AD NUMBER

AD813954

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAY 1967. Other requests shall be referred to US Air Force Rocket Propulsion Laboratory, Attn: RPPR-STINFO, Edwards AFB, CA 93523.

AUTHORITY

AFRPL ltr 20 Dec 1971

AFRPL-TR-67-142

HALOGEN PASSIVATION STUDIES

Contract No. F04611-67-C-0033

W. A. Cannon, W. D. English, and N. A. Tiner

Astropower Laboratory, Missile & Space Systems Division
A Division of Douglas Aircraft Company

TECHNICAL REPORT AFRPL-TR-67-142

May 1967

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards Air Force Base, California

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

AFRPL-TR-67-142

HALOGEN PASSIVATION STUDIES

Contract No. F04611-67-C-0033

W. A. Cannon, W. D. English, and N. A. Tiner

Astropower Laboratory, Missile & Space Systems Division
A Division of Douglas Aircraft Company

TECHNICAL REPORT AFRPL-TR-67-142

May 1967

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards Air Force Base, California

FOREWORD

This report was prepared by Astropower Laboratory, Advance Systems and Technology, Missile and Space Systems Division, Douglas Aircraft Company under Air Force Contract F04611-67-C-0033. The contract was administered by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards Air Force Base, California, with Lt. Ralph Fargnoli as Project Engineer.

This report covers work done on the halogen passivation studies during the period from 1 February 1967 to 30 April 1967. The report was prepared by W. A. Cannon and W. D. English, under the supervision of N. A. Tiner.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

This progress report covers experimental work accomplished during the period 1 February to 30 April 1967. During this time experiments were carried out to further define the reactions of typical system organic contaminants on metal panels with fluorine in the passivation process. Tests with fluorine at 50 psig showed greater reaction than at 15 psig but complete removal did not occur. All residues from passivation treatment of organic contaminants are impact sensitive in LF_2; some react spontaneously and violently with LF_2. Dye penetrant residues in porous cast aluminum are impact sensitive, and are not removed by usual cleaning techniques. Addition of a vacuum bake-out step in the cleaning procedure followed by GF_2 passivation does render the residues insensitive to impact in LF_2. Tungsten-contaminated aluminum (simulating tungsten inclusions in welds) is impact sensitive in LF_2. GF_2 passivation reduces the sensitivity to apparently safe levels, but the optimum passivation conditions have not been determined. Secondary corrosion of F_2-passivated metals in a high-humidity atmosphere containing a low level of HF is greater than corrosion of unpassivated specimens of the same metals. Gases adsorbed in the passive film on metals are being studied by analyzing products desorbed under various conditions. Fluorine, hydrogen fluoride, oxygen and nitrogen are prominent. Conditions for complete desorption have not been defined.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION AND SUMMARY

This is the second quarterly progress report on Contract No. F04611-67-C-0033. It covers work done from 1 February to 30 April 1967. The major objectives of the contract are (1) investigating methods for producing the most suitable passivation films on various alloys to be used for fluorine services; (2) testing effectiveness of passivation procedures on system components; and (3) preparing detailed procedures to obtain the most durable passive surfaces for fluorine service.

The work has been divided into four phases as follows:

Phase I – Passive Surface Investigation
- a. Role of Contaminants
- b. Residual Fluorine
- c. Mechanical Stability

Phase II – Analysis of Passivation Methods

Phase III – Testing of Passivation Methods on Components

Phase IV – Recapitulation of Methods and Preparation of Design Guide for Simple Systems

The major technical effort during the second quarter has been in Phase I. Studies of fluorine reactions with potential system contaminants have been continued. It has been shown that gaseous fluorine passivation at room temperature and at pressures up to 50 psig is ineffective for removing gross organic contamination from metal substrates. Impact sensitive residues are left on organic contaminated metal surfaces exposed to fluorine gas at one atmosphere pressure at room temperature. Minor amounts of organic residues left in porous cast aluminum (grade III porosity) from dye penetrant inspection are apparently removed satisfactorily if the cleaning procedure includes a vacuum bakeout at 105°C (220°F) for 18 hours followed by passivation in fluorine. No impact sensitivity in liquid fluorine was found for 20 specimens so treated.

Tungsten-contaminated aluminum surfaces are impact sensitive in liquid fluorine. Five reactions were noted for 12 specimens. After passivation in gaseous fluorine, only 1 out of 18 specimens reacted when impacted in liquid fluorine.

Studies have been started on measuring corrosion resistance of passive metal surfaces to aqueous HF vapor. In two series of experiments with

2014 aluminum, Monel 400, nickel 200, 316 stainless steel, and copper slightly greater corrosion was noted if surfaces were prepassivated in fluorine gas. The difference with copper was negligible.

Residual absorbed gases from fluorine-passivated surfaces were analyzed with the Aerovac analyzer. Oxygen, fluorine, HF, and nitrogen were prominent in the desorbed gases as well as an unidentified constituent apparently present in the fluorine. Very little water vapor was desorbed from the surfaces.

Preparations have been made for making mechanical stability tests of passivated bellows specimens. Modifications of the bellows test apparatus were necessary to insure safe operation and reliable results; these modifications have now been completed.

SECTION II

EXPERIMENTAL

1. REACTION OF GASEOUS FLUORINE WITH TYPICAL SYSTEM CONTAMINANTS

Investigations of fluorine gas reactions with typical system contaminants have been continued. Additional experiments were carried out by continuously weighing the contaminants while exposing them to flowing fluorine gas. The controlled environment balance especially developed for this purpose is described below.

In view of the relatively slow reactions between gaseous fluorine and typical system contaminants at one atmosphere and room temperature, additional exposures at higher pressures – up to 50 psig – have been carried out. Future plans for conducting exposures to 200 psig and 200°F are being formulated.

a. Exposure of Organics in Controlled Environmental Balance

The controlled environment balance provides for continuously following the weight change of a specimen while it is exposed to flowing fluorine gas. It consists of an Ainsworth single pan analytical balance with a platinum chain hang-down extending through a vertical tube into a cylindrical reaction chamber. The chain terminates in the chamber and supports a specimen pan. Fluorine gas is fed into the chamber at the bottom and is exhausted at the top through a side arm in the vertical tube through which the platinum chain hangs. This arrangement insures that relatively little fluorine gas escapes from the chamber; what does escape is exhausted through the fume hood enclosing the balance assembly. A system of baffles inside the chamber prevents direct impingement of flowing gas on the balance pan. Samples are placed on or removed from the pan through a gasketed closure on the front of the chamber.

Figure 1 gives results for exposing separate samples of petroleum jelly, Pydraul AC, and polyurethane foam to flowing gaseous fluorine in the apparatus at 25°C (77°F). With a flow of fluorine into the chamber of 50 ml/min and with a total chamber volume of 400 ml, several minutes are required for the fluorine concentration to build up to a high level as air is displaced. This probably accounts for the delay in the weight increase shown for the polyurethane specimen. After the initial delay, the specimen showed a continuous gain in weight but at a decreasing rate for the period of exposure. A total weight increase of approximately 13 mg for a specimen of initial weight of 49 mg was observed.

Pydraul AC, 350 mg, was exposed in an aluminum cup (1 inch diameter). After approximately 45 minutes during which a shallow minimum

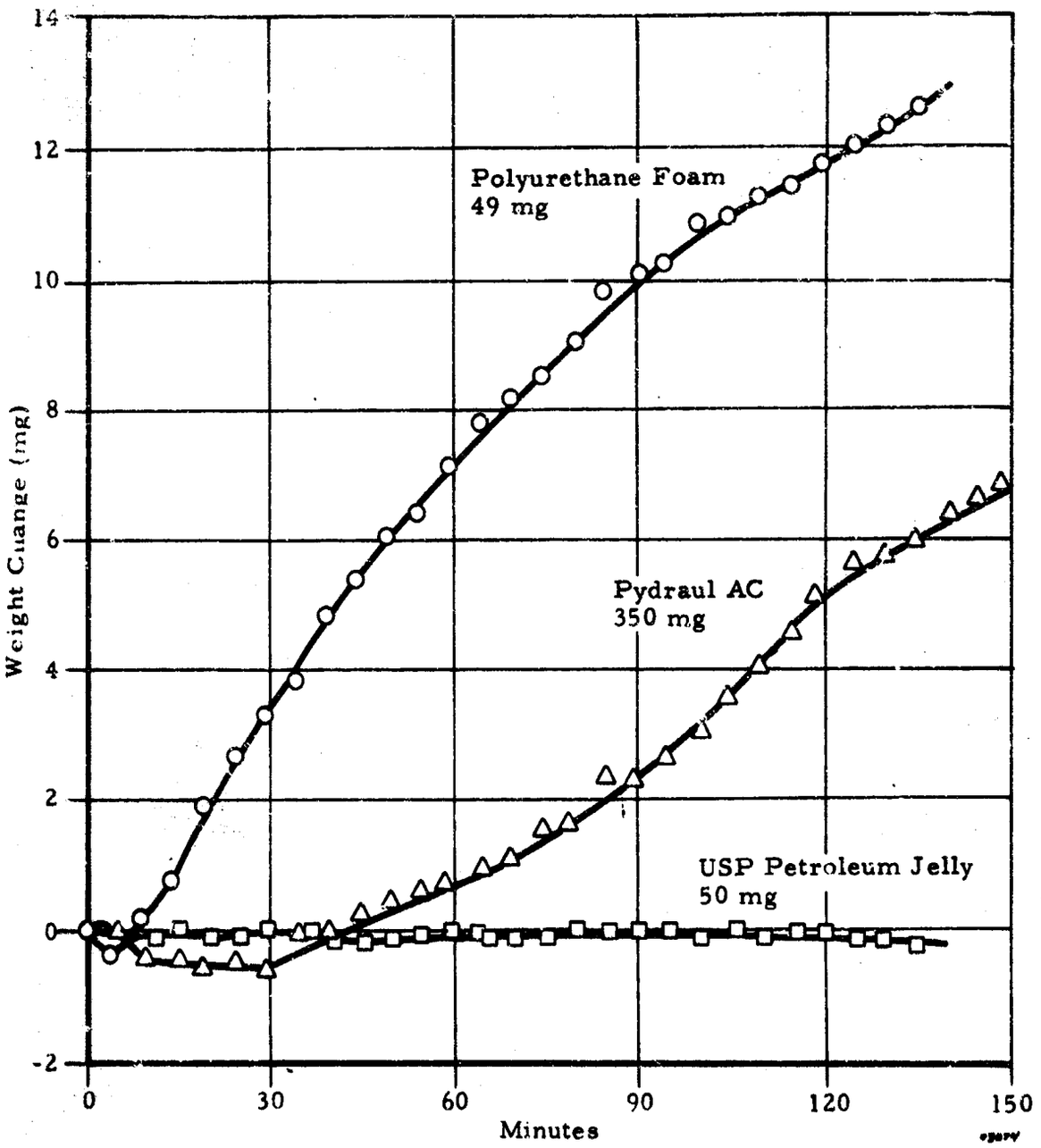


Figure 1. Weight Change as a Function of Time for Some Typical Contaminants. Flowing GF_2 - 25°C (77°F) - One Atmosphere.

in the weight was observed, the specimen weight gradually increased and was still going up after the experiment was terminated in 150 minutes. At this time the Pydraul AC had gained approximately 7 mg as shown in Figure 1.

Petroleum jelly, USP, spread as a thin smear on a one-inch square 304 stainless steel sheet, did not change weight appreciably during 150 minutes exposure in the test apparatus (see Figure 1).

These experiments serve to confirm observations reported previously (Reference 1) concerning the relatively slow reactions between gaseous fluorine and typical system contaminants at one atmosphere and room temperature.

b. Exposure of Organics to High Pressure Fluorine

Several organics were exposed to fluorine at 50 psig and at 25°C (77°F) to compare with results at one atmosphere pressure. The data are summarized in Table I. Although substantially greater reaction is observed compared to one atmosphere pressure, reactions do not yield completely volatile reaction products in any case. One of the two petroleum jelly specimens ignited, while both polyurethane samples ignited. Samples which ignited left carbonaceous residues. Pydraul AC formed semisolid residues with substantial weight increase during exposure. These various residues will be tested for reactivity in LF_2 using the ABMA impact tester.

c. Infrared Analysis of Organic Residues

Infrared spectra were made of residues from the reaction of gaseous fluorine with petroleum jelly USP and Pydraul AC. Spectra from one-hour exposure times at one atmosphere pressure are shown in Figure 2, a and b. These spectra are identical with the materials before exposure, hence it is concluded that reaction with fluorine has not proceeded far enough to yield detectable quantities of products. The samples exposed to fluorine at 50 psig show evidence of considerable C-F bond formation as shown in the spectra of Figure 3, a and b, for one-hour exposure of Pydraul AC and 24-hour exposure of petroleum jelly USP. (The one-hour exposure sample of petroleum jelly USP was not available for analysis because it ignited during the test.) The C-F bond is indicated by the broad absorption band between 7.7 and 9 microns.

2. IMPACT SENSITIVITY OF ORGANIC RESIDUES FOLLOWING PASSIVATION

Type 316 stainless steel impact specimens (discs, 5/8" diameter by 0.016" thick) were individually coated on one side with the following organic contaminants.

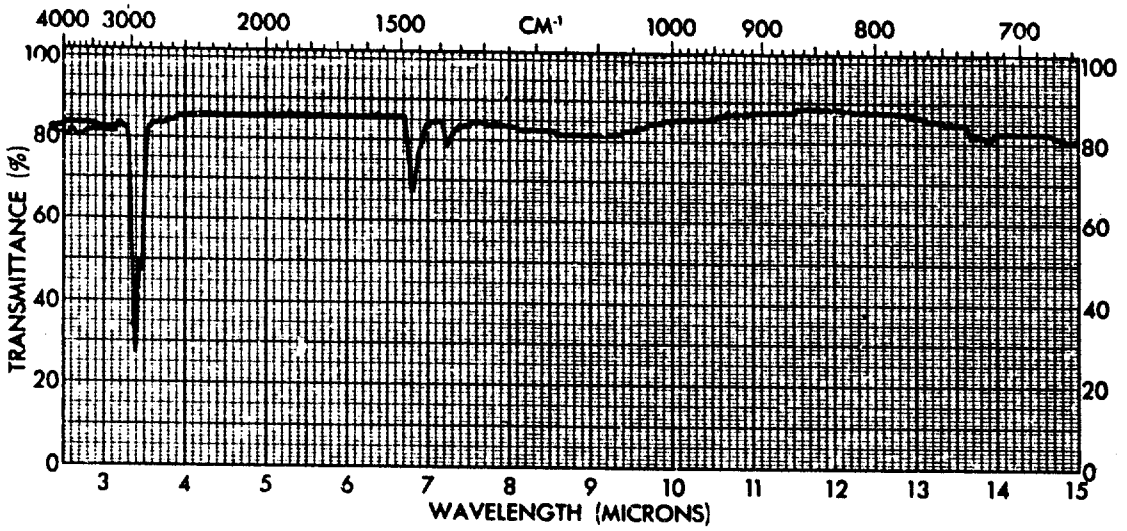
a. Petroleum jelly, USP

b. KEL-F 90 halocarbon grease

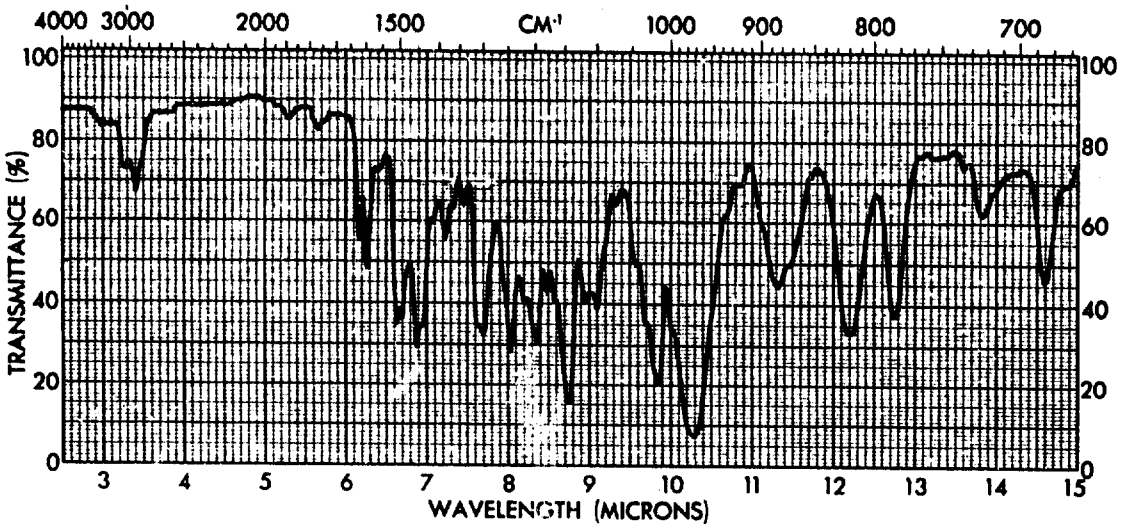
TABLE I. EXPOSURE OF ORGANICS TO HIGH PRESSURE FLUORINE
(50 psig, 77°F)

1-Hour Exposure	Initial Sample Weight	Weight Change	%	Observation
Petroleum Jelly USP	0.0575	-0.0548	-95	Carbon residue
KEL F-90	0.0503	-0.0009	-2	–
Pydraul AC	0.0497	+0.0123	+25	Semi-solid residue
Polyurethane	0.0496	-0.0353	-71	Carbon residue
24-Hour Exposure				
Petroleum Jelly USP	0.0484	+0.0237	+49	Solid film residue
KEL F-90	0.0427	-0.0113	-26	Oily residue
Pydraul AC	0.0528	+0.0243	+46	Brown solid residue
Polyurethane	0.0537	-0.0410	-76	Carbon residue

Petroleum jelly USP and KEL F-90 grease spread on 0.5" x 2" 304 stainless steel panels. Pydraul AC and polyurethane foam contained in ABMA aluminum impact cups (1" dia x 3/4" high).

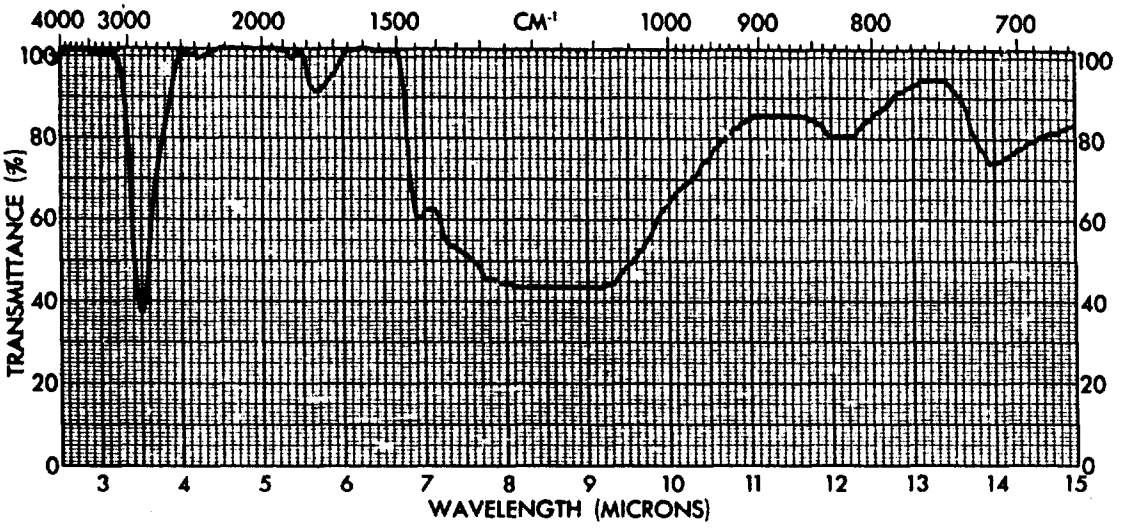


(a) Petroleum Jelly USP Exposed to GF_2 for 1 Hour at One Atmosphere Pressure – 25°C (77°F)

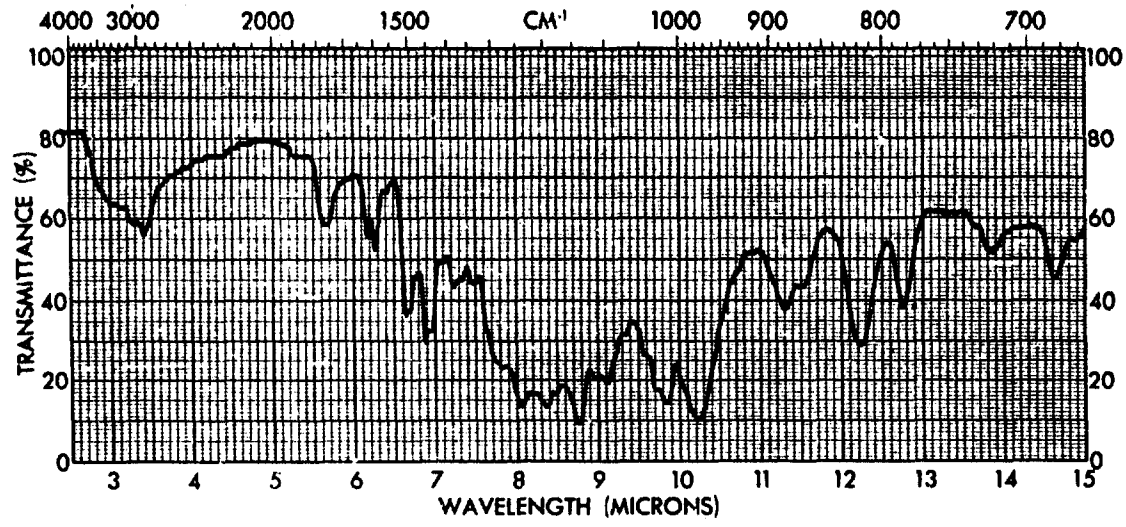


(b) Pydraul AC Exposed to GF_2 for 1 Hour at One Atmosphere Pressure – 25°C (77°F)

Figure 2. Infrared Spectra



(a) Petroleum Jelly USP Exposed to 50 psig Fluorine for 24 Hours at 25°C (77°F)



(b) Pydraul AC Exposed to 50 psig Fluorine for 1 Hour at 25°C (77°F)

Figure 3. Infrared Spectra

c. Acrylic lacquer

d. Polyurethane foam insulation

Contaminant coating was held as nearly as possible to 50 mg per square inch (15 mg per specimen). After applying organic contaminants, the specimens were exposed to a simulated passivation cycle of one-hour exposure to gaseous fluorine at one atmosphere at 25°C (77°F). Following passivation, specimens were impact tested in the modified ABMA tester in liquid fluorine at -195°C (-320°F) at 72 ft-lb energy level (Reference 2). All impacts yielded reactions ranging from moderate to extreme, indicating that all organic residues were impact sensitive. The data are summarized in Table II.

One of the two petroleum jelly coated specimens and one of the two acrylic lacquer coated specimens reacted violently in the liquid fluorine before actual impact. Reactions occurred spontaneously after about 5 seconds contact with liquid fluorine. Neither the KEL-F 90 nor the polyurethane foam contaminated specimens reacted prior to impact. It should be mentioned that the specimens are cooled to -320°F (LN_2 temperature) before the LF_2 is added.

3. IMPACT SENSITIVITY OF DYE PENETRANT RESIDUES

Cast aluminum impact specimens (discs, 0.040" thick by 5/8" diameter) were machined from an A356 aluminum billet of grade III porosity. Specimens were exposed to dye penetrant inspection using Shannon Glow P138A water-washable penetrant. A normal rinse with water was used for removing dye penetrant. After drying, all specimens were vapor degreased in Genesolve D. Fluorescent residues were still present on all specimens after vapor degreasing. These could be detected under low power magnification with ultraviolet illumination. Some of the samples were exposed to a vacuum bakeout at 105°C (220°F) for 18 hours after vapor degreasing. Fluorescent residues could still be detected after vacuum bakeout but the number of fluorescent spots was reduced.

Previous work in this laboratory (Reference 3) has shown that A356 cast aluminum with grade III porosity fails to pass impact tests in liquid fluorine at -320°F when subjected to Penetrex ZL-22 dye penetrant inspection followed by the cleaning and bakeout procedure described in the preceding paragraph. (Shannon Glow P138A used in the current investigation is the equivalent of Penetrex ZL-22. The latter was no longer available for use.) The bare metal, unexposed to dye penetrants, is stable in LF_2 impacts.

In the current investigation, after passivation in gaseous fluorine for 1 hour at one atmosphere pressure at 25°C (77°F), no reactions were obtained in 20 impact specimens in liquid fluorine at -195°C (-320°F) using the modified ABMA test at 72 ft-lb energy (Reference 2). One out of six specimens passivated in gaseous CTF for 1 hour at one atmosphere pressure at 25°C (77°F) reacted on impact and one out of six passivated in

TABLE II. IMPACT SENSITIVITY TESTS
PASSIVATED ORGANIC CONTAMINANTS

Oxidizer – LF_2

Samples – Coatings on 316 Stainless Steel

Ambient Temperature – 54°F, Test Temperature -320°F

Atmosphere – Dry GN_2

Impact Energy – 72 ft-lb

Drop No.	Sample	Type of Reaction				Remarks
		Extreme	Moderate	Faint	None	
1	Blank				x	
2	KEL-F 90		x			
3	KEL-F 90		x			
4	Petroleum Jelly	x				
5	Petroleum Jelly		x			Reacted before impact
6	Acrylic Lacquer		x			
7	Acrylic Lacquer		x			Reacted before impact
8	Polyurethane		x			
9	Polyurethane		x			
10	Blank				x	

gaseous fluorine after normal cleaning, but without the vacuum bakeout, also reacted. The results indicate that fluorine gas passivation is effective in eliminating the impact sensitivity of minor residues of dye penetrants when the cleaning cycle includes a vacuum bakeout treatment.

4. IMPACT SENSITIVITY OF TUNGSTEN-CONTAMINATED SPECIMENS

Inclusions such as those that might be introduced by electrode sputtering in TIG welding were simulated by plasma spraying a mixed aluminum and tungsten powder onto A356 cast aluminum impact specimens. Layers of slightly less than 0.002-inch mean thickness were produced. Three different concentrations of tungsten powder (1%, 3%, and 10% by weight) were studied.

Examination of the specimens by means of a stereo microscope (30X) showed that tungsten grains were definitely present and identifiable in the aluminum coating matrix. The tungsten appeared darker in color, and the crystal grains had much sharper angles than the aluminum, which had partially melted.

The specimens were divided; half were passivated in gaseous fluorine at one atmosphere pressure for 1 hour at 25°C (77°F). Five of twelve unpassivated specimens reacted on impact in the ABMA tester in liquid fluorine at -195°C (-320°F). Only one of eighteen passivated specimens reacted on impact. The data are summarized in Table III.

The results indicate that tungsten particles are impact sensitive in LF_2 and that they become materially less so after passivation. More tests will be required to establish if passivation alone can render tungsten contamination safe.

5. CORROSION OF PASSIVATED SURFACES

a. Procedure

Corrosion test coupons (1" x 3") of 2014 aluminum, Monel 400, nickel 200, 316 stainless steel, and copper were passivated by various techniques, then exposed to 90 - 95% relative humidity at 160°F to determine relative corrosion rates. Unfortunately, the extent of corrosion in one week under these conditions is too slight to discriminate among the passivation methods. Although some tarnishing of copper and Monel 400 takes place the weight changes are generally less than 2 mg per specimen. Stainless steel 316 and nickel 200 undergo weight changes of less than 1 mg per specimen.

A more rigorous corrosion test was devised to induce significant corrosion which may then be used as a basis for comparing passivated surfaces. The test currently used involves exposing the 1" x 3" test coupons to the vapor of 10% aqueous HF solution at 100°F. The vapor tension of HF over the solution is 0.5 torr at 100°F (Reference 4). The test is conducted

TABLE III. IMPACT SENSITIVITY TESTS TUNGSTEN CONTAMINATED CAST ALUMINUM

Oxidizer – LF_2
Samples – A356 Al (Tungsten Contaminated)
Ambient Temperature – 55°F, Test Temperature -320°F
Impact Energy – 72 ft-lb
Atmosphere – Dry GN_2

Drop No.	Sample	Type of Reaction				Remarks
		Extreme	Moderate	Faint	None	
1	A2				x	
2	A2		x			
3	A2			x		
4	B2				x	
5	B2				x	
6	B2				x	
7	B2				x	
8	B2			x		
9	B2				x	
10	C2				x	
11	C2			x		
12	C2			x		
13	A1				x	
14	A1				x	
15	A1				x	
16	A1				x	
17	A1				x	
18	A1				x	
19	B1				x	
20	B1				x	
21	B1		x			Flash, no sound
22	B1				x	
23	B1				x	
24	B1				x	
25	C1				x	
26	C1				x	
27	C1				x	
28	C1				x	
29	C1				x	
30	C1				x	

A1 – 1% W – passivated
B1 – 3% W – passivated
C1 – 10% W – passivated
A2 – 1% W – as deposited
B2 – 3% W – as deposited
C2 – 10% W – as deposited

in a two-quart polypropylene container equipped with a tight fitting lid. Each specimen has a hole on one end through which a horizontal alumina rod extends to support it. Specimens are held apart by alumina spacers. The alumina support rod is in turn held securely in position by a stainless steel frame which stands in the chamber. The aqueous HF solution is placed in a separate small polyethylene container and the entire assembly is placed in a thermostatted oven at 100°F. Preliminary experiments showed the necessity of circulating the vapors to obtain uniform effects, hence a motor driven propeller is provided. Its shaft fits through a hole in the lid of the chamber. A minimum clearance is provided around the propeller shaft.

b. Results and Discussion

Two sets of test coupons of the five alloys mentioned in the preceding section were subjected to the HF corrosion test for 24 hours. One set had been previously passivated by exposure to fluorine gas at one atmosphere pressure for 1 hour at 25°C (77°F) followed by evacuation at the same temperature. One set received the same preparation and corrosion exposure but was not passivated. The relative corrosion of the passivated specimens and controls are shown in Figure 4. In every case the prepassivated coupons suffered greater corrosion, as indicated by the weight changes, than their unpassivated counterparts. The difference is very small for the copper specimens.

Figure 5 gives results for a duplication of the experiment to determine reproducibility of the corrosion. Fairly good reproducibility was demonstrated except for the 316 stainless steel. Although the magnitude of corrosion was significantly different between the two experiments, the relative corrosion of passivated specimens and controls was nearly the same.

6. RESIDUAL GASES FROM PASSIVATED SURFACES

a. Procedure

Eighty grams of 304 stainless steel powder were placed in a bomb, evacuated, and passivated by exposure to fluorine gas at one atmosphere pressure for 1 hour at 25°C (77°F). The surface area of the powder was 1010 cm^2/gram as measured by the krypton gas B.E.T. method. Therefore, the total metal surface area was roughly eight square meters.

Following the passivation cycle, the bomb was evacuated to the best vacuum obtainable with the mechanical oil pump used in the system — roughly 0.5 torr. The evacuation was continued for 15 minutes at room temperature.

The bomb was valved off under vacuum and attached to the inlet system of the Aerovac AVA1 mass spectrometer. The residual gas in the bomb was leaked into the analyzer at a total pressure of 5×10^{-5} torr and the mass spectrum scanned from AMU 12 through 70.

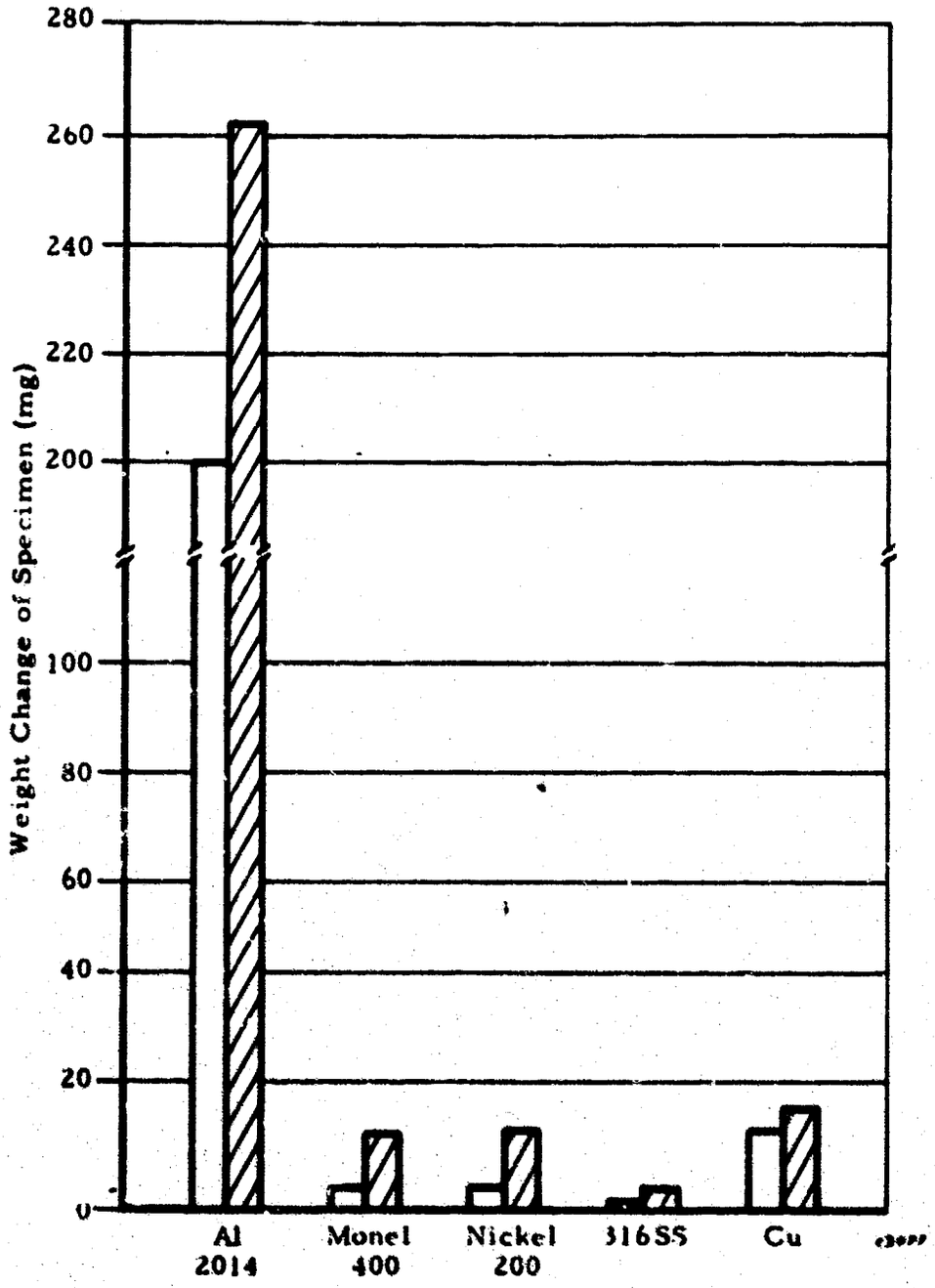


Figure 4. Relative Corrosion of Passivated and Unpassivated Coupons

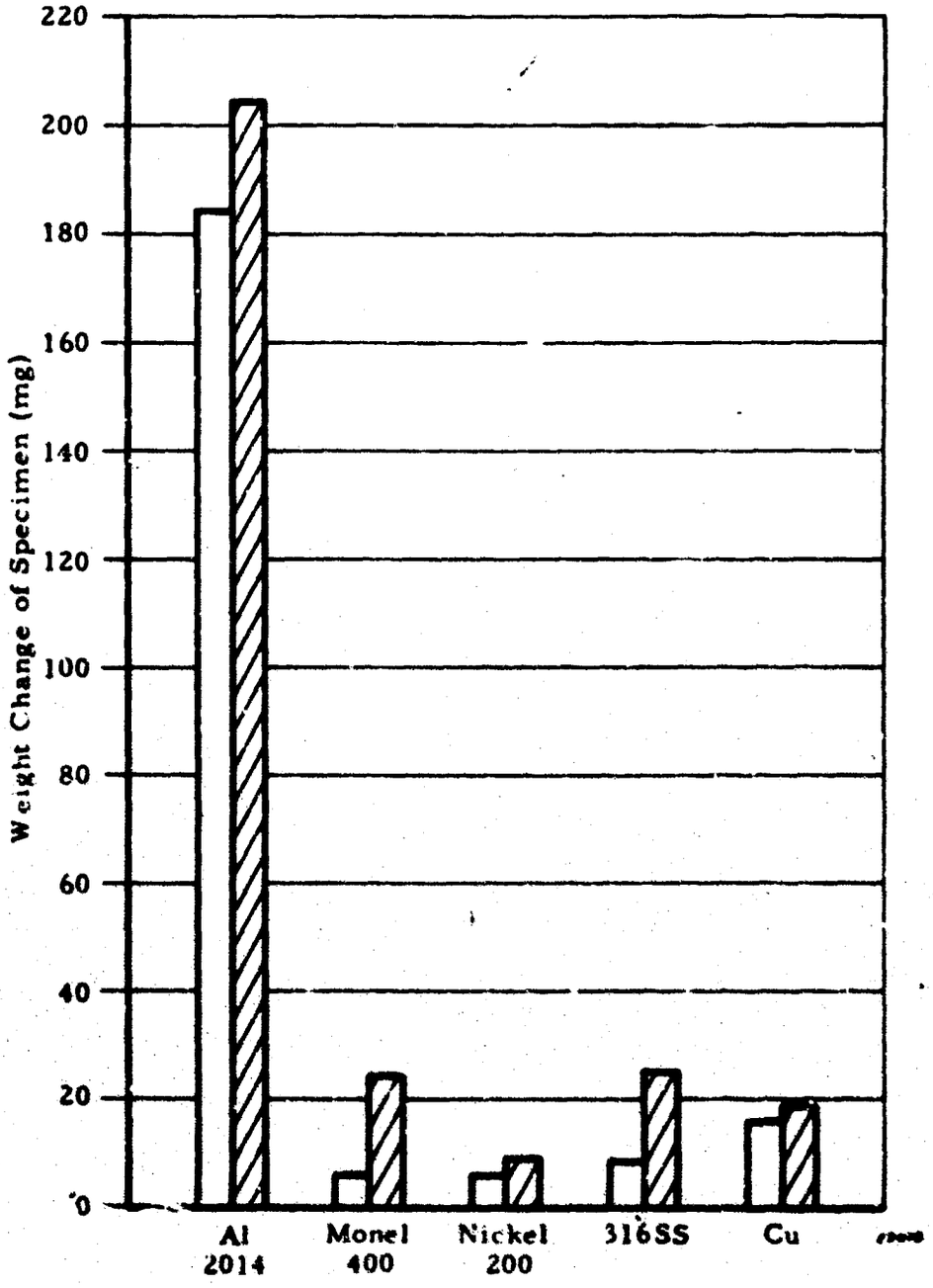


Figure 5. Relative Corrosion of Passivated and Unpassivated Coupons – Second Series

The bomb was again pumped with the mechanical pump for an additional 15 minutes and reattached to the mass spectrometer and an additional scan made over the same mass range. Finally, the bomb was heated to approximately 100°C (210°F) while attached to the mass spectrometer and a third scan made.

b. Results and Discussion

The relative peak heights obtained in the mass analysis for the separate samples are shown in Table IV. The relative peak heights are not directly related to concentration because of the variable response of the instrument to each molecular species. The results are therefore most useful from a qualitative standpoint.

The most prominent peaks in the spectra are due to oxygen, nitrogen, fluorine, HF, and an unknown constituent with AMU of 46. This has been identified in gaseous fluorine from some sources and is evidently strongly adsorbed in the metal powder because it shows up more strongly after heating. Water vapor — AMU 17 and 18 — is not prominent. It is almost absent after the first evacuation of the bomb.

7. MECHANICAL STABILITY TEST

During this period, the rapid screening tester, Douglas drawing #1T13626, was modified for the mechanical stability test program. This modification consisted of welding on a bellows type plunger adapter to replace the unsatisfactory Teflon shaft seal design (see Figure 6). The metal bellows is a hydroformed stainless steel alloy, 21Cr-6Ni-9Mn, produced by Stainless Steel Products, Burbank, California. A set screw port is provided to prevent the plunger shaft from vibrating loose during the flexing test.

The rapid screening tester is being set up in a separate location so that other tests will not interfere with this program.

Previous low cycle fatigue tests on stainless steel and aluminum alloy at Astropower Laboratory indicate an endurance cycle life between 10^4 - 10^5 cycles at or above the materials yield strength stress level. Therefore, tests will be run in the stress range of 65 - 75% yield strength to extend the fatigue life of the metal bellows adapter. These test conditions require using a 0.12-inch cam on the rapid screening tester.

Stainless Steel Products was unable to deliver the hydroformed metal bellows test specimens due to a labor strike. The copper, stainless, nickel alloy metal bellows and a new set of aluminum alloy bellows will be received in the latter part of May.

TABLE IV. MASS SPECTRA OF RESIDUAL GASES FROM PASSIVATED SURFACES

AMU	Probable Ion	Relative Peak Heights Above Background (1) After Initial Evacuation	(2) After Second Evacuation	(3) Bomb Heated
14	N^+	0	0.05	0.05
16	O^+	0.10	0.20	0.20
17	OH^+	0.05	0.10	0.0
18	H_2O^+	0.35	0.0	0.0
19	F^+	0.07	0.2	0.15
20	HF^+	1.6	2.4	2.4
28	$N2^+$, CO^+	1.7	1.9	1.9
32	O_2^+	0.25	0.5	0.6
34	-	0.05	0.1	0.1
44	CO_2^+	0.02	0.0	0.0
46	-	0.25	0.4	0.5
50	-	0.02	0.05	0.1

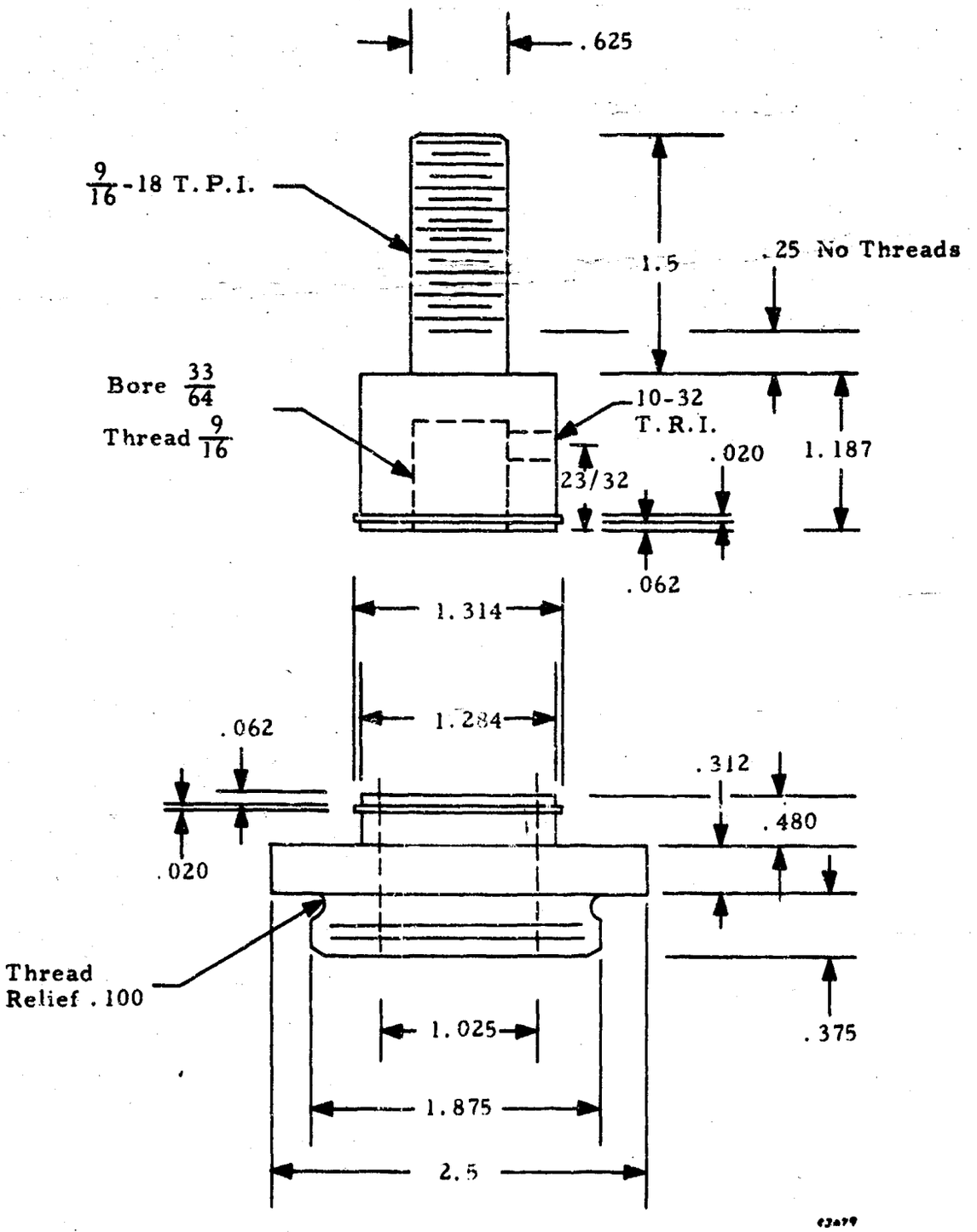


Figure 6. Modification of Rapid Screening Tester Lid

SECTION III

FUTURE WORK

1. PHASE I

The projected Phase I studies will be completed during the next quarter. These will be as follows:

a. Role of Contaminants

In view of the relatively incomplete removal of gross organic system contaminants by fluorine passivation up to 50 psig, a few additional tests will be conducted at temperatures to 200°F and 200 psig. This work is outside the scope of the original proposal work but is necessary to firmly establish the effect of potential system contaminants. No additional costs will be entailed. Reactions of organic materials with chlorine pentafluoride will also be investigated.

b. Effect of Residual Fluorine

The investigation of the residual fluorine left from various passivation methods and its effect on secondary corrosion of metal surfaces will be completed. Methods of removing the adsorbed passivating agent and its reaction products from metal surfaces will be investigated.

c. Mechanical Stability Tests

The flexure tests for passivated bellows specimens is scheduled for completion during the next quarter.

2. PHASE II – ANALYSIS OF PASSIVATION METHODS

Analysis of passivation methods will be made based on the completed Phase I tests.

3. PHASE III – TESTING OF COMPONENTS

A list of recommended components for Phase III studies will be prepared and submitted during the next quarter.

[redacted]

REFERENCES

1. Cannon, W. A., W. D. English and N. A. Tiner, "Halogen Passivation Studies," AFRPL-TR-67-50, February 1967.

2. Spicer, D. R., "Douglas Fluorine and Flox Materials Compatibility Facility," Douglas Report SM-44668, May 1964.

3. Toy, S. M., Personal Communication, Douglas Aircraft Company, April 1967.

4. Ryss, I. G., "The Chemistry of Fluorine and Its Inorganic Compounds," AEC-TR-3927(Part 1), p. 85, United States Atomic Energy Commision, Oakridge, Tennessee, 1960.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Astropower Laboratory
Missile and Space Systems Division
A Division of Douglas Aircraft Company
Newport Beach, California

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

HALOGEN PASSIVATION STUDIES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Quarterly Report — 1 February 1967 through 30 April 1967

5. AUTHOR(S) (Last name, first name, initial)

Cannon, W. A., English, W. D., and Tiner, N. A.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
May 1967	21	4

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
F04611-67-C-0033	AFRPL-TR-67-142
b. PROJECT NO 3148	
c. BPSN 623148	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. Program Element No. 6.24.05.18.4	DAC-59854-Q2

10. AVAILABILITY/LIMITATION NOTICES
This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL (RPPR/STINFO), Edwards, California 93523.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Rocket Propulsion Laboratory Research and Technology Division Air Force Systems Command Edwards Air Force Base, California 93523

13. ABSTRACT

This progress report covers experimental work accomplished during the period 1 February to 30 April 1967. During this time experiments were carried out to further define the reactions of typical system organic contaminants on metal panels with fluorine in the passivation process. Tests with fluorine at 50 psig showed greater reaction than at 15 psig but complete removal did not occur. All residues from passivation treatment of organic contaminants are impact sensitive in LF_2; some react spontaneously and violently with LF_2. Dye penetrant residues in porous cast aluminum are impact sensitive, and are not removed by usual cleaning techniques. Addition of a vacuum bake-out step in the cleaning procedure followed by GF_2 passivation does render the residues insensitive to impact in LF_2. Tungsten-contaminated aluminum (simulating tungsten inclusions in welds) is impact sensitive in LF_2. GF_2 passivation reduces the sensitivity to apparently safe levels, but the optimum passivation conditions have not been determined. Secondary corrosion of F_2-passivated metals in a high-humidity atmosphere containing a low level of HF is greater than corrosion of unpassivated specimens of the same metals. Gases adsorbed in the passive film on metals are being studied by analysing products desorbed under various conditions. Fluorine, hydrogen fluoride, oxygen and nitrogen are prominent. Conditions for complete desorption have not been defined.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fluorine						
Passivation						
Fluorinating Agents						
Chlorine Trifluoride						
Nickel Alloys						
Stainless Steel						
Aluminum Alloys						
Monel						
Contamination						
Hydraulic Fluid						
Halocarbon Grease						
Polyurethane						
Acrylic Lacquer						
Dye Penetrant						
Petroleum Jelly						
Vacuum Impregnation						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.