7

**APCO** ACCESSORY PRODUCTS CO
12484 E. WHITTIER BLVD. WHITTIER, CALIF. 90602 A Textron CO
FLUID CONTROL: SYSTEMS · COMPONENTS

# FLIGHT AND EXPERIMENTAL EXPULSION BLADDERS
# FOR
# MARINER 69

APCO Project Number 764400
JPL Contract No. 951939
Final Report

FACILITY FORM 602

| | |
|---|---|
| N70-14831<br>(ACCESSION NUMBER) | (THRU) |
| 40<br>(PAGES) | 1<br>(CODE) |
| CR-107435<br>(NASA CR OR TMX OR AD NUMBER) | 18<br>(CATEGORY) |

JAN 1970
RECEIVED
NASA STI FACILITY
INPUT BRANCH

PREPARED BY:
John Repar
Rubber Technologist

CONCURRED BY:
John E. Shaw
Project Manager

July 17, 1969

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.

JF11C

# NOTICE

Requests for copies of this report should be referred to:

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Washington 25, D. C.

Attention: AFSS-A

# ABSTRACT

The procedures which were employed in the preparation of hydrazine expulsion bladders for Mariner 69 are described. These were prepared from a butyl rubber compound. A matched aluminum mold with soluble aluminum cores was employed. The process resulted in seamless one-piece bladders.

A compounding study for improving the compatibility and permeability of ethylene propylene copolymer and terpolymers with hydrazine was conducted. It was shown that the choice of inert fillers, such as hydrated silica and clay, caused much less hydrazine decomposition than the employment of carbon black. Some of the permeation data were also extremely low. The hydrazine immersion was conducted at 125°F.

Experimental bladders were produced from one of the compounds which was selected as having the best balance of properties for hydrazine service. Both molding and core dissolution with Compound 10 presented more difficult problems than were encountered with the butyl. The core dissolution procedure was not completely resolved at the end of the program.

Molding of diaphragms, as opposed to bladders, can be accomplished with relative ease with either butyl or ethylene propylene compounds.

# TABLE OF CONTENTS

Page No.

I. Summary 1

II. Introduction 2

III. Technical Discussion 4

A. General 4

B. Compound Development 4

C. Bladder Fabrication Development for Mariner 69 12

D. Production of Bladders for Mariner 69 15

E. Bladder Fabrication from Compound 5 16

F. Bladder Fabrication from Compound 10 17

IV. Conclusions 20

A. Compound Development 20

B. Bladder Fabrication 22

V. Recommendations 24

# LIST OF TABLES

| Table | | Page No. |
|---|---|---|
| I | Compression Set after 7 Days @ 158°F | 7 |
| II | Compatibility with Hydrazine @ 125°F | 8 |
| III | Hydrazine Permeation at Room Temperature | 10 |
| IV | Weight Increases after Hydrazine Immersion @Room Temperature, % | 11 |
| V | Weight Increases of Permeation Test Samples, % | 11 |
| VI | Mold Release Efficiency | 17 |
| VII | Compounding Goals and Attainment | 21 |
| VIII | Compounds | 27 |
| IX | Physical Properties | 28 |
| X | Compound 1 | 29 |
| XI | Compound 2 | 29 |
| XII | Compound 3 | 29 |
| XIII | Compound 4 | 30 |
| XIV | Compound 5 | 30 |
| XV | Compound 6 | 30 |
| XVI | Compound 7 | 31 |
| XVII | Compound 8 | 31 |
| XVIII | Compound 9 | 31 |
| XIX | Compound 10 | 32 |
| XX | Compound FR 6-60-26 | 32 |
| XXI | Molding Record, Compound FR 6-60-26 | 33 |

# LIST OF FIGURES

| | | Page No. |
|---|---|---|
| Figure I | Bladder, Propellant Tank | 34 |
| Figure II | Core Assembly | 35 |

# I. SUMMARY

The need for improved rubber compositions for service in hydrazine as the operational temperature requirements has been increased to 125°F prompted the initiation of a rubber compound development program. All of the proposed compounds were based on ethylene propylene copolymer or terpolymers.

The main effort was directed toward a reduction of hydrazine decomposition. Four compounds, two each based on the copolymer and terpolymer showed a significant improvement over previously qualified compounds. Compounds 8 and 10 were terminated after 135 days of hydrazine immersion. They were restarted and exposed again an additional 328 days before termination, thus suggesting the efficacy of passivation.

There was also an anomaly in which low permeability was accompanied by relatively high hydrazine adsorption. The permeability of Compound 9 was undetectable after one month of exposure while the weight increase after two weeks was 23 percent.

The technique for producing seamless bladders consisted of molding with matched tooling and hollow aluminum cores. The cores were dissolved with caustic solutions.

Bladders were produced for Mariner 69 from Butyl Compound FR 6-60-26. In addition, bladders were also produced from Compound 10, which is based on ethylene propylene terpolymer. The former were produced satisfactorily but the latter presented problems which were not completely resolved at the end of the program.

## II. INTRODUCTION

The use of bladders and diaphragms for the control of liquids in positive expulsion systems, which operate in a zero gravity environment, has been a common practice for many years. The compatibility of flexible materials which come in contact with the fluid has commanded considerable attention.

Hydrazine has presented difficulties which become more severe as exposure times and temperatures are increased. One of the main problems has been hydrazine decomposition. It is spontaneous, to a degree, since control tests which contain no samples also exhibit some decomposition.

There is a wide variation between various materials as effective catalysts. Rubber compounds have caused hydrazine decomposition which has been of sufficient magnitude to be considered undesireable.

The program described in this report was directed toward the development of rubber compositions which would contribute low hydrazine decomposition. Other desireable properties which would make them suitable for use in expulsion bladders include, low permeation to hydrazine and low compression set. Tensile strength, elongation, and Shore hardness values had to be suitable for diaphragm and bladder applications.

The program included the development of a molding technique for producing seamless bladders.

Any one of several techniques might have been employed. But since an O-ring was an integral part to be molded, and since most O-ring sealing elements are molded, it was logical to assume that molding was the optimum technique for making the Mariner 69 seamless bladder. The main problems with the molding technique have been selection of the core material, design and fabrication of a suitable core assembly and removal of the core from a molded bladder.

The approach in this program was to use hollow aluminum cores for light weight as well as to reduce the dissolution time. The cores had to be thick enough so that dimensional stability could be maintained during the molding operation.

Caustic solutions were employed for the dissolution of the cores. These required some study with respect to concentrations, temperatures, and flow rates.

## III. TECHNICAL DISCUSSION

### A. General

The program was conducted in three phases as follows:

A. Compound Development

B. Bladder Fabrication Development

C. Production of Bladders

Pressure rise and permeation tests during hydrazine immersion were conducted by the Jet Propulsion Laboratory.

A mold which was used in preparing experimental expulsion bladders for Mariner 64 was employed in order to produce bladders which were single piece and seamless. The mold and hollow cores were made from aluminum alloy 6061T6.

Figures I and II depict the bladder and core, respectively. The female portion of the mold is conventional in construction and is not shown.

### B. Compound Development

All compounding ingredients are available commercially. The batch size was approximately 1-1/2 pounds. All compounds were Banbury mixed initially in accordance with the following procedure:

| | Operation | Elapsed Time, Minutes |
|---|---|---|
| a. | Add Polymer to Banbury | 0 |
| b. | Add 1/2 of filler(s) | .5 |
| c. | Add balance of filler(s) | 2.0 |
| d. | Remove from Banbury | 5.0 |
| e. | Place on mill | Not Applicable |
| f. | Add vulcanizing agents and blend | 5 (after Step e) |

All experimental compounds in the program were based on ethylene propylene, copolymer and terpolymers.

Standard ASTM slabs and compression set buttons were molded from each compound.

A minimum of three cure times was selected. In several cases additional air oven post cures were employed.

Cure conditions for test samples were selected on the basis of minimum elongation and maximum modulus.

Ten compounds were formulated as shown in Table VIII. Compound 1 is EPR 132 which was developed by the Reaction Motors Division of the Thiokol Corporation. The first four compounds contained HAF carbon black as a filler while the remaining six contained Icecap KE clay, Silene D, or a mixture of both.

The following polymers were included in the program:

| | |
|---|---|
| Nordel 1320 | Dupont |
| Nordel 1440 | Dupont |
| Vistalon 404 | Enjay |
| Vistalon 3509 | Enjay |
| Royalene 301 | U.S. Rubber |

As expected, non-black fillers gave lower tensile strengths (950 to 1700 psi) generally although Royalene 301 Compounds 9 and 10 compared favorably with Compound 1 (1800psi). Elongations did not exhibit any particular trend (180 to 420%).

The hardness values of compounds from terpolymers were generally higher than those from copolymer Vistalon 404 with comparable filler loading.

Curing systems included peroxide, resin and sulfur cures. Peroxide cures gave the best compression set values with Royalene 301 compound 9 having the lowest value, 7.4 percent. It should be noted that tests were conducted for 7 days at 158°F rather than the usual 22 hours. Data is summarized in Table I.

## Table I

### Compression Set after 7 Days @ 158°F

| Compound No. | Peroxide Cure | Resin Cure | Sulfur Cure |
|---|---|---|---|
| 1 | 19.2 | | |
| 2 | 10.7 | | |
| 3 | | | 18.0 |
| 4 | | 24.2 | |
| 5 | 12.2 | | |
| 6 | 22.1 | | |
| 7 | | 18.8 | |
| 8 | | | 35.8 |
| 9 | 7.4 | | |
| 10 | | | 27.6 |

Data at selected cures are shown in Table IX while complete data from each compound appear in Tables X through XIX.

Compound 10, with which the most work was accomplished, had a sulfur bloom. It did not reappear after hydrazine immersion.

Hydrazine immersion tests were conducted at the Jet Propulsion Laboratory. The test for compatibility was accomplished by determining pressure rise. It consisted basically of encapsulating the hydrazine and test sample in a glass container to which a pressure gauge was attached. The temperature was 125°F. The test method is described in Reference 2. Tests were terminated before the pressure rose to fifty pounds per square inch. The data is summarized in Table II.

## Table II

### Compatibility with Hydrazine @ 125°F

| Compound | Days to Termination | Pressure after 60 days, psi |
|---|---|---|
| Fargo FR6-60-26 | 29 | -- |
| Parker E515-8 | 17 | -- |
| Stillman SR722-70 | 23 | -- |
| 1 | 28 | -- |
| 2 | 23 | -- |
| 3 | 4 | -- |
| 4 | 4 | -- |
| 5 | -- | 17 |
| 6 | 110 | 30 |
| 7 | 13 | -- |
| 8 | 135* | 14 |
| 9 | 20 | -- |
| 10 | 135* | 6 |
| Blank | -- | 4.5 |

*Restarted and run for an additional 328 days before termination.

All of the compounds which contained carbon black were terminated prior to 30 days. Interestingly, the four compounds which were still under test after 60 days had a wide range of characteristics. Compounds 5 and 6 are based on peroxide cured copolymers while compounds 8 and 10 are sulfur cured terpolymers. The performance of Compounds 7 and 9 is not readily explicable; the presence of contamination in the rubber is a possibility.

It should be noted that compounding with fillers other than carbon black arose from the fact that hydrazine decomposition products consist only of hydrogen, nitrogen, and ammonia. Therefore, it was assumed that the decomposition was due to the presence of catalysts. Since the filler comprises a major fraction of most rubber compounds, it was suspected that the effect from a large amount of filler would mask that of minute residual quantities of vulcanizing agents such as sulfur.

The use of plasticizers and other additives was avoided in order to minimize contamination of hydrazine by leaching and also to limit the number of possible reactions with hydrazine to a minimum. Passivation was effective since Compounds 8 and 10 which were terminated at 135 days, were reimmersed and went for 328 days before termination.

The hydrazine permeation tests were conducted in accordance with Reference 3. The test sample has a permeation area of one square inch. The hydrazine which permeated was collected and titrated for qualitative determinations. The weight change test was performed with the use of weighing bottles since hydrazine is quite volatile.

A very interesting phenomenon was the association of low permeation with high hydrazine adsorption. The hydrated silica and clay fillers appeared to have a high affinity to hydrazine while simultaneously showing excellent compatibility. Compound 9, for example, had a weight gain of 22.91% after 286.5 hours and yet had no detectable permeation at the end of 759.25 hours of exposure. Conversely, Compound 8 had a weight increase of only 4.95% while the permeation test was discontinued at 140.75 hours when the rate had already risen to .334 milligrams per square inch per hour. The weight increases were approximately linear from 70 to 286.5 hours of hydrazine immersion. The test samples which were employed in permeation determinations were also weighed. In comparing the results of weight increases in Tables IV and V, it is evident that the values are much lower in Table V. This is due to the fact that hydrazine is in contact with one side of the sample only in permeation tests, while the entire sample is immersed during weight increases determinations.

The samples for permeation tests ranged in thickness from 0.052 to 0.067 inches which was similar to the thickness of the bladders.

Table III

Hydrazine Permeation at Room Temperature

| Compound No. | First Measurable Permeation, Hrs. | $Mg/in^2/Hr.$ After 759.25 Hrs. |
|---|---|---|
| 5 | 90.5 | .015 |
| 6 | 593.25 | .014 |
| 7 | 412.25 | .032 |
| 8 | 68.5 | .334* |
| 9 | --- | 0 |
| 10 | 593.25 | .022 |

*Terminated at 140.5 hours.

ORIGINAL PAGE IS
OF POOR QUALITY

## Table IV

### Weight Increases
### After Hydrazine Immersion @ Room Temperature, %

| Compound No. | 70 Hrs. | 167 Hrs. | 286.5 Hrs. |
|---|---|---|---|
| 5 | 1.09 | 1.73 | 2.04 |
| 6 | 5.10 | 8.81 | 12.91 |
| 7 | 7.75 | 12.79 | 18.01 |
| 8 | 6.66 | 5.20 | 4.95 |
| 9 | 8.35 | 15.15 | 22.91 |
| 10 | 7.66 | 11.73 | 16.85 |

## Table V

### Weight Increases
### of
### Permeation Test Samples, %

| Compound No. | After 759.25 Hours @ Room Temperature |
|---|---|
| 5 | 0.53 |
| 6 | 4.59 |
| 7 | 6.40 |
| 8 | 3.87 |
| 9 | 7.65 |
| 10 | 5.70 |

## C. Bladder Fabrication Development for Mariner 69

Fargo Rubber compound FR6-60-26 was employed in flight bladders for Mariner 69, based on previous qualification for Mariner 64.

The mold and cores were made from Aluminum Alloy 6061T6. The female half of the mold was conventional with guide pins and flash grooves. The cores, however, were hollow and machined to match the female half of the mold. They were made as two hemispheres which slide together in a precision fit. The assembly as shown in Figure II had a steel insert. The insert could be disassembled by rotating the outer portion until the nut loosened and thus permitted two halves of a split washer to fall There was clearance to pull out the insert and shake out the split washer. The insert had a hole through the center which acted as a vent.

The centerline of the mold was the same as that of the core as shown in Figure II. This position of the parting line permitted accurate molding of the critical O-ring seal member. The main difficulty was the tearing of bladders or ribs near the parting line during bladder and core extraction following completion of the molding cycle.

The rubber was milled out to a thin sheet (.04 inches thick) and placed on the core at room temperature. The entire core was covered evenly. Additional strips were placed on what would become the top and bottom during molding in order to adjust the amount of rubber present by weight.

The female portion of the mold was cooled below 300°F for loading. The covered core was placed in the preheated lower mold cavity and the upper half fitted over it. The assembly was then placed in the hot press and pressure applied. Cure time commenced when the mold reached 305°F. Cure temperatures ranged from 305°F to 330°F. The core and bladder were extracted from the mold after completion of the molding cycle. A water emulsion of DC6 Silicone mold release was employed and no difficulties were encountered in removing the core from the mold.

The bladder was trimmed, visually inspected again, and leak tested while still on the core. The O-ring section was the most critical. Subsequently, the mold was reworked slightly in order to improve the parting line on the O-ring.

If a defect was visible, the rubber was removed and the core was reused in a subsequent molding cycle.

Ten heats were run in order to establish bladder fabrication procedures from Fargo Rubber Compound FR6-60-26. Five bladders passed leak tests successfully and three of the aluminum cores were dissolved. A record of these ten heats is given in Table XVIII.

All exterior surfaces could be inspected visually while the bladder was on the core. The O-ring section could be examined in its entirety. Air bubbles could be detected readily. Wall thickness could not be measured too well but scrap bladders were measured and found to be within print tolerances.

The initial leak test while the bladder was on the core was accomplished without difficulty.

The aluminum core was dissolved by pumping a 10% solution (by weight) of Aluminux into it at 120°F and a flow rate of one gallon per minute. Aluminux is a sodium hydroxide base which contains chelating agents. Completion of core dissolution was apparent with the cessation of hydrogen evolution.

Core dissolution progressed satisfactorily until pump failure occurred. Dryout of precipitates on the bladder surfaces presented considerable difficulty during cleaning operations. It was necessary to evert the bladders in order to reach all interior surfaces. The process of eversion caused damage to the ends of several ribs and was eliminated during the later production phase. Bladders were leak-tested by pressurizing with air to 1 psi and submerging in water for three minutes. No evidence of leakage was allowed.

Bladders were washed with a 1% solution of Basic H solution after core dissolution. Deposits from core dissolution were removed by scrubbing with a nylon brush and liquid honing. Final cleaning consisted of washing with a 1% solution of Basic H followed by a rinse with deionized water.

## D. Production of Bladders for Mariner 69

The fabrication and processing procedures which were developed under the previous section were employed in the production of bladders from Fargo Rubber Tutyl Compound FR-6-60-26. Physical properties of the batches are given in Table XV.

Difficulties in sheeting the rubber to the desired thickness and free from air bubbles initially caused considerable rejections in the production run. The incidence of air bubbles in a scrap part usually consisted of only one or two. There was no pattern with respect to location of the bubbles.

The core dissolution procedure was expanded in order to include provisions for pump failure. Basically, the bladder was completely submerged in either Aluminux solution or water until the core was dissolved. This minimized deposition of precipitate on the bladder surface and simplified cleaning. It was possible to eliminate eversion from the cleaning process and thus reduced the possibility of damaging bladders.

Forty-seven heats were run in order to produce eight bladders.

The bladders were maintained in the molded configuration during storage and shipment.

## E. Bladder Fabrication from Compound 5

Nine heats were run in efforts to produce bladders. Three bladders were submitted for further processing but failed leak tests.

Four of the remaining bladders were torn during removal and the remaining two had excessive backrind. This is an extremely rough condition at the parting line which cannot be trimmed satisfactorily. The compound had satisfactory molding characteristics as far as flow and molded appearance were concerned. Knitting was not as good as that of most butyl compounds. The undercut position of the ribs at both ends of the bladder was the major cause of rupture. Cooling of the mold to 200°F or less before attempting extraction was tried but no bladder with satisfactory characteristics was produced.

The loading of sheeted compound on the core was considerably more difficult with Compound 5 as compared to Butyl. It has very little surface tackiness and therefore the preform tended to disassemble.

## F. Bladder Fabrication from Compound 10

Twenty-five heats were run in order to produce six bladders from Compound 10. As in the case of Compound 5, the loading of the mold with thin sheets of material was complicated by the lack of tackiness. The molding characteristics of this compound are generally good.

During early heats, tearing of the ribs was experienced; therefore, the mold was reworked so that the ends of the ribs were radiused. There was also incidence of ruptures due to mold adhesion which initiated a mold release study. Data is summarized in Table VI.

Table VI

Mold Release Efficiency

| Surface | Rating |
|---|---|
| * Lubeco MR-98 | Excellent |
| ** Microseal 200-1 | Good |
| ** Microseal 100-1 | Good |
| * Lubeco 7046 | Good |
| Silicone Spray | Fair |
| Mica Dust | Poor |
| Fluorocarbon Spray | Poor |

*Lubeco, 1322 S. Alameda, Compton, California, 90221
**Microseal Corporation, 16322 S. Figueroa, Gardena, Calif. 90247

Since the mold is made of aluminum, Microseal 200-1 was selected as the safest compromise coating to apply. Lubeco Coating MR-98 was superior but required a temperature of 500°F during application as compared to 350°F for the 200-1. Lubeco MR-98 should be ideal for steel molds.

Spray type lubricants were not sufficiently effective to be used alone. The lubricant on the core of the mold tended to gather at the parting line and caused flow lines on the interior of the bladders.

In addition to lubrication, it was necessary to cool the mold below 200°F while the mold was still under hydraulic pressure in order to extract the bladders from the mold satisfactorily.

It should be mentioned that Compound 10 tends to adhere to the mold more severely with each successive molding cycle despite cleaning of the mold with either methyl ethyl ketone or toluene if bare metal is employed.

Weight control of the stock prep was employed during the entire program. Even though the aluminum shells which comprise the cores were of substantial thickness (3/8"), they would still distort when uneven loads were imposed.

The molding procedure which produced satisfactory bladders from Compound 10 consisted of the following steps:

a. Load mold at 250°F.
b. Raise hydraulic pressure to desired level in seven equal steps at one minute intervals (up to 300 tons).
c. Hold at working hydraulic pressure for a minimum of 15 minutes or until stock ceases flowing.
d. Raise temperature to curing level (320°F).
e. Hold at cure temperature for one hour.
f. Cool mold to 200°F or less with working hydraulic pressure applied.
g. Release hydraulic pressure and open mold <u>slowly</u>.

Leak testing, trimming, and inspection presented no problems.

The core dissolution procedure required further study and revision. It was found that Aluminux at 10% concentrations were injurious to Compound 10, causing surface degradation. Heavy deposits of Aluminum oxide adhered tenaciously to the surface. After a short study, the procedure which evolved consisted of the following steps:

a. Prepare a solution of sodium hydroxide with a 2.5% concentration.
b. Adjust the temperature to 110 ±10°F.
c. Add bladder and core.
d. Commence pumping at the rate of one gallon per minute.
e. Change solution after two days.
f. Continue dissolution until hydrogen evolution ceases.

Approximately 15 days were required to complete the core dissolution. Despite the decrease in concentration and temperature, the core dissolution continued to be cause for concern.

There was a discoloration of the rubber and one of the bladders developed localized blisters during the post cure period.

## IV. CONCLUSIONS

### A. Compound Development

Data indicates that both ethylene propylene copolymers and terpolymers may be compounded for service in hydrazine. Fillers which are considered inert in this work showed an improvement over carbon black with respect to hydrazine decomposition. Hydrazine permeation was found to be low while weight increase in some cases were high.

Although the compression set data of compounds which showed up best in hydrazine decomposition tests were not among the lowest, they were not so high as to preclude satisfactory O-ring sealing.

In comparing the physical properties of Compounds 5, 6, 8, and 10, Compound 10 has the best balance of properties for bladder applications; next would be Compound 5, 6, and 8, respectively.

The following table shows the aims of compound development and the degree of achievement. The pressure rise of Compound 10 (6 psi) when compared with the blank (4.5 psi in 60 days) indicates that the pressure rise criteria has been met. This was the primary effort in the compounding program.

## Table VII

## Compounding Goals and Attainment

| Criteria | Desired | Actual | | | |
|---|---|---|---|---|---|
| | | 5 | 6 | 8 | 10 |
| 1. Permeability, mg/in2/hr | 001 | * | * | * | * |
| 2. Compatibility, psi rise in 60 days | 2 | 17 | 30 | 14 | 6 |
| 3. Elongation, % | 325 ±25 | 190 | 300 | 420 | 360 |
| 4. Tensile Strength, psi | 3000 | 1300 | 1050 | 950 | 1600 |
| 5. Shore A Hardness | 75 ±5 | 65 | 57 | 79 | 79 |
| 6. Compression Set, % | 20 max | 12.2 | 22.1 | 35.8 | 27.6 |

*See Table III, Page 10.

## B. Bladder Fabrication

Molding, in accordance with the procedures which were employed in this program, produced bladders of high quality and required no extensions of existing print tolerances. The techniques are applicable to bladders of 11 inches or less in diameter without qualification. Bladders of larger size can certainly be fabricated but the upper limit in size is not immediately obvious. Bladders which are 20 inches in diameter should be feasible. Shapes which are other than spherical are similarly possible.

The molding technique offers several advantages. Among these are wall thickness control (whether constant thickness or tapered), precision molding of sealing elements and incorporation of continuous or segmented ribs.

The processes of trimming and leak test are satisfactory.

Inspection techniques of bladders on cores permits visual evaluation of slightly over 50% of the surface area with the O-ring sealing section being entirely exposed. The hazard exists that an internal flaw may be present in the bladder which will not be detected until the core is dissolved. The cores are relatively expensive and, therefore, should only be dissolved when assurance of a suitable bladder has been ascertained.

The core dissolution presented virtually no problem with the Butyl compound. However, Compound 10 was much more sensitive and required a revision of the procedure in order to include lower temperatures and concentrations of caustic in order to achieve slower reactions and closer controls. Even then, results were not entirely satisfactory as evidenced by discoloration and blistering of Compound 10.

## V. RECOMMENDATIONS

Since the pressure rise data shows a considerable improvement when inert fillers, rather than carbon blacks, are employed, the prospects of compounding Butyl rubber for low hydrazine decomposition appears particularly attractive and should be pursued. Butyl rubbers are well known for lower permeation to gases than ethylene propylene rubbers and, therefore, continue to be considered where exposure to hydrazine and gases is required.

Vango of the Jet Propulsion Laboratory has suggested varying the filter level in order to study the permeation and weight changes in greater detail.

Since passivation by presoak in hydrazine was found to be effective, it should be optimized.

Additional properties such as tensile strength, elongation, modulus, hardness, and volume swell should be studied during hydrazine immersion tests.

Bladders are much more difficult to produce than diaphragms; therefore, compounds which look promising should be evaluated in the diaphragm configuration prior to seamless bladder fabrication. JPL tooling is available for this purpose.

It is likely that cores can be constructed which are capable of disassembly. This is primarily a design problem of obtaining dimensional stability during application of the molding pressure.

Radiographic evaluation of the internal cleanliness of rubber compositions is sensitive enough to detect particles as small as .005" in diameter. One of the most common types of contamination is metal particles. It is recommended that radiographic analysis be incorporated in future work in order to check homogeneity of test samples and also to provide a tool for measuring cleanliness of finished products.

## REFERENCES

1. N. B. Levine, H. Krainman, and J. Green, *Positive Expulsion Bladders for Storable Propellants*, AFML-TR-65-379, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, January 1966.

2. S. P. Vango, *Technique of Evaluating Bladder Materials Suitable for Possible Use with Hydrazine*, Space Programs Summary 37-17, Volume IV, Pages 37 and 38, Jet Propulsion Laboratory, Pasadena, California, 1962.

3. S. P. Vango, *Determination of Permeability of Cast Teflon Sheet to Nitrogen Tetroxide and Hydrazine*, TM 33-55, Jet Propulsion Laboratory, Pasadena, California, August 25, 1961.

TABLE VIII COMPOUNDS

| INGREDIENT | * COMPOUNDS 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | SOURCE |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Vistalon 404 | 100 | 100 |  |  | 100 | 100 |  |  |  |  | Enjay Chemical Co. |
| Vistalon 3509 |  |  |  | 100 |  |  | 100 |  |  |  | Enjay Chemical Co. |
| Nordel 1440 |  |  | 100 |  |  |  |  | 50 |  |  | E.I Dupont DeNemours Co. Inc |
| Nordel 1320 |  |  |  |  |  |  |  | 50 |  |  | E.I Dupont DeNemours Co. Inc. |
| Royalene 301 |  |  |  |  |  |  |  |  | 100 | 100 | U.S. Rubber Co. |
| Vistanex |  |  |  | 5 |  |  |  |  |  |  | Enjay Chemical Co. |
| HAF Carbon Black | 50 | 60 | 60 | 65 |  |  |  |  |  |  | Vulcan 3, Cabot Corp. |
| Icecap KE Clay |  |  |  |  | 100 | 40 | 40 |  |  |  | Burgess Pigment Co. |
| Precipitated Hydrated Silica |  |  |  |  |  | 30 | 40 | 80 | 65 | 65 | Silene D Pittsburg Plate & Glass Corp. |
| Zinc Oxide |  |  | 5 | 5 |  |  |  | 5 |  | 5 | Protex 168 New Jersey Zinc Co. |
| Stearic Acid |  |  |  | 1 |  |  |  |  |  |  | L. A. Chemical Co. |
| Dicup 40C | 10 | 7 |  |  | 7 | 7 |  |  | 7 |  | Hercules Powder Co. |
| Sulfur |  | .2 | 1.5 |  |  |  |  | 1.5 |  | 1.5 | L. A. Chemical Co. |
| Polyhalomethyl Phenol Resin |  |  |  | 12 |  |  | 12 |  |  |  | ST 1055, Schenectady Chemicals, Inc. |
| Vinyl Silane |  |  |  |  | 1 | 1 | 1 |  | 1 |  | A-172, Union Carbide Corp. |
| Tri-Allyl Cyanurate |  |  |  |  | 1.5 | 1.5 |  |  | 1.5 |  | American Cyanamid Co. |
| Tetra Methylthiuram Monosulfide |  |  | 1.5 |  |  |  |  | 1.5 |  | 1.5 | Thionex, E.I. Dupont De Nemours Co., Inc. |
| Mercapto Benzothiazole |  |  | .5 |  |  |  |  | .5 |  | .5 | Captax, RT Vanderbilt Co. Inc. |
| TOTAL | 160 | 167.2 | 168.5 | 188 | 209.5 | 179.5 | 193 | 188.5 | 174.5 | 173.5 |  |

* Parts per hundred of rubber by weight

# TABLE IX

## PHYSICAL PROPERTIES

| COMPOUND NUMBER | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Press Cure, Minutes @310°F | 45 | 30 | 30 | 60 | 30 | 60 | 45 | 45 | 45 | 60 |
| Air Oven Cure, Hours @ 350°F | -- | -- | -- | -- | -- | -- | 16 | -- | -- | 4 |
| Original Properties | | | | | | | | | | |
| Tensile Strength, psi | 1800 | 2750 | 2750 | 2600 | 1300 | 1050 | 1250 | 950 | 1700 | 1600 |
| Elongation, % | 350 | 340 | 300 | 260 | 190 | 300 | 230 | 420 | 180 | 360 |
| 200% Modulus, psi | 590 | 1130 | 1600 | 1870 | ---- | 600 | 1125 | 650 | ---- | 925 |
| Hardness, Shore A | 63 | 67 | 75 | 78 | 65 | 57 | 72 | 79 | 75 | 79 |
| After 7 days @ 158°F | | | | | | | | | | |
| Compression Set, % | 19.2 | 10.7 | 18 | 24.2 | 12.2 | 22.1 | 18.8 | 35.8 | 7.4 | 27.6 |

### TABLE X

Compound 1

| Physical Properties | | | |
|---|---|---|---|
| Cure, Minutes @ 310°F | 30 | *45 | 60 |
| Tensile Strength psi | 1850 | 1800 | 2000 |
| Elongation % | 360 | 350 | 390 |
| 200% Modulus, psi | 675 | 590 | 575 |
| Hardness, Shore A | 63 | 63 | 62 |

*Selected Cure

### TABLE XI

Compound 2

| Physical Properties | | | |
|---|---|---|---|
| Cure, Minutes @ 310°F | *30 | 45 | 60 |
| Tensile Strength, psi | 2750 | 2750 | 2750 |
| Elongation, % | 340 | 340 | 350 |
| 200% Modulus, psi | 1130 | 1100 | 1025 |
| Hardness, Shore | 67 | 68 | 67 |

*Selected Cure

### TABLE XII

Compound 3

| Physical Properties | | | |
|---|---|---|---|
| Cure, Minutes @ 310°F | 15 | *30 | 45 |
| Tensile Strength, psi | 2625 | 2750 | 2750 |
| Elongation, % | 310 | 300 | 310 |
| 200% Modulus, psi | 1400 | 1600 | 1550 |
| Hardness, Shore A | 75 | 75 | 75 |

*Selected Cure

## TABLE XIII

### Compound 4

| Physical Properties | | | |
|---|---|---|---|
| Cure Minutes @ 310°F | *30 | 45 | 60 |
| Tensile Strength, psi | 2750 | 2600 | 2600 |
| Elongation, % | 340 | 300 | 260 |
| 100% Modulus, psi | 1290 | 1570 | 1370 |
| Hardness, Shore A | 76 | 77 | 78 |

*Selected Cure

## TABLE XIV

### Compound 5

| Physical Properties | | | |
|---|---|---|---|
| Cure Minutes @ 310°F | *30 | 45 | 60 |
| Tensile Strength, psi | 1300 | 1300 | 1300 |
| Elongation, % | 190 | 195 | 190 |
| 100% Modulus, psi | 550 | 520 | 560 |
| Hardness, Shore A | 65 | 65 | 64 |

*Selected Cure

## TABLE XV

### Compound 6

| Physical Properties | | | |
|---|---|---|---|
| Cure, Minutes @ 310°F | 30 | 45 | *60 |
| Tensile Strength, psi | 1050 | 1000 | 1050 |
| Elongation, % | 310 | 300 | 300 |
| 200% Modulus, psi | 550 | 600 | 600 |
| Hardness, Shore A | 57 | 57 | 57 |

*Selected Cure

### TABLE XVI
### Compound 7

| Physical Properties | | | | | | |
|---|---|---|---|---|---|---|
| Press Cure, minutes @ 310°F | 30 | 45 | 60 | 45 | 30 | *45 |
| Oven Cure, hours @ 350°F | -- | -- | -- | 4 | 16 | 16 |
| Tensile Strength, psi | 1325 | 1525 | 1350 | 1075 | 1125 | 1250 |
| Elongation, % | 940 | 800 | 740 | 430 | 200 | 230 |
| 200% Modulus | 225 | 300 | 350 | 600 | 1125 | 1125 |
| Hardness, Shore A | 65 | 65 | 65 | 69 | 74 | 72 |

*Selected Cure

### TABLE XVII
### Compound 8

| Physical Properties | | | |
|---|---|---|---|
| Cure, Minutes @ 310°F | 30 | *45 | 60 |
| Tensile Strength, psi | 1000 | 950 | 950 |
| Elongation, % | 410 | 420 | 410 |
| 200% Modulus, psi | 675 | 650 | 650 |
| Hardness, Shore A | 81 | 79 | 83 |

*Selected Cure

### TABLE XVIII
### Compound 9

| Physical Properties | | | |
|---|---|---|---|
| Cure, Minutes @ 310°Fq | 30 | *45 | 60 |
| Tensile Strength, psi | 1700 | 1700 | 1900 |
| Elongation, % | 180 | 180 | 180 |
| 200% Modulus, psi | -- | -- | -- |
| Hardness, Shore A | 73 | 75 | 75 |

*Selected Cure

## TABLE XIX
### Compound 10

| Physical Properties | | | | |
|---|---|---|---|---|
| Press Cure, Minutes @310°F | 30 | 45 | 60 | *60 |
| Oven Cure, hours @ 350°F | -- | -- | -- | 4 |
| Tensile Strength, psi | 1800 | 1625 | 1775 | 1600 |
| Elongation, % | 610 | 580 | 610 | 360 |
| 200% Modulus, psi | 425 | 500 | 475 | 925 |
| Hardness, Shore A | 67 | 72 | 72 | 79 |

*Selected Cure

## TABLE XX
### Compound FR 6-60-26

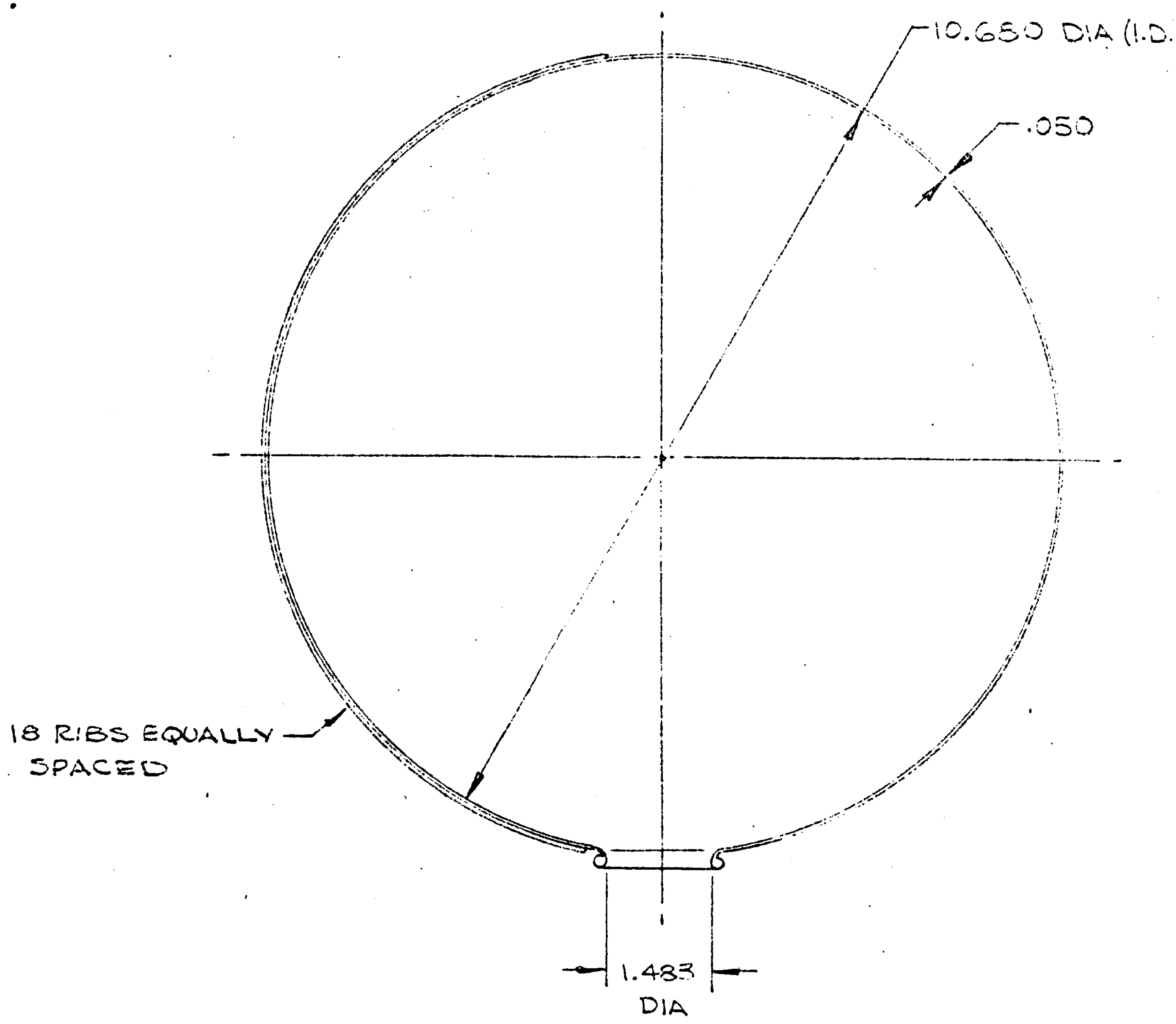
| Physical Properties | | | | |
|---|---|---|---|---|
| Batch No. | None | 528 | 528 | 529 |
| Cure, Minutes @ 310°F | 40 | 40 | 60 | 60 |
| Tensile Strength, psi | 1165 | 2100 | 2150 | 2225 |
| Elongation, % | 355 | 630 | 520 | 505 |
| 200% Modulus, psi | 450 | 375 | 550 | 775 |
| Hardness, Shore A | 50 | 58 | 60 | 65 |

## TABLE XXI

## Molding Record

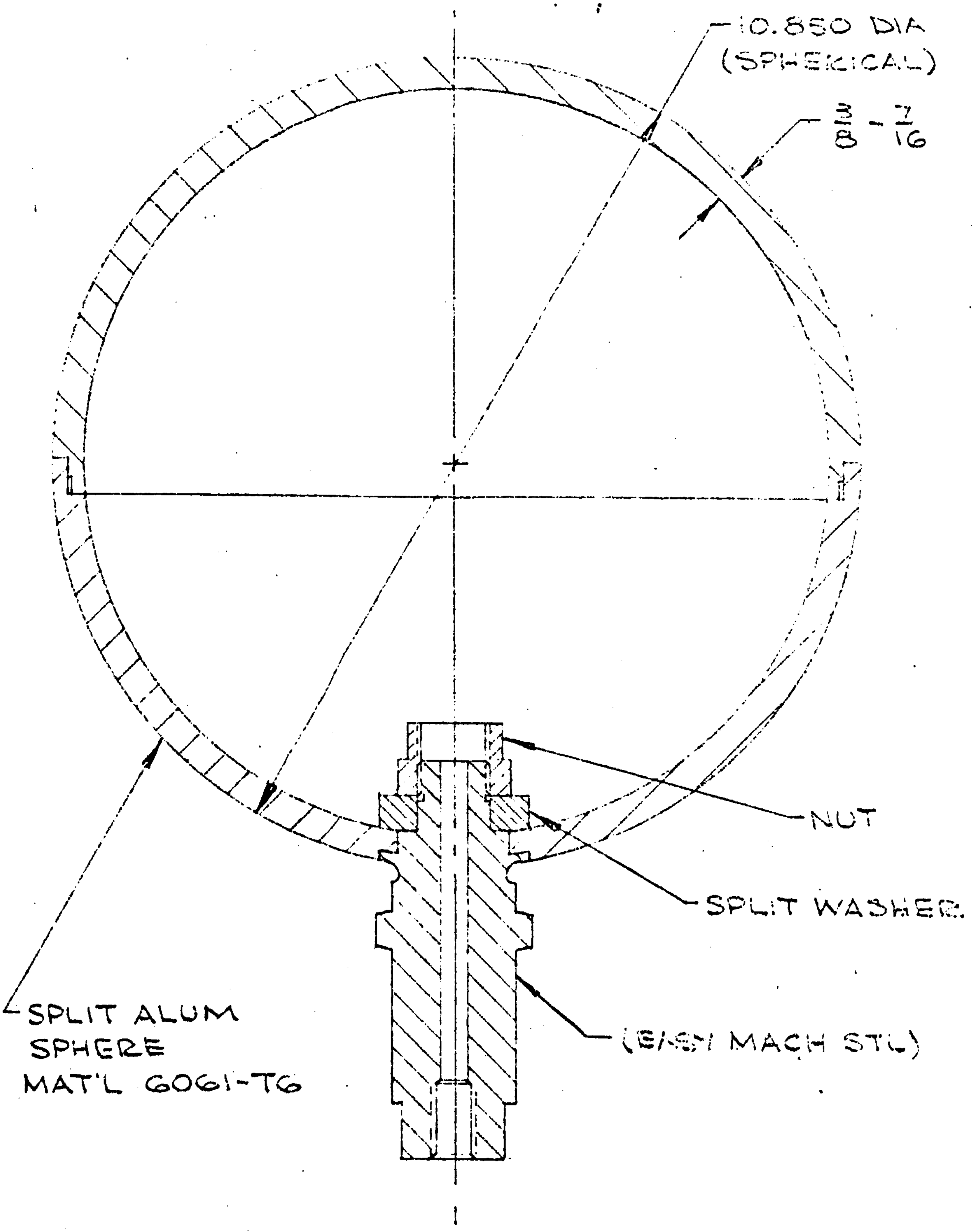
## Compound FR 6-60-26

| Heat No. | Batch No. | Wt. of Stock Ounces | Loading Temp °F | Cure @ 310°F Minutes | Results |
|---|---|---|---|---|---|
| 1 | 528 | 16 | 305 | 40 | Air bubbles, heavy flash, discarded |
| 2 | 528 | 15 | 310 | 40 | Passed leak test, dissolved core |
| 3 | 528 | 14 | 180 | 40 | Backrind broke through surface, discarded |
| 4 | 528 | 15 | 225 | 40 | Passed leak test, appeared under cured, discarded |
| 5 | 528 | 14 | 215 | 40 | Air bubbles discarded |
| 6 | 528 | 13 3/4 | 255 | 40 | Passed leak test, in storage |
| 7 | 528 | 15 | 225 | 40 | Backrind, discarded |
| 8 | 528 | 13 1/2 | 280 | 60 | Air bubbles, discarded |
| 9 | 528 | 13 3/4 | 285 | 60 | Passed leak test, core dissolved |
| 10 | 529 | 13 3/4 | 280 | 60 | Passed leak test, core dissolved |



BLADDER, PROPELLANT TANK

FIGURE I



CORE ASSEMBLY

FIGURE II