

COMPATIBILITY TESTING OF SPACECRAFT MATERIALS AND SPACE-STORABLE LIQUID PROPELLANTS

FINAL REPORT ADDENDUM

ΒY

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ONE SPACE PARK + RECONDO BEACH, CALIFORNIA

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1. INTRODUCTION

This document is an addendum to the Final Program Report (Reference 1) describing work performed by TRW Systems for the Jet Propulsion Laboratory under Contract 953486 during the period March 6, 1974 through May 15, 1974. The principal objective of this program was to obtain vital, long-term propellant/material of construction compatibility information for design of a liquid propulsion system using liquid fluorine or FLOX (88/12 w/w F_2/O_2 mixtures). The final report (Reference 1) provides descriptions of the new low cost method for conducting compatibility measurements at cryogenic temperatures together with the results of post test characterization of the two test materials, aluminum 2219-T87 alloy and titanium 6A1-4V alloy and the propellants after exposure durations of 36 and 45 weeks. This addendum documents the results of post test characterization after exposure durations of 61 and 70 weeks and provides an overview of the total test program through analysis of results as a function of the four exposure durations. Definitive information has been extracted from the test program regarding the compatibility of the the two test materials in the presence of liquid fluorine and FLOX. However, extended storage periods are recommended to ascertain whether these changes continue as a function of time to such an extent that they could seriously affect the reliability of the materials when used as hardware in advanced missions to outer planets which will require exposure to the propellants for periods as long as five to ten years.

1.1 OBJECTIVES

The objective of the work described in this addendum to the Final Report, Contract 953486, consisted of post test characterization of the propellants and metal test specimens which had been maintained in contact at $-320^{\circ}F + 10^{\circ}F (77^{\circ} \pm 4^{\circ}K)$ for durations of 61 and 70 weeks.

1.2 SPECIFIC TASK

The objective described above was accomplished through implementation of Task IV, Phase III and IV, Post Test Characterization activities of the propellants, test materials and interaction products on test termination. Phase III consisted of post test characterization of the following units after storage for 61 weeks:

- One (1) capsule containing aluminum and liquid fluorine
- Two (2) capsules containing titanium and liquid fluorine
- One (1) capsule containing aluminum and FLOX
- One (1) capsule containing titanium and FLOX
- One (1) capsule containing liquid fluorine
- One (1) capsule containing liquid FLOX

Phase IV consisted of the post test characterization of propellant and test specimens and the interaction products of propellants with the specimens and/or capsules of the remaining units after a total storage time of 70 weeks.

2. TASK III - POST TEST CHARACTERIZATION

2.1 PHASE III - POST TEST CHARACTERIZATION

Phase III consisted of opening five capsules after storage from 13 November 1972 to 17 January 1974 (61 weeks) containing propellant and double dogbone specimens, removing propellant for analysis, removing the specimens, analyzing the propellant residues, if present, and submitting the specimens to mechanical testing and metallurgical analysis. Also characterized were two control specimens to provide time zero information. The specimens characterized in Phase III are delineated in Table I. The specimen number corresponds to those identified in Reference 1. The methods used for the post test characterization were identical to those reported in

| | | TA | ABLE 1 | [|
|-------|-----|------|--------|------------------|
| PHASE | III | POST | TEST | CHARACTERIZATION |

| Specimen Number | Material | Liquid Propellant Exposure |
|--------------------|------------|----------------------------------|
| 7226 | Al 2219T87 | FLOX |
| 7204 | Al 2219T87 | Fluorine |
| 7228 | Ti 6A1-4V | FLOX |
| 7212 | Ti 6A1-4V | Fluorine |
| 7216 | Ti 6A1-4V | Fluorine |
| 7242 | Al 2219T87 | None (Control) |
| 7248 | Ti 6A1-4V | None (Control) |

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Reference 1 except that pitting analysis was repeated with previous specimens for the purpose of comparing pitting conditions of all specimens using the <u>same</u> observational criteria by the <u>same</u> analyst. This approach was undertaken at this time to avoid variation in judgment between individuals performing the analysis at different times which was the case in earlier work. Quantitative assessment is difficult because none of the specimens showed more than minimal superficial surface corrosion.

2.1.1 Microscopic Examination

Microscopic examination includes examination of specimen surfaces up to 32X using a stereo-microscope. Photographs showing general surface appearance of these specimens are presented in Appendix A as Figures A.1 through A.4. Except for the control specimens, all exposed specimens showed surface discolorations. A mapping of the surface appearance is better depicted in pictorial sketches presented in Appendix B as Figures B.1 through B.5. It is apparent that discoloration was more severe with titanium than with aluminum for both FLOX and F_2 exposures. Also FLOX seems to produce greater surface attacks (discoloration) than F_2 . These observations are again shown at slightly higher magnifications in Appendix C as Figures C.1 through C.11 which showed selected views of typical discolored areas.

2.1.2 Light Optical Microscopic and Scanning Electron Microscopic Examination

Microscopic examination of these specimen surfaces was conducted by using both light optical microscope and scanning electron microscope. Light optical microscope photographs are shown in Appendix D as Figures D.1 through D.6 and Scanning Electron Microscope (SEM) photographs are shown in Appendix E as Figures E.1 through E.12. In comparing the microstructures between the control specimens and the exposed specimens it is apparent that the surface topography of both titanium alloy and aluminum alloy has changed as the result of propellant exposures. The changes were not obvious with the aluminum for the following reasons:

- The aluminum alloy was not significantly affected by the exposure, and
- The aluminum specimens were initially chemically etched from acid cleaning prior to exposure.

As a general observation from these photomicrographs, vapor phase exposure seems to be less severe than liquid phase exposure. However, it is not obvious that FLOX has more or less effect on either the aluminum alloy or the titanium alloy than F_2 .

2.1.3 Pitting Analysis

Metallographic cross-sections of test specimens were used to perform quantitative pitting analysis. Typically, the profiles of the reacted surfaces are as shown in Appendix F as Figures F.1 through F.8. A field width of 0.08 cm linear surface from each specimen was analyzed by counting the number of pits and measuring the pit sizes. By assuming uniform distribution the pit concentration was calculated in 10^4 number per cm². By assuming circular cross-section on the surface the pit size was computed in 10^{-7} cm² area. The pit depth was calculated as linear height in microns, μ , $(10^{-4}$ cm). Table II summarizes results of Phase III analysis. It is difficult to draw conclusions from these results because the amount of corrosion exhibited by all specimens was extremely small. The corrosive effect on the aluminum alloy is insignificant. For the titanium alloy there seems to

| Specimen No. | Mat1 | Phase | Medium | Pit Concentration 10 ⁴ Number/cm ² | Pit Size 10 ⁻⁷ cm ² | Pit Depth µ |
|-----------------|------|---------|----------------|---|---|----------------|
| 7228 | Ti | Liquid | FLOX | 5. | 0.4 to 7. | 5. & Below |
| 7226 | Al | Liquid | FLOX | 3. | 0.1 to 4. | 4. & Below |
| 7228 | Ti | Vapor | FLOX | 0.7 | 0.8 to 5. | 8. & Below |
| 7226 | Al | Vapor | FLCX | 5. | 0.2 to 7. | 5. & Below |
| 7204 | Al | Liquid | F ₂ | 2. | 0.8 to 8. | 6. & Below |
| 7212 | Ti | Liquid | F ₂ | 4. | 0.1 to 6. | 8. & Below |
| 7216 | Ti | Liquid | F ₂ | 9. | 0.8 to 6. | 5. & Below |
| 7204 | Al | Vapor | F ₂ | 2. | 0.2 to 9. | 5. & Below |
| 7212 | Ti | Vapor | F ₂ | 0.5 | 0.2 to 3. | 4. & Below |
| 7216 | Ti | Vapor | F ₂ | 4. | 0.2 to 10. | 8. & Below |
| 7242 | A1 | Control | Vac | 0.7 | 1. to 6. | 4. & Below |
| 7248 | Ti | Control | Vac | 0.02 | 0.1 to 1. | 2. & Below |

TABLE II SUMMARY OF PITTING ANALYSIS RESULTS

be an increase in pit concentration and size as a result of exposure. However, one could not conclude readily from these results that the pitting condition becomes increasingly worse with time. One reason for this difficulty was that exposure time for these specimens may be still too short for quantitative assessment.

2.1.4 Characterization of Residues from Phase III Specimens

Table III provides the results of specimen weight measurements prior to and after propellant exposure together with analyses of the water extracted material from the surface of the specimens. These latter data were obtained to provide a basis for comparison with the studies being performed by the Boeing Company for JPL under Contract NAS7-789. These samples were obtained by washing the vapor and liquid exposed surfaces of the double dogbones and the inside surfaces of the glass capsules with 10 ml of water (adjusted pH 7.5) using a 5-ml pipet to dispense the water. After washing a minor amount of residue was retained on the specimens. These residues were examined by electron microprobe analysis as described below.

Electron microprobe analyses were performed on corrosion products and surface deposits which are easily removed from a number of specimens. Spectral scans were run on these powder samples to determine the atomic elements present. Quantitative estimates were made using the X-ray intensity results from the spectral scan data. Results are summarized in Table IV.

The white powder which showed high concentrations of Ti, O, and Si and low to medium concentrations of F, and C are most likely composed of oxides and fluorides of titanium and silicon (TiO_2, TiF_4, SiO_2) . The source of silicon was probably the glass capsules, however, no etching of the containers was observed. It is puzzling that the residue from Specimen 7216 was reddish brown in color and contained high percentage of carbonaceous material.

2.1.5 <u>Tensile Properties After Exposure</u>

Table V shows tensile test results of the Phase III specimens as well as four control (unexposed) specimens. Based on these results, it can be concluded that there were no deleterious effects on either tensile strength or ductility (elongation) of Ti-6Al-4V titanium or 2219-T87 aluminum alloys from exposure to liquid or vapor FLOX and F_2 . The tensile tested specimens as shown in Appendix G as Figures G.1 through G.4 indicated ductile fracture.

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| TABLE III | |
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| | |
| | L |

COMPOSITION OF SPECIMEN SURFACE WASHINGS FUR PHASE III CHARACTERIZATION

| [| | | | Ţ | | T | T | ភ ភ | 1 |
|-------------------|----------|--|--|--|---------------------|---------|------------|--|--------------------|
| | > | . I I I | 202 202 202 | | 111 | | ı | 1 🖓 🔗 | |
| ļ : | = | 111 | 875 175 600 | 475 75 25 | 225 50 225 | | ı | - <25 ^a <25 ^a | |
| bu M | u۳ | 6.5 7.5 2.0 | 1.0 0.5 0.5 | 0.5 0.5 0.0 | 0.5 0.0 1.0 | | U | <0.5 ^a <0.5 ^a <0.5 ^a | .002% HF |
| leight, | 5 | 000 | 111 | 8 8 1 | 1 1 1 | | 1 | ן ני עריי עריי | ined <0 |
| acted W | Ге | 200 200 1 | 87 13 89 | 87 82 4 | 168 8 158 | | ı | - 27 - 19 - 19 | nt conta |
| Extr | AI | 450 520 80 | 100 50 | 803 | 533 | | \$ | ء ما | Propellar |
| <u>ج</u> | 24 - | 10.0 10.5 10.2 | 10.3 10.5 1.0 | 275 190 10 | 15.4 18.7 3.1 | | 8 | - 2.8 0.0 | a a |
| Weight Change | g | -0.0011 | +0.0037 | -0.0006 | +0.0016 | +0.0016 | 0 | 01 1 | |
| Initial Weight | D | 3.0789 | 4.8803 | 4.8820 | 4.9396 | 3.1104 | 3.1003 | 4.8612 - - | fethod |
| Sample | Location | Al-F ₂ Liquid Al-F ₂ Gas Capsule | Ti-F ₂ Liquid Ti-F ₂ Gas Capsule | Ti-F ₂ Liquid Ti-F ₂ Gas Capsule | Ti-FLOX | A1-FLOX | Al-Control | Ti-Control F ₂ Control Capsule FLOX Control Capsule | it of Analvtical N |
| Sample | No. | 7204 | 7216 | 7212 | 7228 | 7226 | 7242 | 7248 | al im |

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| MICROPROBE ANALYSIS OF CORROSION PRODUCTS | | | | | | | | | |
|---|---|------------|-----------------|--|--|--|--|--|--|
| AND SURFACE DEPOSITS FROM PHASE ITI | | | | | | | | | |
| Specimen 7228 7228 7216 | | | | | | | | | |
| Propellant Exposure | FLOX Liquid | FLOX Vapor | Fluorine Liquid | | | | | | |
| Deposit Color | Deposit Color White White Reddish Brown | | | | | | | | |
| <u>Elemental Content</u> | | | | | | | | | |
| Oxygen | Oxygen High High - | | | | | | | | |
| Carbon | Carbon Low Medium High | | | | | | | | |
| Titanium High High High | | | | | | | | | |
| Silicon High High Medium | | | | | | | | | |
| Fluorine | Medium | Medium | Medium | | | | | | |

TABLE IV

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| TABLE V |
|---------|
|---------|

TENSILE TEST RESULTS OF PHASE III PROPELLANT EXPOSED AND CONTROL SPECIMENS

| Specimen Number | Propellant Exposure | Yield Strength KSI 0.2% Offset | Ultimate Tensile Strength, KSI | Elongation % in 1 Luch |
|--------------------|-------------------------|-----------------------------------|-----------------------------------|---------------------------|
| 7242-1 | Control-Al | 53.6 | 65.9 | 8 |
| 7242-2 | Control·Al | 54.0 | 67.6 | 9 |
| 7248-1 | Control-Ti | 140.5 | 150.4 | 13 |
| 7248-2 | Control-Ti | 140.2 | 150.0 | 13 |
| 7216 | Vapor-F ₂ | 139.4 | 150.0 | 14 |
| 7216 | Liq-F2 | 139.3 | 150.4 | 13 |
| 7228 | Liq-FLOX | 138.8 | 148.4 | 16 |
| 7228 | Vapor -F LOX | 138.9 | 150.0 | 13 |
| 7204 | Liq-F ₂ | 55.6 | 68.0 | 10 |
| 7204 | Vapor-F ₂ | 55.2 | 68.4 | 8 |
| 7226 | Liq -F LOX | 54.6 | 67.4 | 10 |
| 7226 | Vapor -F LOX | 54.8 | 67.7 · | 9 |
| 7212 | Liq-F2 | 139.3 | 149.2 | 14 |
| 7212 | Vapor-F ₂ | 138.6 | 148.4 | 15 |

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2.2 PHASE IV - POST TEST CHARACTERIZATION

Chemical-metallurgical post test characterization of Phase IV samples was implemented on tests terminated on 25 March 1974. These specimens had a total of 70 weeks storage in contact with the propellants. The specimens characterized in Phase IV are identified in Table VI.

| Specimen No. | Material | Liquid Propellant Exposure |
|-----------------|------------|----------------------------------|
| 7218 | A1-2219T87 | None (control) |
| 7246 | Ti-6A1-4V | None (control) |
| 7202 | A1-2219T87 | F ₂ |
| 7224 | A1-2219T87 | FLOX |
| 7230 | Ti-6A1-4V | FLOX |
| 7222 | A1-2219T87 | FLOX |
| 7206 | A1-2219T87 | F ₂ |
| 7236 | Ti-6A1-4V | FLOX |
| 7238 | A1-2219T87 | FLOX |

SPECIMENS CHARACTERIZED IN PHASE IV

TABLE VI

2.2.1 Microscopic Examination

Microscopic examination included examination of specimen surfaces up to 32X using a stereo-microscope as shown in Figures A.5 through A.9. Except for the two control specimens all exposed specimens showed surface discoloration. However, surface chemical attack appeared to be very superficial and there was no evidence of gross corrosion occurring in any of the specimens examined. A mapping of the surface appearance is depicted in pictorial sketches presented in Appendix B, Figures B.6 through B.10. It is apparent that discoloration was more pronounced in the titanium specimens (7230 and 7236) than with the aluminum specimens. Slightly higher magnification views are shown in Appendix C, Figures C.12 through C.27 for selected areas.

2.2.2 Light Optical Microscopic and Scanning Electron Microscope Examination

Microscopic examination of the Phase IV specimen surfaces was conducted by using both light optical microscope and scanning electron microscope (SEM). Light optical photographs are shown in Appendix D, Figures D.7 through D.14 and SEM photos are shown in Appendix E, Figures E.13 through E.28. It is apparent by comparing the SEM photos that the Ti-6A1-4V specimens exhibited a chemically etched surface as shown in Figures E.15, E.16, E.25 and E.26. There was a slight modification of the aluminum alloy surface structure although a cracked coating of unknown material was noted on aluminum specimen 7238 (Figures E.17 and E.18).

2.2.3 Pitting Analysis

Metallographic cross-sections were performed on test specimens for quantitative pitting analysis. The profiles of typical reacted surfaces are shown in Appendix F as Figures F.9 through F.26. A field width of 0.08 cm linear surface as examined at 400 - 1000X was used for pit counts and pit size determinations. By assuming uniform distribution the pit concentration was calculated in number of pits per cm². By assuming circular pit geometry on the surface, the pit size was computed in cm² area. The pit depth was calculated as linear height in μ . Table VII summarizes results of pitting analysis for the Phase IV specimens.

2.2.4 Characterization of Residues from Phase IV Specimens

Table VIII provides the results of Phase IV specimen weight changes and characterization of 10 ml water extractions of the test specimens and glass capsules to determine the build-up of metals on the specimen surfaces. The procedure for extraction of the specimens was described in Section 2.1.4.

Electron microprobe analyses were performed on corrosion products and surface deposits that were easily removed from a number of specimens. Spectral scans were run on these powder samples which had been air dried at room temperature. Semi-quantitative estimates were made for each detectable element using the X-ray intensity outputs. Results are summarized in Table IX. The white powder from Specimen 7238 is most likely an oxide or hydroxide of aluminum. The deposits (both white and black) from Specimen 7236 are probably different forms of mixed oxides of Ti and Si. The high oxygen content

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| Spec. No. | Alloy | Exposure | Medium | Pit Concentrati 104 Number/cm ² | on P | it Size 10 ⁻⁷ cm ² | Pit Depth µ |
|--------------|-------|-------------|----------------|---|------|--|----------------|
| 7246 | Ti | (Control-1) | Vac | 0.05 | 0.1 | to 0.3 | 0.9 & Below |
| | Ti | (Control-2) | Vac | 0.3 | 0.03 | to 0.3 | 3. & Below |
| 7202 | A1 | Vap | F ₂ | 3 | 0.03 | to 3 | 4. & Below |
| | A1 | Liq | F ₂ | 7 | 0.1 | to 6 | 6. & Below |
| 7224 | A1 | Vap | FLOX | 3 | 0.03 | to 1 | 6. & Below |
| | A1 | Liq | FLOX | 2 | 0.1 | to 6 | 6. & Below |
| 7230 | Ti | Vap | FLOX | 5 | 0.0 | to 5 | 2. & Below |
| | Ti | Liq | FLOX | 7 | 0.1 | to 50 | 4. & Below |
| 7222 | A1 | Vap | FLOX | 3 | 0.3 | to 3 | 6. & Below |
| | A1 | Liq | FLOX | 3 | 0.5 | to 6 | 4. & Below |
| 7206 | A1 | Vap | F ₂ | 3 | 0.1 | to 5 | 7. & Below |
| | A1 | Liq | F ₂ | 4 | 0.03 | to 6 | 9. & Below |
| 7236 | Ti | Vap | FLOX | . 4 | 0.1 | to 8 | 4. & Below |
| | Ti | Liq | FLOX | 9 | 1.0 | to 60 | 8. & Below |
| 7238 | A1 | Vap | FLOX | 3 | 0.1 | to 7 | 6. & Below |
| | A1 | Liq | FLOX | 3 | 0.3 | to 8 | 5. & Below |
| 7218 | A1 | (Control-1) | Vac | 2 | 0.1 | to 6 | 4. & Below |
| | A1 | (Control-2) | Vac | 2 | 0.03 | to 6 | 5. 2 Below |

TABLE VII SUMMARY OF PHASE IV PITTING ANALYSIS RESULTS '

found in the gray-black deposit from Specimen 7202 may be due to formation of aluminum oxide after exposing the specimen to air. It is not likely that the F_2 environment or the etched glass capsule is the source of such high oxygen content in the surface deposit.

2.2.5 <u>Tensile Properties</u>

Table X shows tensile test results of the Phase IV group of exposed specimens as well as two control (unexposed) specimens. Two tensile test specimens were derived from each double dogbone specimen. Based on these results as well as results from previous reports in this program the same conclusion may be drawn; that is, there were no deleterious effect on either the

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TABLE VIII

COMPOSITION OF SPECIMEN WASHINGS FOR PHASE IV SAMPLES

| | | Initial | Weight | | Ext | racted W | eight, | 6 4 | | بين ميني 1997 - ميني |
|-----------------|-----------------------------------|--------------|--------------|----------------|--------------|-------------|------------------|-------------|------------|-------------------------|
| Specimen No. | Specimen Location | Weight, g | Change, g | Fa | Al | Fe | 5 | Mn | 1i | > |
| 7202 | Al-F2 Liquid | 3.0892 | +0.0026 | 4- | 2600 2700 | 120 134 | ~- | <0.5 5.0 | 11 | 1 L |
| | Al-F ₂ uas Capsule | | | 10 | 630 | 10 | | <6.0 | 1 | 1 |
| 7206 | Al-F ₂ Liquid | 3.0604 | -0.0004 | ، ۲ | 1080 | 142 164 | <u> </u> | <0.5 4.0 | 11 | 1 1 |
| | Al-F ² Gas Cansule | | | ~ ~ | 210 | 16 | - ~ | 2.0 | 1 | 1 |
| 6665 | Al-FLOX Liquid | 3.0466 | +0.0008 | 10 | 1270 | 150 | ~~ | 2.0 2.0 | I 1 | 1 1 |
| 1 | A1-FLOX Gas | | | 010 | 1000 | 8 8 8 | | 0.5 | | ı |
| | rapsu re | | | | 5300 | 001 | ø | 7.5 | 1 | ł |
| 7224 | Al-FLOX Liquid | 3.0265 | 1700.04 | 01 | 5300 | 86 |]= | 6.0 | I | 1 |
| | Al-FLUX Gas Cansule | | | := | 550 | 10 | 2 | 7.0 | 1 | I |
| 1 | | 2 007E | 9000 | ~ | 950 | 114 | 2 | <0.5 | ı | 1 |
| 7238 | Al-FLOX LIQUID | 3.00/0 | | 10 | 1830 | 138 | m | °0.5 | ı | 1 |
| | AI-FLUX GAS | | | 10 | 150 | ω | 2 | <0•5 <0 | ı | 1 |
| | | A 8008 | -0.0012 | 10 | 150 | 52 | 2 | <0.5 .0 | 300 | |
| /230 | Ti-FLOX Gas | |))) | 01 | 100 | 52 | ، س ر | ⊖ < v. r | <10 <10 | |
| | Capsule | | | רכ | 230 | 7 | 1 I | | | JEO |
| 7236 | Ti-FLOX Liquid | 4.8965 | -0.0013 | ດເ | 2000 | 72 | | °.0 €.5 | | 001 |
| | Ti-FLOX Gas | | | 10 | 600 | 12 | ~ ~ | <0.5 | 400 | <10 |
| 0102 | Al_Control | 3,0696 | 0 | ı | I | 1 | I | ١ | I | 1 |
| 017/ | | A OAED | C. | 1 | I | 1 | ı | I | ı | I |
| 7246 | Ti-Control | 4.0409 | þ | | | | | ļ | ſ | C F |
| | F ₂ Control Cancule | | | - | 260 | 30 | \ | <0.5 | | 2 |
| | FLOX Control | | | 7 | 290 | 8 | 27 | <0.5 | <10 | <10 |
| | capsule | | | | | | | | | |

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^aPropellant contained <0.002% HF

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| Specimen No. | 7202 | 7238 | 7236 | 7236 |
|---------------------|-----------------------|-------------|------------|------------|
| Propellant Exposure | F ₂ Liquid | FLOX Liquid | FLOX Vapor | FLOX Vapor |
| Deposit Color | Gray-black | White | White | Black |
| Elemental Content | | | | |
| 0 | High | High | High | High |
| Fe | Medium | Low | Low | - |
| Ti | - | - | High | High |
| A1 | High | High | Low | Medium |
| F | High | Low | Low | Low |
| V | - | - | - | Low |
| Si | Medium | Medium | High | High |

TABLE IX MICROPROBE ANALYSIS OF CORROSION PRODUCTS AND SURFACE DEPOSITS

tensile strength or ductility (elongation) of Ti-6Al-4V and Al-2219T87 alloy from liquid or vapor FLOX and F_2 exposures. The tensile tested specimens, shown in Appendix G as Figures G.5 through G.9 indicated ductile fracture.

3. CONCLUSIONS AND RECOMMENDATIONS

Subtle changes in the extent of chemical compatibility of aluminum and titanium alloys with FLOX and fluorine propellants over exposure periods up to 70 weeks have been detected. Gross properties, such as mechanical properties, were not significantly affected during the storage period. The most significant changes were observed on a microscale regarding the extent of chemical compatibility through an analysis of the pitting results as a function of storage time. These results are summarized in Table XI. This table lists both the pit concentration and pit size as a function of exposure duration, specimen type, and exposure environment.

Inspection of Table XI reveals that a great deal of variability exists between replicate analyses which tends to minimize the number of clear-cut conclusions which can be drawn from the data. However, the following general trends can be inferred from the Table XI data:

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| Specimen No. | Alloy | Propellant Exposure | Yield Strength Ksi 0.2% Offset | Ultimate Tensile Strength, Ksi | Elongation % in l-inch |
|-----------------|-------|------------------------|---|---|---------------------------|
| 7246-1 | Ti | Control | 141.2 | 150.0 | 17 |
| 7246-2 | Ti | Control | 141.8 | 149.6 | 13 |
| 7218-1 | Al | Control | 55.6 | 68.4 | 10 |
| 7218-2 | Al | Control | 55.6 | 68.4 | . 9 |
| 7202L | A1 | F ₂ | 54.7 | 67.7 | 10 |
| 7202V | Al | F_2 | 54.2 | 67.4 | 11 |
| 7206L | A٦ | $\overline{F_2}$ | 54.2 | 67.6 | 9 |
| 7206V | Al | F_2 | 54.4 | 67.5 | 9 |
| 7222L | Al | FLOX | 55.3 | 68.3 | 9 |
| 7222V | A1 | FLOX | 55.1 | 68.2 | 9 |
| 7224L | A1 | FLOX | 55.3 | 68.2 | 10 |
| 7224V | A1 | FLOX | 54.0 | 66.8 | 10 |
| 7230L | Ti | FLOX | 140.5 | 150.0 | 14 |
| 7230V | Ti | FLOX | 138.6 | 149.2 | 15 |
| 7236L | Ti | FLOX | 141.9 | 152.9 | 15 |
| 7236V | Ti | FLOX | 142.3 | 151.1 | 16 |
| 7238L | A1 | FLOX | 54.3 | 67.5 | 10 |
| 7238V | Al | FLOX | 55.5 | 68.5 | 11 |

TABLE X TENSILE TEST RESULTS

TABLE XI SUMMARY OF PITTING AS A FUNCTION OF EXPOSURE DURATION

| | | | | | | Exposure Dura | ation, weeks | | | |
|----------|----------|----------|---|--|---|------------------------------|---|---|---|--|
| | | | 'n | | 4 | 15 1 | Q | | 12 | 0 |
| Material | Exposur | <u>و</u> | Conc. 19 ⁴ No/cm ² | Size 10 ⁻⁷ cm ² | Conc. 10 ⁴ No/cm ² | Size 10 ⁻⁷ cm2 | Conc. 10 ⁴ No/cm ² | Size 10 ⁻⁷ cm ² | Conc. 10 ⁴ No/cm ² | Size 10 ⁻⁷ cm ² |
| | Vac | mun | | | | | 0.02 | 0.1 - 1. | 0.05 0.3 | 0.1 - 0.3 0.03 - 0.3 |
| ٨ | | Liquid | | | 3. | 61 - 7 6 | 4. 9. | 0.1 - 6 0.8 - 6 | | |
| ₽~FAð | Fluorine | Vapor | | | ъ. | 9.2 - 7 | 7.5 4. | $\begin{array}{ccc} 0.2 & - & 3\\ 0.2 & - & 10\\ \end{array}$ | | |
| Rutaet | | Liquid | 4. | 9.5 - 2. | 2. | 0.1 - 3n | 5. | 0.4 - 7. | 7. 9. | 3.1 - 50. 1 60. |
| ÷1 | FLOX | Vapor | 2. | 0.1 - 1. | э. | 0.1 - 8 | 9.7 | 0.8 - 5. | 5. 4. | 0.1 - 5. 0.1 - 5. |
| | Vac | uur. | | | | | 0.7 | 1 6. | 2. 2. | 9.1 - 6. 0.03 - 6. |
| Ĺ | | Liquid | | | 0.7 | 0.ī - 3. | 2. | 0.8 - 8. | 7. 4. | 0.1 - 6. 0.03 - 6. |
| 810122 | Fluorine | Vapor | | | 0.2 | 0.1 - 1. | 2. | 0.2 - 9. | 3. 3. | $\begin{array}{rrrr} 0.03 &- & 3.\\ 0.1 &- & 5. \end{array}$ |
| տուլտոլ | | Liquid | | | 0.1 | 0.4 - 33 | з. | 0.1 - 4. | | 0.1 - 6. 0.5 - 6. 0.3 - 8. |
| ¥ | FLOX | Vapor | | | 0.3 | 0.1 - 8. | 0.7 | 9.8 - 5. | | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |

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-14-

- Corrosive attack is extremely small on Ti-6Al-4V and Al-2219T87 alloys in liquid or vapor fluorine and FLOX environments for exposure as long as 70 weeks.
- The degree of corrosive attack appears to be more severe in the FLOX environment than in the fluorine environment.
- There appears to be a trend showing that A1-2219T87 is more corrosion resistant than Ti-6A1-4V in FLOX environments.
- Inconclusive data exist regarding the comparative resistance between the two metals in fluorine environment.
- The pitting condition of FLOX exposed Ti-6Al-4V appears to worsen with time, particularly in terms of pit size. The pit diameter was increased by two orders of magnitude after 16 months.

The findings of this program, particularly the differences of pitting as a function of storage duration provide the basis for the recommendation to extend the storage duration to improve on the definition of the effects of storage time. Clearly, the 70-week durations are insufficient to ascertain whether the observed corrosive phenomena rate levels off or accelerates as a function of time. These key data are needed to obtain unequivocal evidence to make valid extrapolations for hardware commitments of advanced missions to outer planets.

APPENDIX A MICROSCOPIC EXAMINATION OF SPECIMENS

This appendix contains photographs of microscope examination of the nine test specimens.



Figure A.1 Control Test Specimens

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Aluminum - Fluorine - Side Two



-18-







-19-



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7216

Titanium - Fluorine - Side Two Figure A.4. Tensile Test Specimens After Propellant Immersion



Figure A.5. Tensile Test Specimens After Vacuum Exposure

-21-





-22-





Figure A.7. Tensile Test Specimens After Propellant Exposure

-23-

Aluminum - Flox - Side 1

| 722 | 4 |
|----------------------------|--------|
| | |
| VAPOR | LIQUID |
| | 5) |
| 720 | 6 |
| Aluminum - Fluorine - Side | e 1 1X |

Aluminum - Flox - Side 2



Aluminum - Fluorine - Side 2IXFigure A.8. Tensile Test Specimens After Propellant Exposure

-24-





Figure A.9. Tensile Test Specimens After Propellant Exposure

-25-

Mapping of Surface Appearance of Double Dogbone Specimen No. 7212 (Ti-6A1-4V) After Exposure to Fluorine

Figure B.1.

APPENDIX B PICTORIAL SKETCHES OF POST TEST SPECIMENS

This appendix contains ten pictorial sketches of post test specimens.



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Mapping of Surface Appearance of Double Doggone Specimen No. 7204 (2219-T87 A1) After Exposure to Fluorine Figure B.3.

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SPECIMEN NO. 7228

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Mapping of Surface Appearance of Double Dogbone Specimen No. 7228 (Ti-6Al-4V) After Exposure to FLOX Figure B.5.

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Figure B.6. Mapping of Surface Appearance of Double Dogbone Specimens 7202 and 7230 After Exposure

Specimen No. 7202 - Al-2219T87 - Fluorine

-32-



Figure B.7. Mapping of Surface Appearance of Double Dogbone Specimens 7224 and 7236 After Exposure

-33-



Figure B.8. Mapping of Surface Appearance of Double Dogbone Specimens Nos. 7222 and 7238 After Exposure

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-34--


Figure B.9. Mapping of Surface Appearance of Double Dogbone Specimens Nos. 7206 and 7246 After Exposure

Specimen No. 7206 - Al-2219T87 - Fluorine

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-35-







APPENDIX C

SELECTED VIEWS OF TYPICAL DISCOLORED AREAS OF SPECIMENS

This appendix contains twenty-seven 8X and 32X of selected discolored areas of test specimens.



-37-



Figure C.2. Specimen No. 7226 - A1-2219T87 - FLOX Vapor Exposure

-38-



32X



-39-



Figure C.4. Specimen No. 7204 - Al-2219T87 - Fluorine Vapor Exposure





32X Figure C.5. Specimen No. 7204 - Al-2219T87 - Fluorine Liquid Exposure



(b) 32X Figure C.6. Specimen No. 7212 - Ti-6A1-4V - Fluorine Vapor Exposure

-42-



Figure C.7. Specimen No. 7212 - Ti-6A1-4V - Fluorine Liquid Exposure

-43-



(b)

Figure C.8. Specimen No. 7216 - Ti-6A1-4V - Fluorine Vapor Exposure

-44-





-45-





Figure C.10. Specimen No. 7228 - Ti-6A1-4V - FLOX Vapor Exposure



(a)



Figure C.11. Specimen No. 7228 - Ti-6A1-4V - FLOX Vapor Exposure



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-48-



(A) Ti-6Al-4V Specimen No. 7246



(B) A1-2219T87 Specimen No. 7218
Figure C.13. Control Specimens (32X)

-49-



Figure C.14. Specimen No. 7202 - A1-2219T87- FLOX Liquid Exposure

- 50 -



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Figure C.15. Specimen no. 7202 - Al-2219T87 - FLOX Vapor Exposure

-51.-



Figure C.16. Specimen No. 7206 - A1-2219T87 - Fluorine Liquid Exposure



Figure C.17. Specimen No. 7206 - A1-2219T87 - Fluorine Vapor Exposure

-53-



(A)



(B) 32X Figure C.18. Specimen No. 7236 - Ti-6A1-4V - FLOX Liquid Exposure









8X



-55-



(B)

Figure C.20. Specimen No. 7222 - A1-2219T87 - FLOX Liquid Exposure



(B)

Figure C.21. Specimen No. 7222 - A1-2219T87 - FLOX Vapor Exposure





Figure C.22. Specimen No. 7238 - A1-2219T87 - FLOX Liquid Exposure

-58-



Figure C.23. Specimen No. 7238 - A1-2219T87 - FLOX Vapor Exposure





Figure C.24. Specimen No. 7224 - A1-2219T87 - FLOX Liquid Exposure

-60-





Figure C.25. Specimen No. 7224- A1-2219T87 - FLOX Vapor Exposure

-61-



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Figure C.26. Specimen No. 7230 - Ti-6A1-4V - FLOX Liquid Exposure

-62-





(B)

32X

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Figure C.27. Specimen No. 7230 - Ti-6A1-4V - FLOX Vapor Exposure

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APPENDIX D

DETAILED MICROSCOPIC EXAMINATION OF TEST SPECIMENS

This appendix contains fourteen photographs of vapor and liquid exposed sections of the test specimens at 400X magnification.



(b) Surface Structure of Control Specimen No. 7242 - Al-2219-T87

Figure D.1. Surface Microstructure of Control Specimens

-65-

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(b)

Figure D.2. Surface Microstructures of Vapor Side (a) and Liquid Side (b) of Specimen No. 7226 Al-2219T87 - (FLOX Exposure)



(a)



400X



-67-



(a)



(b)

400X

Figure D.4. Surface Microstructure of Vapor Side (a) and Liquid Side (b) of Specimen No. 7212 Ti-6A1-4V - (Fluorine Exposure)



(a)



400X

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(b)



(a)



400X

400X

Figure D.6. Surface Microstructure of Vapor Side (a) and Liquid Side (b) of Specimen No. 7228 Ti-6A1-4V - (FLOX Exposure)

-70-



(a) Specimen 7218 A1-2219T87



400X (b) Specimen 7246 Ti-6A1-4V

Figure D.7. Surface Microstructure of Control Specimens -71-


Figure D.8. Surface Microstructures of Vapor Side (A) and Liquid Side (B) of Specimen No. 7230 - Ti-6A1-4V - (FLOX Exposure)



(A)



(B)

400X

Figure D.9. Surface Microstructures of Vapor Side (A) and Liquid Side (B) of Specimen No. 7206 - A1-2219T87 - (Fluorine Exposure)



Figure D.10. Surface Microstructures of Vapor Side (A) and Liquid Side (B) of Specimen No. 7202 - A1-2219T87 - (Fluorine Exposure)





Figure D.il. Surface Microstructures of Vapor Side (A) and Liquid Side (B) of Specimen No. 7236 - Ti-6Al-4V - (FLOX Exposure)



Figure D.12. Surface Microstructures of Vapor Side (A) and Liquid Side (B) of Specimen No. 7238 - A1-2219T87 - (FLOX Exposure)



(A)



Figure D.13. Surface Microstructures of Vapor Side (A) and Liquid Side (B) of Specimen No. 7222 - A1-2219T87 - (FLOX Exposure)

-77-



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Figure D.14. Surface Microstructures of Vapor Side (A) and Liquid Side (B) of Specimen No. 7224 - A1-2219T87 - (FLOX Exposure)

-78-

APPENDIX E

SCANNING ELECTRON MICROSCOPE EXAMINATION OF TEST SPECIMENS

This appendix contains twenty-eight scanning electron microscope figures of propellant test specimens.





-79-

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(b) 500X Figure E.2. SEM Photo of Surface of Specimen No. 7242 Aluminum Control

-80-





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(b) 500X



-81-



(a) 250X



(b) 500X





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(a) 250X



(b) 500X



-83-



(a) 250X



(b) 500X





(a) 250X



(b) 500X

Figure E.7. SEM Photo of Surface of Specimen No. 7212 Ti-6A1-4V - Fluorine Vapor Exposure

-85--

47.989 P.72



(a) 250X





-86-



(a) 250X



Figure E.9. SEM Photo of Surface of Specimen No. 7228 Ti-6A1-4V - FLOX Vapor Exposure





(b) 500X

Figure E.10. SEM Photo of Surface of Specimen No. 7228 Ti-6A1-4V - FLOX Liquid Exposure





(b) 500X



-89- -----

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(b) 500X



-90-



Figure E.13. SEM Photo of Surface of A1-2219T87 Control Specimen No. 7218

-91-



Figure E.14. SEM Photo of Surface of Ti-6A1-4V Control Specimen No. 7246

-92-



Figure E.15. SEM Pholo of Surface of Ti-6A1-4V Specimen No. 7230 (FLOX Liquid Exposure)

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Figure E.16. SEM Photo of Surface of Ti-6Al-4V Specimen No. 7230 (FLOX Vapor Exposure)

-94-

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Figure E.17. SEM Photo of Surface of Al-2219T87 Specimen No. 7238 (FLOX Liquid Exposure)

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-95-



Figure E.18. SEM Photo of Surface of A1-2219T87 Specimen No. 7238 (FLOX Vapor Exposure)



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Figure E.20. SEM Photo of Surface of A1-2219T87 Specimen No. 7224 (FLOX Vapor Exposure)

-98-



500X

Figure E.21. SEM Photo of Surface of A1-2219T87 Specimen No. 7222 (FLOX Liquid Exposure)



(B)

500X

Figure E.22. SEM Photo of Surface of A1-2219T87 Specimen No. 7222 (FLOX Vapor Exposure)



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Figure E.23. SEM Photo of Surface of A1-2219T87 Specimen No. 7206-A1 (Fluorine Liquid Exposure)

-101-



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SEM Photo of Surface of A1-2219T87 Specimen No. 7206 (Fluorine Liquid Exposure) Figure E.24.

-102-

500X



Figure E.25. SEM Photo of Surface of Ti-6A1-4V Specimen No. 7236 (FLOX Liquid Exposure)

-103-



Figure E.26. SEM Photo of Surface of Ti-6A1-4V Specimen No. 7236 (FLOX Vapor Exposure)



-105-



Figure E.28. SEM Photo of Surface of A1-2219T87 Specimen No. 7202 (Fluorine Liquid Exposure)

-106-

APPENDIX F

METALLOGRAPHIC CROSS-SECTION OF PRE- AND POST TEST SPECIMENS

This appendix provides twenty-six figures of metallographic crosssection of pre- and post test specimens.



Figure F.1. Cross-section of FLOX Vapor Exposed Portion of Specimen No. 7226 (A1-2219T87) Showing Reacted Surface Profile

-107-




-109-





Figure F.5. Cross-section of Fluorine Vapor Exposed Portion of Specimen No. 7204 (A1-2219T87) Showing Reacted Surface Profile

-111-



← Aluminum



Figure F.6. Cross-section of Fluorine Liquid Exposed Portion of Specimen No. 7204 (Al-2219T87) Showing Reacted Surface Profile

-112-



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Titanium

- 0.000 CM

400X

1000X

Nickel Plate Reacted Surface

Titanium

E 0.000 CM E 0.001 CM E 0.002 CM

0.005 CM

Figure F.9. Cross-Section of Ti-6A1-4V Control Specimen No. 7246-1.

-115-

Nickel Plate Reacted Surface Titanium - 0.000 CM t 0.005 см 400X Nickel Plate Reacted Surface Titanium E 0.000 CM E 0.001 CM E 0.002 CM 1000X

Figure F.10. Cross-Section of Ti-6A1-4V Control Specimen No. 7246-2

-116-



-117-







Figure F.14. Cross-section of Fluorine Vapor Exposed Portion of Specimen No. 7206-Al Showing Reacted Surface Profile.

-120-





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75

Nickel Plate Reacted Surface

Titanium





-122-



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1000X

Figure F.20. Cross-Section of Fluorine Vapor Exposed Portion of Specimen No. 7202 Showing Reacted Surface Profile

-126-

4.40



-127-



-128-





-130-







Figure F.26. Cross-Section of FLOX Vapor Exposed Portion of Specimen No. 7224 Showing Reacted Surface Profile

APPENDIX G POST TENSILE TEST SPECIMENS

This appendix contains nine figures of post tensile test specimens prior to and after propellant exposure.



Titanium 1.3X





-133-



Aluminum - Fluorine 1.3X



-134-



Aluminum - FLOX 1.3X

7216 V

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17216 L

Titanium - Fluorine 1.3X Figure G.3. Tensile Tested Specimens -135-



Titanium - Fluorine 1.3X



Aluminum - FLOX 1.3X Figure_G.4._ Tensile Tested Specimens

-136-

4, 1

7218 VACUUM 7218 VACUUM ∿ 1.3X Aluminum - Vacuum (Control)

1



Titanium - Vacuum (Control) \sim 1.3X Figure G.5. Tensile Tested Coupons

7230LIQUID





Titanium - FLOX

 $\sim 1.3X$



Figure G.6. Tensile Tested Coupons

-138-



Figure G.7. Tensile Tested Coupons

-139-



7202 LIQUID



Aluminum - Fluorine \sim 1.3X Figure G.8. Tensile Tested Coupons

-140-



Aluminum - FLOX \sim 1.3X

Figure G.9. Tensile Tested Coupons