. cruciform	Detonation
7	1	0.350	Squib and 8 - 3/32 in. strands	Long, slow inefficient burn
8	1	0.350	Squib and 12-3/32 in. strands	No ignition
9	2	0.350	12-ft coil of resistance wire for hot wire ignition	Wire burn-through No ignition

It became apparent from these firings that an unusual combination of heat flux and igniter duration was required for the successful ignition of the modified eutectic formulations.

When propellant strands were used as auxiliary ignition material, insufficient ignition occurred; i.e., either no ignition at all or a delayed ignition which finally resulted in a long slow inefficient burn. It is significant to note that increasing the number of strands used decreased the ignition probability. A possible explanation is that increasing the number of strands increased the chamber pressure which, in turn, increased the burning rate of the strands and decreased the ignition duration. Tests 1 and 2 with four strands resulted in two "soft" ignitions in two attempts. Tests 4, 5, and 7 with eight strands resulted in one ignition for three attempts. Test 8 with twelve strands was unsuccessful. The strand material was completely consumed in all tests.

With a cruciform grain used as auxiliary ignition material, apparent over-ignition occurred. Test 3 resulted in overpressurization and motor failure when the nozzle shear assembly failed. Test 6 resulted in an actual detonation. The motor tube and nozzle body fragmented into shrapnel. In these cases the difficulties may involve grain breakup caused by the ignition shock, followed by rapid ignition and overpressurization.

Test 9, utilizing a hot wire type ignition, was unsuccessful because the resistant wire burned through prior to ignition. The cause may have been a short circuit caused by a bridge of molten eutectic.

Tests 1, 2, and 7 were unlike all previous tests in that combustion was "intermediate" to incomplete ignition or blow-up. Disassembly of motor parts and examination of the residue after the firings showed that extremely poor combustion efficiency had resulted. Although the burning had been self-sustaining, large globules of molten aluminum and decomposed eutectic had remained behind. There were several other indications of poor combustion efficiency. Throughout the duration of runs, the exhausts had been white and smoky indicating much unburned particulate matter; pressure traces never showed chamber pressures very much above atmospheric pressure; and chuffing sounds were frequently heard during the runs. Because of the combination of ignition difficulties and poor combustion efficiency, no hybrid firings were made.

Three additional solid firings were made in which a combination of higher heat flux and increased igniter duration was provided.

In one motor 2-1/4 inch magnesium-Teflon strands were cemented to the inside perforation. The higher heat resulted from approximately 3-4 times as much material as test motors 1 and 2 above. The increased duration resulted from the increased diameter of the strands and the application of inhibitor along the sides of the strands to mechanically restrict the rate of burning. This motor resulted in no ignition although burnout of the strand material was complete.

The other two motors used the same basic ignition scheme but three strands were used in one and four in the other. The motor with three strands ignited and burned slowly and inefficiently much in the manner of the previous successful ignitions. A white, smoky exhaust was observed with much particulate matter. Examination of the motor after firing showed large globules of aluminum and eutectic in a molten, decomposed state. The final motor (4 ignition strands) overpressurized on ignition.

FUEL SLURRY DEVELOPMENT

An auxiliary phase of this project was the investigation of the feasibility of using dense added-fuel in the hydrazine injectant. The theoretical advantages are quite striking and were shown in Table 1. A major problem encountered was that of crystal growth and recrystallization of triaminoguanidine (TAG) from solution on thermal cycling. Samples of N_2H_4, N_2H_4 - TAG slurry, N_2H_4 - TAG - 5 - aminotetrazole solution, and N_2H_4 - TAG - cellulose acetate (CA) gel were evaluated for thermal cycling properties. The results are shown in Table 9.

TABLE 9.   Results of Thermal Cycling Tests

Composition	Observation after 120 cycles[a]	Observation after 480 cycles[a]
N_2H_4 (99%)	No effect	No effect
N_2H_4 + TAG 50% slurry	No effect	Hard mass of crystals
N_2H_4 + TAG + AT solution	Some crystal formation	Increased crystal formation
N_2H_4 + TAG + CA gel	No effect	Porous crystals

[a]One cycle: 20-75°C at 12 minute periods.

It is significant to note the severity of these tests. The temperature extremes were 20 to 75°C, much greater than for a normal day's variation. The 120 cycle tests could be considered as equivalent to well over 4 months' storage, and the 480 cycle tests could be considered as equivalent to over 16 months' normal storage. The conclusion reached was that TAG does recrystallize from N_2H_4 whether in gel, slurry, or solution

form. However, it was also concluded that slurries and gels of TAG in N_2H_4 can indeed be made and used even though not on a long term storage basis.

DISCUSSION OF RESULTS

Description of problem areas and the attempts to solve them have been included in individual sections of the test. A few of the concepts will be discussed in more detail here.

Ignition Problems

Throughout the entire project, development of suitable ignition techniques was a continuing problem. Slab and strand burning tests, laboratory gas flame experiments, and motor firings all indicated unusual requirements of heat flux and igniter duration for successful ignition. The results from the laboratory gas flame ignitions and hot plate cook off of small samples would indicate that igniter duration is of extreme importance. The probable explanation lies in the marginal self-sustaining nature of aluminized eutectic during the early phase of burning (in lab tests, samples would sometimes be burning in a gas flame and then extinguish when the flame was removed). No completely satisfactory ignition technique was developed but several successful ignitions were achieved. Additional work of a more fundamental nature would be required in this area in a continuation of the project.

Combustion Mechanism and Problems - Solid Alone

Consideration of the results of strand and slab burning tests, DTA, motor firings, and principal thermal reactions of the aluminized eutectic system led to a crude combustion model of this system burning as a pyrotechnic as shown in Fig. 8.

The figure represents a simplified picture of the region close to the surface of the burning propellant. The AP-LP eutectic begins to melt at a depth below the surface where the temperature has reached approximately 200°C. Somewhat closer to the surface, where the temperature range is 300-400°C, ammonium perchlorate will decompose into gaseous products. In the temperature region of 450-500°C, the lithium perchlorate will decompose into lithium chloride and oxygen. Closer to the surface, where the temperature exceeds 600°C, the lithium chloride will melt, and finally the Al particles will melt at 660°C.
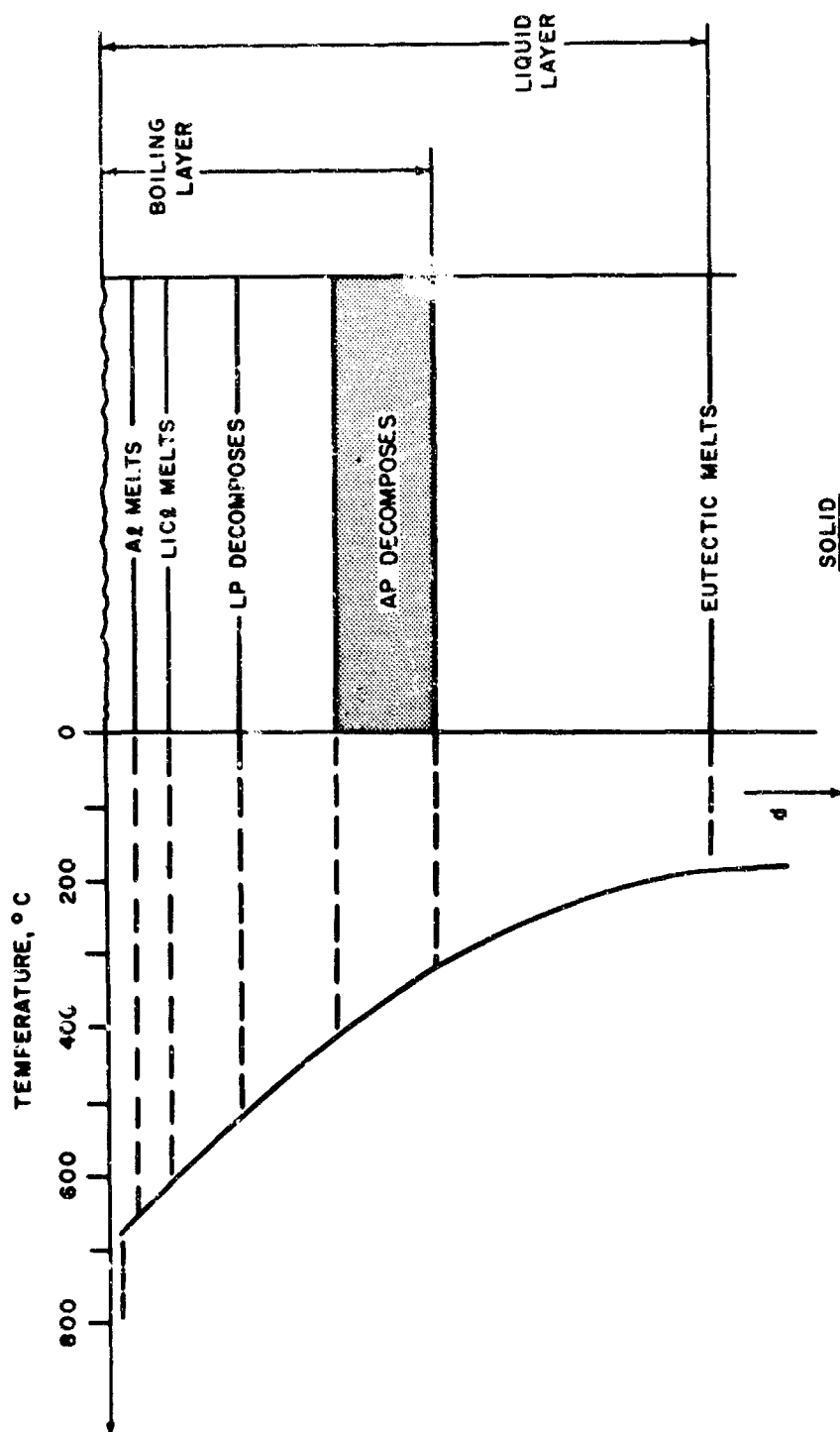
FIG. 8. Temperature vs Depth Schematic for Burring Aluminized AP/LP Eutectic.

The real picture is, of course, more complicated. The temperature gradient will be modified by endothermic melting processes and exothermic decomposition reactions. The vigorous gas evolution will tend to churn up and mix the various strata of the liquid layer and to project droplets of partly decomposed mixture into the gaseous combustion zone. The important factor of consideration is the existence of a liquid surface layer consisting of molten aluminum, lithium chloride, and partly decomposed eutectic, disturbed by vigorous bubbling of oxidizing gases formed in an underlying layer of the liquid.

It is generally recognized that it is difficult to ignite aluminum particles and that a fairly high temperature is required for ignition. This condition is met in solid propellants where the matrix surrounding the metal particles has a high flame temperature. However, in the case of the aluminized eutectic, the temperature of the gases from the deflagrating material is quite low. The flame temperature of pure ammonium perchlorate is approximately 930°C (Ref. 7). In the aluminized eutectic, 2/3 of the ammonium perchlorate has been replaced by lithium perchlorate. The LP must be considered as a diluent, since it decomposes into lithium chloride and oxygen with only small heat release (-6.7 kcal/mole) and since the oxygen generated cannot react with the already oxidizer-rich gases of the ammonium perchlorate. Whereas pure AP sustains burning under pressure, the AP/LP eutectic would not sustain burning in any tests conducted in this project. It therefore appears that the aluminized eutectic can only burn if the aluminum participates in the combustion, and as previously mentioned, a powerful ignition is required to achieve ignition of aluminum.

Another factor to be considered is the low volatility of the lithium chloride. The boiling point of LiCl is 1400°C at atmospheric pressure, and is estimated to be 2200°C at 1,000 psi. This means that, unless there is a very high surface temperature, or unless LiCl reacts to make more volatile components, the content of LiCl in the surface layer of the solid will increase during combustion. This will tend to slow down the combustion by diluting the other ingredients, by retaining the metal particles, and by acting as a barrier to heat transfer. If the amount of LiCl becomes sufficiently great, it will stop the combustion before all of the other ingredients are gasified or expelled and result in a serious loss in combustion efficiency.

These considerations point out the importance of heating rates for good combustion efficiency.

At low heating rates the temperature gradient through the solid grain will not be high and there will be a fairly deep layer of liquid at the surface. Because of the long stay time, the molten metal may tend to agglomerate at the surface and to be released in large droplets that will burn slowly, if at all. The combustion zone will move further away from the surface and

reduce the feedback of heat to the surface. If the heating rate is suffi-
ciently low, the eutectic will gasify without entraining the metal and
leave behind a mixture of molten aluminum and lithium chloride. This
behavior was observed in many of the motor firings where the ignition
system was the principal heat source. In addition, because the relatively
deep layer of liquid formed at low heating rates is susceptible to erosion
by gas flow parallel to the surface, a mixture of metal and partly decom-
posed eutectic can accumulate at the rear end of the motor or be washed
out of the nozzle. The behavior was also observed in several static
firing attempts.

At high heating rates, the temperature gradient of the solid will be
steep and the liquid layer at the surface will be thin. The gasification
may be sufficiently rapid to make possible the release of individual metal
particles from the surface before they have had time to agglomerate.
The small particles would burn rapidly in the high local concentration of
oxidizing gases and a high temperature flame front could be established
close to the surface. This might permit sufficiently effective feedback
of heat to the surface to maintain the high temperature gradient, and
the high rates of gasification and particle release, thus establishing steady
state conditions.

Films of burning strands of aluminized eutectic taken at various
pressures tend to confirm the existence of such different combustion
regimes. At pressures of 1,100-1,400 psi the combustion was observed
to be irregular and droplets of a burning mixture were ejected. At
higher pressures (1,500-1,800 psi) the combustion was more regular,
the flame front was closer to the surface, the surface was calm, there
was no ejection of burning droplets, and there was a smaller scatter of
the burning rate data.

Good steady state combustion of the solid in motor firings was not
achieved in this program and the results of all the tests performed indi-
cate that it would be an extremely difficult accomplishment. The values
of heating rates, temperature gradients, and chamber pressures required
for successful operation apparently cover a quite narrow range below
which, low efficiency and incomplete burns result, and above which, over-
pressurization or detonation occurs.

Combustion Problems - Hybrid System

With the addition of hydrazine to the aluminized eutectic system
some new factors must be considered. Assuming equilibrium conditions,
complete oxidation of the aluminum would utilize about 3/4 of the oxygen
available from the deflagration of the eutectic. If the rest of the oxygen
reacted with the hydrazine, a little less than 1/2 of the hydrogen in the
hydrazine would be consumed. The remainder would be available as working
fluid.

However, in the practical situation, the excess hydrogen would probably compete with the aluminum for the available oxygen. Under these conditions there would be a loss in overall heat release, since the heat of hydrogen-oxygen reaction is less than half of the heat of the aluminum-oxygen reaction, on an oxygen equivalence basis. If equilibrium conditions were reached, the unreacted Al would subsequently have to react with water vapor, but it is probable that the chamber residence time would be insufficient to complete this reaction. Furthermore, this reaction would also tend to extend the combustion zone away from the grain surface and reduce feedback of heat to the surface.

The net effect of these considerations is that the presence of hydrazine would adversely affect the combustion of the solid. In the static firings conducted with hydrazine there was evidence to this effect even in those cases where the hydrazine was successfully ignited. In some firings, the hydrazine immediately extinguished the solid combustion; in others, there was a finite period of hydrazine monopropellant operation followed by extinguishment.

The most promising line to follow seemed to be to try to establish effective combustion of the solid phase as a monopropellant in such a way that injection of the liquid phase would not interfere with the primary combustion of the solid phase. A logical extension of this concept would be to consider the solid phase as the main energy source and the liquid phase primarily as a working fluid.

CONCLUSIONS

The following conclusions have been derived from the work.

1. The oxidizer eutectic/metal/hydrazine fuel systems are promising as highly energetic hybrid propellant systems according to theoretical performance calculations. The use of dense fuel additives to the liquid increase the theoretical performance.

2. The most promising system, from the standpoint of processability and hazard presented, was the LP-AP/Al hydrazine fuel slurry.

3. Hydrazine fuel slurries with TAG can be processed and used, although perhaps not on a long term storage basis.

4. Binderless solid formulations have good stress/modulus mechanical properties, but very poor elongation.

5. Aluminum powder alone is a substantial reinforcement agent for mechanical properties in this type of system.

6. Binderless solid formulations can be processed successfully without undue hazard. Carbonaceous fuel additives increase the hazard level.

7. The ignition and combustion characteristics of the LP-AP/Al solid can be modified by the use of additives. Differential Thermal Analysis was found to be a useful tool for the screening of such additives.

8. The solid phase burned satisfactorily in pressure bombs. Strand burning tests indicated pressure exponents greater than unity for most formulations.

9. Pressure exponents of less than unity in the solid phase were achieved in strand burning tests by the addition of carbonaceous fuel and the reduction of aluminum powder content in the basic system.

10. The solid phase did not burn satisfactorily in rocket motors with this system. Two types of combustion regimes were observed with the basic system: (a) slow, extremely inefficient burning and/or decomposition, and (b) overpressurization with blow-up or detonation.

11. In motor firings with modified systems, the same general types of combustion regimes described above were observed. It is probable that a greater increase in fuel content or decrease in aluminum content is required for satisfactory combustion in the motor environment than in pressure bombs.

12. The differences in pressure bomb and motor behavior for this system is apparently attributable to a great sensitiveness of this system to environmental differences such as static versus dynamic flow conditions and heat transfer.

13. Further increases in fuel content or decreases in aluminum content would defeat the purpose and concept of binderless systems and seriously decrease the theoretical potential of the system.

14. Injection of liquid hydrazine in some rocket motors appeared to impair the combustion of the solid.

15. The most likely method of making this a workable system in motors would be to establish efficient, stable pyrotechnic burning of the solid phase based upon the concept of the solid as the primary energy source and the liquid phase as a working fluid source

16. Stable, efficient pyrotechnic burning required of the solid phase in motors was not achieved in this study and in order to do so, an xtensive research and development effort would be required.

On the basis of the above conclusions, and primarily because of the great problems encountered in the attempts to produce good motor combustion characteristics, work on binderless oxidizer/metal hydrazine fuel slurry hybrid systems was terminated.

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and experimentally for their suitability as high per-
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theoretically to a propellant with a measured density of 1.92 g/cm^3 and a measured specific impulse of 260 lb-sec/lb. A binderless system comprised of a solid phase of ammonium perchlorate-lithium perchlorate eutectic, reinforced with aluminum metal, was selected for scale-up and development. The liquid phase of the system was hydrazine or a slurry of added fuel in hydrazine. The results of investigations in the areas of combustion research, safety and compatibility studies, process development, ignition, motor firings, and fuel slurry development are reported.

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