NASA CONTRACTOR
REPORT

NASA CR-161431

STUDY OF ETCHANTS FOR CORROSION-RESISTANT METALS, SPACE SHUTTLE EXTERNAL TANK

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(NASA-CR-161431) STUDY OF ETCHANTS FOR CORROSION-RESISTANT METALS, SPACE SHUTTLE EXTERNAL TANK (Martin Marietta Aerospace) 26 p HC A03/MF A01 CSCL 11F

N80-25414

Unclas
G3/26 22418

January 11, 1980

Prepared for

NASA-George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

NASA CR-161431

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January 11, 1980

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MATERIALS ENGINEERING

TEST REPORT

NO. ETTR-52

Revision A

METAL ETCHANTS PRIOR TO PENETRANT INSPECTION

JANUARY 11, 1980

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1.0 INTRODUCTION

All metal parts, materials, and welds which are mechanically disturbed and require penetrant inspection must be etched prior to that inspection step. Etching removes metal smears that might mask defects.

Metals used in the Space Shuttle External Tank(ET) which require etching prior to penetrant inspection are aluminum alloys, austenitic stainless steels, nickel base alloys, and titanium alloys (annealed). Etchants for austenitic stainless steels, nickel base alloys, and titanium alloys were selected for evaluation in this study after a review of applicable MMC, Boeing, McDonnell Douglas and Rockwell International specifications (References 1-10).

2.0 OBJECTIVES

The objectives of this program were to study and formulate acceptable etchant concentrations and application and removal procedures for etching austenitic stainless steel, nickel base alloys and titanium alloys (annealed) employed on the ET.

The etchant solutions were to be capable of removing a minimum of 0.4 mils of surface material in less than one hour, at a rate such that control could be exercised.

3.0 CONCLUSIONS

3.1 There was no intergranular attack of 6AL-4V titanium, 21-6-9, A-286, or Inconel 718 by the solutions tested, given the respective processing conditions.

3.2. 6AL-4V:

The standard HNO_3/HF solution, paragraph 5.2.1, can be effectively utilized to remove 0.4 mils surface material in less than one hour; see tables I thru IV for etchant solution, technique, and rate.

3.3. Inconel 718:

Two solutions, $HCl/HNO_3/NiCl_2/FeCl_3/CrO_3$, paragraph 5.2.3, and HCl/H_2O_2, paragraph 5.2.4, can be effectively utilized to remove 0.4 mils surface material in less than one hour; see tables VII and IX for respective etchant solution, technique, and rate.

3.4. A-286 and 21-6-9:

Three solutions $FeCl_3/HNO_3/H_3PO_4$, paragraph 5.2.2, $HCl/HNO_3/NiCl_2/FeCl_3/CrO_3$, paragraph 5.2.3, and HCl/H_2O_2, paragraph 5.2.4, can be effectively utilized to remove 0.4 mils surface material in less than one hour; see tables VI, VII, and IX for respective etchant solution, technique, and rate.

3.5. Cab-O-Sil was a satisfactory thickener for solutions $FeCl_3/HNO_3/H_3PO_4$, paragraph 5.2.2, and $HCl/HNO_3/NiCl_2/FeCl_3/CrO_3$, paragraph 5.2.3, reducing etch rate.

4.0 RECOMMENDATIONS

The MMC specification governing etching of studied materials should be appropriately revised per the study conclusions.

5.0 MATERIALS

5.1 Specimens - Metal specimens, 1½" x 3" were made from 0.25" 6AL-4V titanium, 0.25" 718 Inconel, 0.063 A-286 CRES and 0.040" 21-6-9 CRES. Specimens were alkaline cleaned prior to etchant tests.

5.2 Etchant Solutions - Etchant solutions were made up from technical and reagent grade chemicals to obtain the given make-up for each solutions except Pasa-Jell 101 which is a proprietary solution. These solutions are described as follows.

5.2.1 Standard HNO_3/HF

5.2.1.1 Solution Make-Up

Chemical	A	B	C	D
HNO_3 (42°Bé), fl oz/gal	40	60	40	60
HF (70%), fl oz/gal	2.7	2.7	6.4	6.4
Water, DM	Balance			
Temperature, °F	75/140			

5.2.1.2 Portions of solutions B and C were also thickened with Cab-O-Sil to brush consistency and used at 75°F.

5.2.2 $FeCl_3/HNO_3/H_3PO_4$

5.2.2.1

Solution Make-Up Chemical	Amount
$FeCl_3$, fl oz/gal	57.5
HNO_3, fl oz/gal	19.3
H_3PO_4, fl oz/gal	9.6
Water, DM	Balance
Temperature, °F	75/140

5.2.2.2 A portion of the above solution was also thickened with Cab-O-Sil and used at 75°F.

5.2.3 $HCl/HNO_3/NiCl_2/FeCl_3/CrO_3$

5.2.3.1 Solution Make-Up Chemical	Amount
HCl, fl oz/gal	75
HNO_3, fl oz/gal	10.3
$NiCl_2$ $6H_2O$, oz/gal	1.28
$FeCl_3$, fl oz/gal	46
CrO_3, oz/gal	51
Water, DM	Balance
Temperature, °F	75/140

5.2.3.2 A portion of the above solution was also thickened with Cab-O-Sil and used at 75°F.

5.2.4 HCl/H_2O_2

Solution Make-Up: 50% HCl (20°Be') and 50% H_2O_2 (30% Stabilized).

5.2.5 Low HNO_3/HF No. 1

5.2.5.1 Solution Make-Up Chemical	Amount
HNO_3, fl oz/gal	12.8
HF, fl oz/gal	3.8
Water, DM	Balance
Dissolved Ti, oz/gal	.3
Temperature, °F	75/140

5.2.5.2 A portion of the above solution was thickened with Cab-O-Sil and used at 75°F.

5.2.6 Low HNO_3/HF No. 2

5.2.6.1 Solution Make-Up

Chemical	A	B	C	D
HNO_3 (42°Bé), fl oz/gal	20	20	20	20
HF (70%), fl oz/gal	5	5	2.6	2.6
Iron (Fe), oz/gal	---	3.4	1.0	3.4
Wetting Agent, Dynes/cm (See 5.2.7.3)	---	--- 31-32	--- 31-32	---
Water, DM		Balance		
Temperature, °F		75°F		

5.2.6.2 A portion of solution B was thickened with Cab-O-Sil and used at 75°F.

5.2.7.3 The surface tension of two portions of solutions B and C were reduced with Ultrawet K (Atlantic-Richfield) to 31-32 dynes/cm and the solutions used at 75°F.

5.2.7 Pasa-Jell 101 - This is a proprietary blend of mineral acids, activators and inhibitors. It is of brush consistency and used at 75°F. (Products Research and Chemical Corporation)

6.0 TEST PROCEDURES

Duplicate specimens of each metal were weighed prior to and after etching in each solution at different temperatures and times. The etch rates were then determined by weight difference. Results are recorded in Table I through Table XIII. The absence of intergranular attack was determined by direct observation and 10X magnification.

7.0 DISCUSSION OF RESULTS AND CONCLUSIONS

7.1 Intergranular Attack - There was no intergranular attack of any metal surfaces tested by the solutions and respective processing conditions.

7.2 Thickening Agents - Two thickening agents were tried; barium sulfate and Cab-O-Sil.

7.2.1 Barium sulfate was quickly discounted after the first use. A large amount is required to provide a thickened version which remains thickened after application. The resultant mixture is very unreactive. Reducing the amount of barium sulfate to achieve reasonable etch rates results in a mixture that separates too easily for practical use.

7.2.2 Cab-O-Sil was found satisfactory for solutions 5.2.2, 5.2.3, 5.2.5 and 5.2.6 (Tables VI, VII, VIII and XI). It appears that for solutions 5.2.1 (Tables II and III) where the HF/HNO_3 ratio is greater than 1 to 7, too much of the HF is neutralized by Cab-O-Sil (silica). All solutions were thickened at the time of use and not stored.

7.3 Etchant Effects - The criterion for selected etchants was that each should be capable of removing .4 mil/side in less than one hour.

7.3.1 Standard Nitric/Hydrofluoric Acids Solutions (See Tables I through IV).

a) The criterion was met for 6AL-4V titanium.
b) The criterion was not met for A-286 and Inconel 718, except for A-286 at 140°F (Table IV conditions). No test was performed on 21-6-9, which is expected to behave like A-286.

7.3.2 Pasa-Jell 101 (Table V). This solution was totally ineffective on 6Al-4V titanium, A-286, 21-6-9 and Inconel 718.

7.3.3 $FeCl_3/HNO_3/H_3PO_4$ (Table VI).

a) The criterion was met for A-286, 21-6-9, by both immersion and brush application (non-thickened and thickened with Cab-O-Sil), although the etch rate of the thickened version was considerably reduced.
b) This solution was totally ineffective on 6AL-4V and Inconel 718.

7.3.4 $HCl/HNO_3/NiCl_2/FeCl_3/CrO_3$ (Table VII)

a) The criterion was met for A-286, 21-6-9, and Inconel 718 by both immersion and brush application (non-thickened and thickened with Cab-O-Sil). The etch rate of the thickened version was also reduced.
b) An activation step (depassivation) is required in HCl solution (30-50 oz/gal) prior to etching.
c) This solution was ineffective on 6AL-4V titanium.

7.3.5 Low HNO_3/HF (Table VIII)

a) This solution greatly exceeded the criteria for 6AL-4V titanium by immersion and should not be considered safe for use on titanium.
b) The thickened version (Cab-O-Sil) was satisfactory for 6AL-4V titanium.
c) The criterion is not met for A-286 at 75°F or Inconel 718 at 75°F or 140°F.
d) The solution could be heated for use on A-286.

7.3.6 Low HNO_3/HF (Tables X through XIII)

a) The criterion was met for 6AL-4V titanium. The etch rate varied considerably, and for the solution with low HF and high Fe build-up (Table XIII) it was reduced below the criterion.

b) Brush application of the non-thickened version was satisfactory but the thickened version was ineffective (Table XI).

c) Reducing the surface tension reduced the etch rate (Table XI).

7.3.7 HCl/H_2O_2 (Table IX)

a) The criterion is met in less than two minutes immersion for A-286, 21-6-9 and Inconel 718.

b) This is a rather unstable solution but can be used effectively by immersion or brush application.

8.0 REFERENCES

1. Martin Marietta Aerospace STP 5007, Cleaning, Descaling, and Passivation of Corrosion and Heat Resistant Steels and Nickel Alloys.

2. Boeing BAC 5751, Cleaning, Descaling and Surface Preparation of Various Alloys.

3. Boeing BAC 5753, Cleaning, Descaling and Surface Preparation of Titanium and Titanium Alloys.

4. Boeing BAC 5758, Cleaning, Descaling and Surface Preparation of Nickel and Cobalt Base Alloys.

5. Boeing BAC 5759, Chemical Milling of Steel.

6. Boeing BAC 5792, Chemical Milling of Nickel and Cobalt Alloys.

7. McDonnell Douglas DPS 41003, Surface Treatment of Corrosion Resistant Steels.

8. McDonnell Douglas DPS 41013, Surface Treatment of Heat and Corrosion Resistant Nickel Base Alloys.

9. McDonnell Douglas DPS 41450, Cleaning and Etching Titanium.

10. Rockwell International MPPRA 1103-003-50, Etching of Machined Metal Surfaces for Penetrant Inspection.

11. Martin Marietta Aerospace STP 5015, Cleaning Titanium Alloys.

TABLE I: NITRIC/HYDROFLUORIC ACID SOLUTION A

Make-up: 40 fl oz HNO_3 (42°Be) and 2.7 fl oz HF (70%)/gal; balance: demineralized water.

Immersion Application

Metal Etched	Temperature	Metal removed, mils, for stated time			
		15 minutes	30 minutes	45 minutes	60 minutes
Titanium 6Al-4V	75°F	.45	.61	.76	.87
	140°F	.50	1.00	1.37	1.72
A 286	75°F	.007	.016	.024	.031
	140°F	.042	.080	.114	.143
Inconel 718	75°F	.001	.002	.003	.004
	140°F	.005	.015	.023	.030

TABLE II: NITRIC/HYDROFLUORIC ACID SOLUTION B

Make-up: 60 fl oz HNO_3 (42°Be') and 2.7 fl oz HF (70%)/gal; balance: demineralized water

	Metal Etched	Temperature	Metal removed, mils, for stated time			
			15 minutes	30 minutes	45 minutes	60 minutes
Immersion	Titanium 6Al-4V	75°F	.17	.35	.53	.70
		140°F	.41	.76	1.13	1.48
	A-286	75°F	.008	.016	.026	.033
		140°F	.086	.161	.220	.285
	Inconel 718	75°F	.003	.007	.009	.011
		140°F	.020	.039	.046	.060
Brush	Thickened with CAB-O-SIL					
	Titanium 6Al-4V	75°F	.015	.025	.038	.050

TABLE III: NITRIC/HYDROFLUORIC ACID SOULUTION C

Make-up: 40 fl oz HNO_3 (42°Be') and 6.4 fl oz HF (70%)/gal; balance demineralized water

	Metal Etched	Temperature	Metal removed, mils, for stated time			
			15 minutes	30 minutes	45 minutes	60 minutes
Immersion	Titanium 6Al-4V	75°F	1.09	1.72	2.26	2.76
		140°F	1.33	--	--	--
	A-286	75°F	.027	.043	.056	.070
		140°F	.102	.182	.253	.316
	Inconel 718	75°F	.006	.009	.012	.014
		140°F	.036	.064	.088	.111
Brush	Thickened with CAB-O-SIL	75°F	.016	.040	.060	.082
	Titanium 6Al-4V					

TABLE IV: NITRIC/HYDROFLUORIC ACID SOLUTION D

Make-up: 60 fl oz HNO_3 (42°Be') and 6.4 fl oz HF (70%)/gal; balance: demineralized water

Immersion Application

Metal Etched	Temperature	Metal removed, mils, for stated time			
		15 minutes	30 minutes	45 minutes	60 minutes
Titanium 6Al-4V	75°F	.50	.94	1.39	1.78
	140°F	1.48	--	--	--
A-286	75°F	.024	.046	.070	.090
	140°F	.224	.370	.500	.654

TABLE V: PASA-JELL-101
(as received)
Brush Application

Metal Etched	Temperature	Metal removed, mils, for stated time			
		15 minutes	30 minutes	45 minutes	60 minutes
Titanium 6Al-4V	75°F	.001	.002	.002	.002
	90°F	.001	.003	.004	.005
A-286	75°F	nil	nil	nil	nil
	90°F	nil	.001	.002	.002
Inconel 718	75°F	nil	nil	nil	nil
	90°F	nil	nil	nil	nil

TABLE VI: $FeCl_3/HNO_3/H_3PO_4$

Make-up: 57.5 fl oz $FeCl_3$, 19.3 fl oz HNO_3 (42°Be'), 9.6 fl oz H_3PO_4 (85%)/gal; balance demineralized water

	Metal Etched	Temperature	Metal removed, mils, for stated time		
			5 minutes	10 minutes	15 minutes
Immersion	Titanium 6Al-4V	75°F	nil	nil	nil
	A-296	75°F	.36	.78	1.59
	Inconel 718	75°F	nil	nil	nil
	21-6-9	75°F	.40	.75	1.45
Brush Application	A-286	75°F	.28	.54	.78
	21-6-9	75°F	.21	.44	.67
	Thickened with CAB-O-SIL				
	A-286	75°F	.18	.35	.45
	21-6-9	75°F	.19	.35	.57

TABLE VII: $HCl/HNO_3/NiCl_2/FeCl_3/CrO_3$

Make-up: .6 gal HCl, .08 gal HNO_3 (42°Be'), 1 lb $NiCl_2 \cdot 6H_2O$, 1.8 lb $FeCl_3$, .40 lb CrO_3/gal; balance:HCl

	Metal Etched	Temperature	Metal removed, mils, for stated time		
			5 minutes	10 minutes	15 minutes
Immersion	Titanium 6Al-4V	75°F	.001	.001	.001
	A-286	75°F	.26	.62	1.04
	Inconel 718	75°F	.38	.72	1.05
	21-6-9	75°F	.28	.63	1.03
Brush Application	A-286	75°F	.11	.20	.30
	Inconel 718	75°F	.17	.32	.47
	21-6-9	75°F	.18	.33	.50
	Thickened with CAB-O-SIL				
	A-286	75°F	.22	.48	.70
	Inconel 718	75°F	.14	.38	.55
	21-6-9	75°F	.22	.47	.71

TABLE VIII: LOW HNO3/HF NO. 1

Make-up: 12.8 fl oz HNO_3 (42°Be'), 3.8 fl oz HF (70%)/gal; balance: demineralized water

	Metal Etched	Temperature	Metal removed, mils, for stated time			
			15 minutes	30 minutes	45 minutes	60 minutes
Immersion	Titanium 6Al-4V	75°F	1.03	1.76	2.31	2.40
		140°F	3.55	--	--	--
	A-286	75°F	.027	.040	.046	.055
		140°F	.224	.370	.500	.654
	Inconel 718	75°F	.002	.004	.005	.005
		140°F	.003	.003	.003	.003
Brush	Thickened with CAB-O-SIL Titanium 6Al-4V	75°F	.10	.25	.40	.61

TABLE IX: HCl/H_2O_2

Make-up: 50% HCl ($20^oBe'$), 50% H_2O_2 (30% Stabilized)

Immersion Application

Metal Etched	Temperature	Metal removed, mils, for stated times		
		1 minute	2 minutes	3 minutes
A-286	75^oF	.31	.63	1.39
Inconel 718	75^oF	.36	.45	1.56
21-6-9	75^oF	.41	.76	1.48

TABLE X: LOW HNO_3/HF NO. 2A

Make-up: 20 fl oz HNO_3 (42°Be'), 5 fl oz HF (70%)/gal; balance: demineralized water

Immersion Application

Metal Etched	Temperature	Metal removed, mils, for stated time			
		5 minutes	10 minutes	15 minutes	30 minutes
Titanium 6Al-4V	75°F	.44	.77	1.02	1.57
A-286	75°F	.008	.010	.015	.021
Inconel 718	75°F	.001	.001	.002	.002
21-6-9	75°F	.006	.006	.007	.011

TABLE XI: LOW HNO_3/HF NO. 2B

Make-up: 20 fl oz HNO_3 (42°Be'), 5 fl oz HF (70%), 3.4 oz Fe/gal; balance demineralized water

	Metal Etched	Temperature	Metal removed, mils, for stated time			
			5 minutes	10 minutes	15 minutes	30 minutes
Immersion	Titanium 6Al-4V	75°F	.24	.43	.59	1.05
	A-286	75°F	.001	.001	.002	.003
	Inconel 718	75°F	.001	.002	.003	.008
	21-6-9	75°F	nil	nil	nil	nil
Brush Application	Titanium 6Al-4V	75°F	.30	.60	.85	1.22
	Thickened with CAB-O-SIL					
	Titanium 6Al-4V	75°F	nil	nil	nil	nil
	31-32 Dynes/cm		15 minutes	30 minutes	45 minutes	60 minutes
	Titanium 6Al-4V	75°F	.12	.21	.30	.37

TABLE XII: LOW HNO_3/HF NO. 2C

Make-up: 20 fl oz HNO_3 (42°Be'), 2.6 fl oz HF (70%), 1 oz Fe/gal; balance demineralized water

Immersion Application

Metal Etched	Temperature	Metal removed, mils, for stated time			
		5 minutes	10 minutes	15 minutes	30 minutes
Titanium 6Al-4V	75°F	.45	.78	1.12	1.96
A-286	75°F	.001	.008	.012	.016
Inconel 718	75°F	.001	.001	.002	.003
21-6-9	75°F	nil	.001	.001	.003
31-32 Dynes/cm					
Titanium 6Al-4V	75°F	---	---	.984	---

TABLE XIII: LOW HNO_3/HF NO. 2D

Make-up: 20 fl oz HNO_3 (42°Be'), 2.6 fl oz HF (70%), 3.4 oz Fe/gal; balance demineralized water
Immersion Application

Metal Etched	Temperature	Metal removed, mils, for stated time			
		5 minutes	10 minutes	15 minutes	30 minutes
Titanium 6Al-4V	75°F	.011	.023	.032	---
A-286	75°F	nil	nil	nil	---
Inconel 718	75°F	nil	nil	nil	---
21-6-9	75°F	nil	nil	nil	---

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