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THE SURFACE PREPARATION OF ALUMINUM ALLOYS USING THE PHOSPHORIC ACID CONTAINMENT SYSTEM FOR REPAIR

SUSÀN S. SALIBA
University of Dayton Research Institute
300 College Park Avenue
Dayton, OH 45469-0168

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AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
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NOTICE

JAMES J. MAZZA
Project Engineer
Materials Integrity Branch

MICHAEL F. HITCHCOCK
Chief
Materials Integrity Branch

GARY K. WAGGONER
Chief
Systems Support Division

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14 ABSTRACT

The Phosphoric Acid Containment System (PACS) was developed by The Boeing Company and is intended to provide on-aircraft phosphoric acid anodization of aluminum surfaces. The first objective of this investigation was to determine if the PACS produces a surface equivalent to the phosphoric acid tank system. The second objective was to evaluate the PACS procedure against Air Force maintenance criteria and ascertain if operator sensitivity is an issue. In addition, the PACS unit was used to study the effects of various operating parameters on the quality of the prepared aluminum surface. The operating, or processing, variables examined included voltages/currents other than those recommended in the operating procedure, anodization time/acid flow rate over the aluminum, orientation of the surface being anodized, temperature of the surface being anodized, effect of a delay between completion of acid flow and initiation of rinse, effect of fasteners on vacuum integrity and methods to seal leaks, effect of screen type, effect of type and amount of breather material, effect of the addition of sodium bicarbonate to the rinse water, and the size of the surface being anodized. Wedge test panels were made with the PACS-prepared surfaces to determine the integrity of the bond between the surface preparation and the adhesive. In addition, the surface morphology of the aluminum surface was characterized. Wedge test results indicated that the PACS-prepared aluminum surfaces were as good as those prepared using the standard phosphoric acid anodize (PAA) procedure. In addition, the morphology of the PACS and PAA surfaces were similar in overall oxide layer structure, but differed in oxide layer thickness. Based on the wedge test results, the ranges for the PACS operating or processing parameters were determined.

15. SUBJECT TERMS

Surface Preparation Technique, Phosphoric Acid Containment System (PACS), Repair of Aluminum, Wedge Test, Surface Morphology

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TABLE OF CONTENTS

Section **Page**

LIST OF FIGURES

Figure **Page**

LIST OF FIGURES (Concluded)

LIST OF TABLES

PREFACE

This report covers the work performed by the University of Dayton Research Institute (UDRI), Dayton, Ohio 45469-0168, during the period from June 1, 1992 through December 31, 1993. It was carried out under Air Force Contract No. F33615-89-C-5643. The work was administered under the direction of Robert Urzi and Mark Kistner of the Systems Support Division of the Air Force Materials Directorate, Wright Laboratory, Wright-Patterson Air Force Base, Ohio. James J. Mazza (WL/MLSE) was the Program Project Engineer for this program.

The work described herein was conducted at UDRI in the Plastics, Adhesives, and Composites Laboratory of the Materials Engineering Division. The Principal Investigators on this program were D. Robert Askins and Susan S. Saliba. The majority of the laboratory work was conducted by L. Dee Pike, Laura Purcell, and Christine Schulte.

The report was submitted by the author for publication in September 1994.

SECTION 1
INTRODUCTION

Aircraft repair bonding of aluminum surfaces requires the use of surface preparation techniques prior to adhesive application. Mechanical bond strength and environmental durability tests have shown phosphoric acid anodizing to be a superior surface treatment when compared to other methods, such as chromic acid anodizing and sulfuric acid-sodium dichromate etch [1-3].

Currently, phosphoric acid anodization is carried out in large tanks or through the phosphoric acid nontank anodizing (PANTA) system, in which phosphoric acid is applied to the surface in gel form. Although these processes produce superior bonding surfaces, there are drawbacks in terms of logistics and operator exposure to phosphoric acid using these techniques. Typically, the parts requiring repair are not easily removed for dipping into anodizing tanks. Recognizing the problems associated with the existing phosphoric acid anodization processes, the Boeing Company developed the Phosphoric Acid Containment System (PACS), which successfully accomplishes anodization without having to remove the aluminum part to be repaired. The PACS unit is currently being manufactured by ATACS Products, Inc. of Tukwila, WA.

SECTION 2
APPROACH

The first objective of this investigation was to determine if the PACS produces an equivalent to the phosphoric acid tank system. The second objective was to evaluate the PACS procedure against Air Force maintenance criteria and ascertain if operator sensitivity is an issue. The last objective was accomplished by conducting a round robin test effort with four depots.

Two types of tests were used for anodized aluminum surface evaluation: wedge tests and surface morphology characterization. Wedge tests were conducted to determine the integrity of the bond between the surface preparation and the adhesive. Surface morphology tests were conducted to compare the morphology of the standard phosphoric acid anodization (PAA) prepared surfaces with the morphology of the PACS prepared surfaces. Both oxide structure and thickness were documented. The sequence of activities used for this investigation is outlined in Figure 1. The PACS Model 0810 was utilized for all experimentation. This unit consists of a portable control panel which allows for the control of vacuum, voltage, and current. In addition, acid and water recovery bottles as well as connective tubing are utilized to contain the acid medium during anodization. Figure 2 illustrates the PACS Model 0810 control panel.

2.1 ANODIZATION PROCEDURE

Prior to the anodization procedure the area to be repaired was abraded with 3M Company Scotchbrite (fine) under tap water and solvent wiped until a water break-free surface was obtained. The area was then vacuum bagged. The stacking sequence which is illustrated in Figure 3, included the area to be repaired, four layers of breather material, and inner and outer vacuum bag. The inner bag contains the phosphoric acid during the anodization and the outer bag provides protection in the event of a leak in the inner bag. An inlet acid hose was placed in the lower right corner of the inner bag and was then attached to the control panel in accordance with the operating manual supplied by ATACS Products, Inc. [4]. An outlet acid hose was placed in the upper left corner and was then attached to the unit. Note that all hoses are color coded making it nearly impossible for the operator to improperly connect them. Subsequently, the anode wire was connected from the aluminum panel to the control panel while the cathode wire was connected from the screen to the control panel.

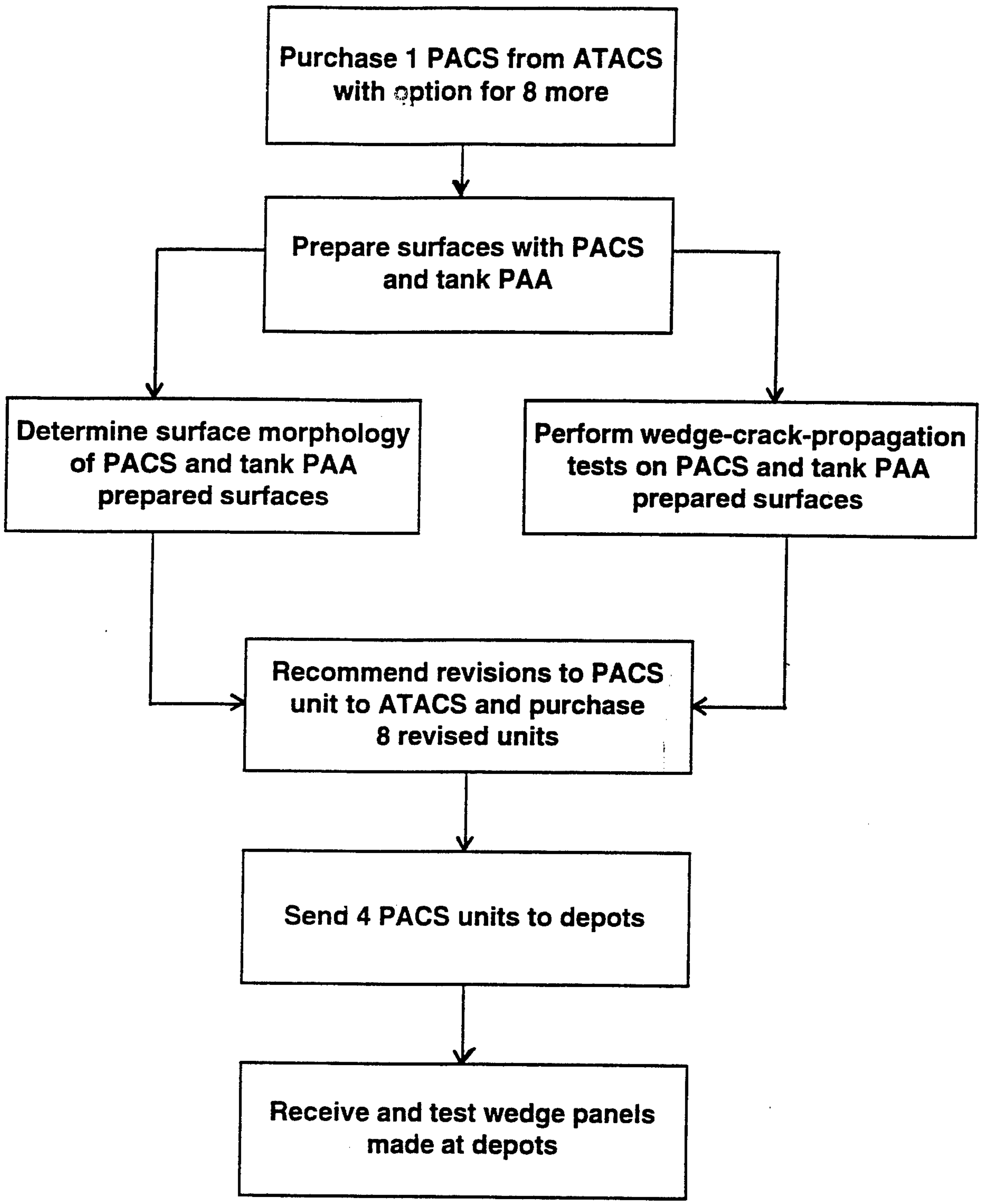


Figure 1. Task 1 Activity Sequence

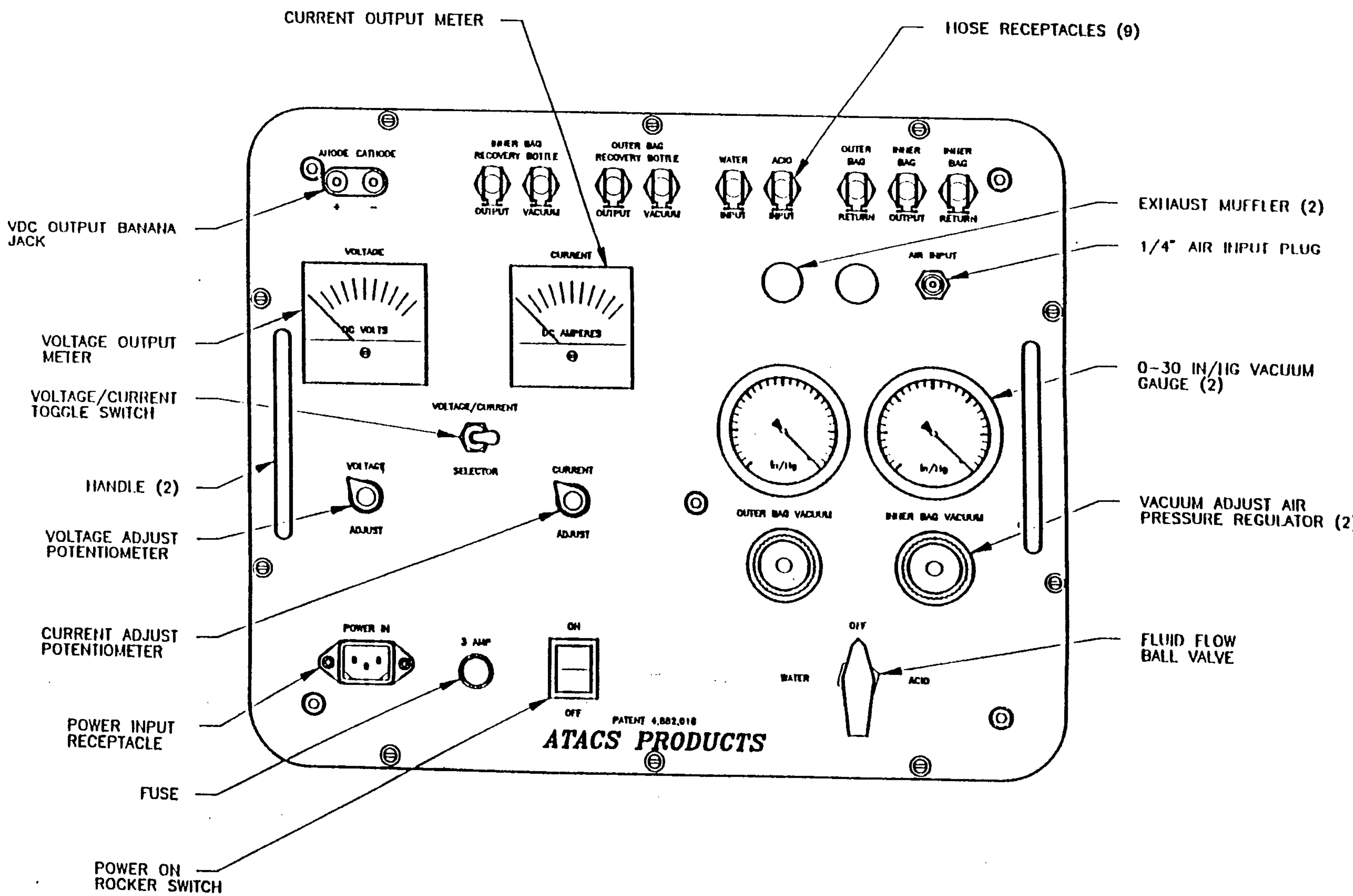


Figure 2. Phosphoric Acid Containment System (PACS) Control Panel

A - Brown-Coded Inner Vacuum Bag Output Hose

B - Green-Coded Inner Vacuum Bag Return Hose

C - Yellow-Coded Outer Vacuum Bag Return Hose

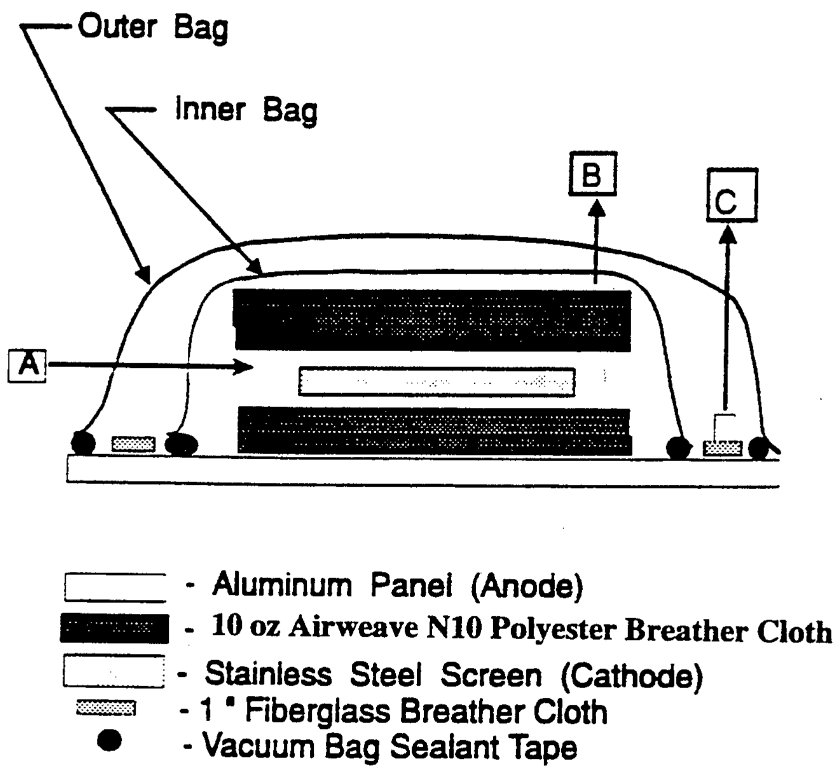


Figure 3. Stacking Sequence of Repair Area Lay-Up

In order to initiate anodization, a continuous air supply of 100 to 180 psi was attached to the air input plug on the control panel. The inner and outer vacuum gauges on the control panel were then used to regulate the vacuum level in both bags to approximately 15 in Hg. A collapsible container filled with 2 liters of 12% phosphoric acid was connected to the control panel through designated tubing. Once the vacuum was stable, the acid/off/water valve on the control panel was turned to the acid position to allow acid flow through the inlet hose over the panel. The flowrate of the acid was controlled so that the acid was in contact with the aluminum surface for 25 minutes. Once the inner bag was saturated with acid (approx. 5 min for an 8" X 8" area repair), the power was turned on to initiate the anodization process. Both voltage and current can be controlled. The acceptable range for amperage is 1-7 amps/sq. ft. and for voltage is 6-10 VDC. At the end of the anodization process, the acid/off/water valve was placed in the off position. A 4-liter collapsible water bottle was then connected to the control panel and the acid/off/water valve was turned to the water position. Once the 4 liters of water were drawn through the system, the anodization procedure was completed. At this point the power was turned off. The pH of the breather material and aluminum was checked with litmus paper upon completion of the procedure. When the pH was less than 3, additional water was flushed through the system prior to removal of the bagging material. Once the anodization procedure was complete, the diluted acid that had collected in the recovery bottles was neutralized using sodium bicarbonate.

2.2 THE WEDGE TEST

Wedge test panels were utilized to determine the effectiveness of the PACS unit, and to compare existing wedge test data on PAA prepared panels to those prepared using the PACS unit. The wedge test panels were prepared and tested in accordance with ASTM D 3762 where the specimens were aged in a 140°F, 95-100% RH environment. Table 1 outlines the test plan followed for this work.

2.3 SURFACE MORPHOLOGY CHARACTERIZATION

Aluminum panels (2024-T3 bare and clad, 7075-T6 bare) were anodized utilizing both the PAA and PACS techniques for surface morphology comparisons. A Hitachi Field Emission Scanning Electron Microscope (SEM) was used to produce stereo pair photographs of the anodized surfaces. A stereoviewer was then used to examine the stereo pairs, providing a view of the surface morphology in 3-D. A parallax bar attached to the stereoviewer was used to measure oxide layer dimensions. In addition, Auger

TABLE 1

TEST PLAN FOR PREPARED WEDGE TEST SPECIMENS

Alloys (2)	2024-T3 bare, 7075-T6 bare
Surface preparations (2)	PACS, tank PAA
Primer (1)	Cytec's BR 127
Adhesives (2)	3M's AF-163-2, Cytec's FM 73
Cure Conditions (1)	Manufacturer's recommended
Type tests and replicates: surface morphology analysis wedge crack (140°F, 95-100% RH)	 2 10 (two sets of 5)
TOTAL WEDGE SPECIMENS	80

Electron Spectroscopy (AES) was used to measure the overall thickness of the oxide layer. AES is a surface sensitive technique which can detect all elements except hydrogen that are present at levels >0.5% within 3nm of a sample surface. AES can also determine composition as a function of depth when used in combination with an argon sputtering technique.

2.4 ROUND ROBIN TEST EFFORT

The round robin test effort included both wedge and peel testing. As stated above the wedge crack panels were prepared and tested in accordance with ASTM D 3762 where the specimens were aged in a 140°F, 95-100% RH as well as 140°F, 5% salt fog environment. The peel panels were prepared and tested in accordance with ASTM D 3167 at RT.

SECTION 3
DISCUSSION OF RESULTS

Both wedge test panels and surface morphology characterization were utilized not only to compare PAA and PACS prepared surfaces, but also to determine the effects of several procedural variables on the quality of the anodized aluminum that results while using the PACS unit. In addition, wedge test and peel results are included from the round robin test effort.

3.1 WEDGE TEST

Wedge test panels were prepared and tested as discussed in Section 2.2. All the panels were primed with BR 127 and bonded with either FM 73 or AF 163-2. The wedge test results for the 2024-T3 bare aluminum specimens that were anodized by either the PAA or PACS techniques are presented in Tables 2 and 3. Graphical representations of these results are illustrated in Figures 4 and 5. For both adhesives, the specimens that were anodized using the PACS technique showed crack growths similar to the baseline PAA prepared surfaces. Wedge test results for 7075-T6 bare aluminum specimens that were anodized by either the PAA or PACS techniques are presented in Tables 4 and 5. Graphical representations of these results are illustrated in Figures 6 and 7. For both adhesives, the specimens that were anodized using the PACS technique showed crack growths similar to the baseline PAA prepared surfaces.

3.1.1 Effect of PACS Processing Variables

The effect of PACS processing variables on the wedge test results were studied. The operating or processing variables examined include:

1. Voltages/currents other than those recommended in the operating procedure,
2. Anodization time/acid flow rate over the aluminum,
3. Orientation of the surface being anodized,
4. Temperature of the surface being anodized,
5. Effect of a delay between completion of acid flow and initiation of rinse,
6. Effect of fasteners on vacuum integrity, and methods to seal leaks,
7. Effect of screen type,
8. Effect of type and amount of breather material,
9. Effect of the addition of Sodium Bicarbonate to the rinse water, and
10. Size of the surface being anodized.

TABLE 2

COMPARISONS OF PAA AND PACS ANODIZED Al 2024-T3 BARE WEDGE TEST PANELS FABRICATED USING BR 127 PRIMER AND FM 73 ADHESIVE

Specimen (1)	Surface Prep.	Adhesive	CUMULATIVE WEDGE TEST (In) Time (hours)						
			0	1	4	8	24	168	672
T3PAAFM1-1	PAA	FM 73	1.10	1.19	1.21	1.21	1.33	1.44	1.44
T3PAAFM1-2	PAA	FM 73	1.11	1.19	1.21	1.21	1.26	1.39	1.43
T3PAAFM1-3	PAA	FM 73	1.18	1.22	1.27	1.30	1.41	1.47	1.51
T3PAAFM1-4	PAA	FM 73	1.14	1.18	1.21	1.23	1.29	1.53	1.53
T3PAAFM1-5	PAA	FM 73	1.14	1.23	1.27	1.27	1.34	1.42	1.57
		Average	1.13	1.20	1.23	1.24	1.33	1.45	1.50
T3PAAFM2-1	PAA	FM 73	1.14	1.22	1.25	1.29	1.35	1.47	1.58
T3PAAFM2-2	PAA	FM 73	1.10	1.19	1.23	1.26	1.32	1.41	1.56
T3PAAFM2-3	PAA	FM 73	1.12	1.21	1.26	1.29	1.36	1.46	1.57
T3PAAFM2-4	PAA	FM 73	1.14	1.25	1.32	1.38	1.43	1.58	1.67
T3PAAFM2-5	PAA	FM 73	1.10	1.19	1.24	1.29	1.34	1.47	1.55
		Average	1.12	1.21	1.26	1.30	1.36	1.48	1.59
T3PCSFM1-1	PACS	FM 73	1.26	1.26	1.26	1.30	1.35	1.45	1.57
T3PCSFM1-2	PACS	FM 73	1.16	1.21	1.21	1.28	1.35	1.40	1.49
T3PCSFM1-3	PACS	FM 73	1.21	1.25	1.25	1.25	1.33	1.42	1.48
T3PCSFM1-4	PACS	FM 73	1.19	1.24	1.30	1.30	1.30	1.40	1.45
T3PCSFM1-5	PACS	FM 73	1.18	1.18	1.21	1.21	1.27	1.38	1.48
		Average	1.20	1.23	1.25	1.27	1.32	1.41	1.49
T3PCSFM2-1	PACS	FM 73	1.15	1.20	1.20	1.25	1.33	1.41	1.49
T3PCSFM2-2	PACS	FM 73	1.25	1.34	1.34	1.34	1.42	1.55	1.55
T3PCSFM2-3	PACS	FM 73	1.16	1.25	1.27	1.27	1.33	1.47	1.47
T3PCSFM2-4	PACS	FM 73	1.20	1.28	1.28	1.28	1.39	1.48	1.56
T3PCSFM2-5	PACS	FM 73	1.22	1.28	1.28	1.28	1.39	1.44	1.56
		Average	1.20	1.27	1.27	1.28	1.37	1.47	1.53

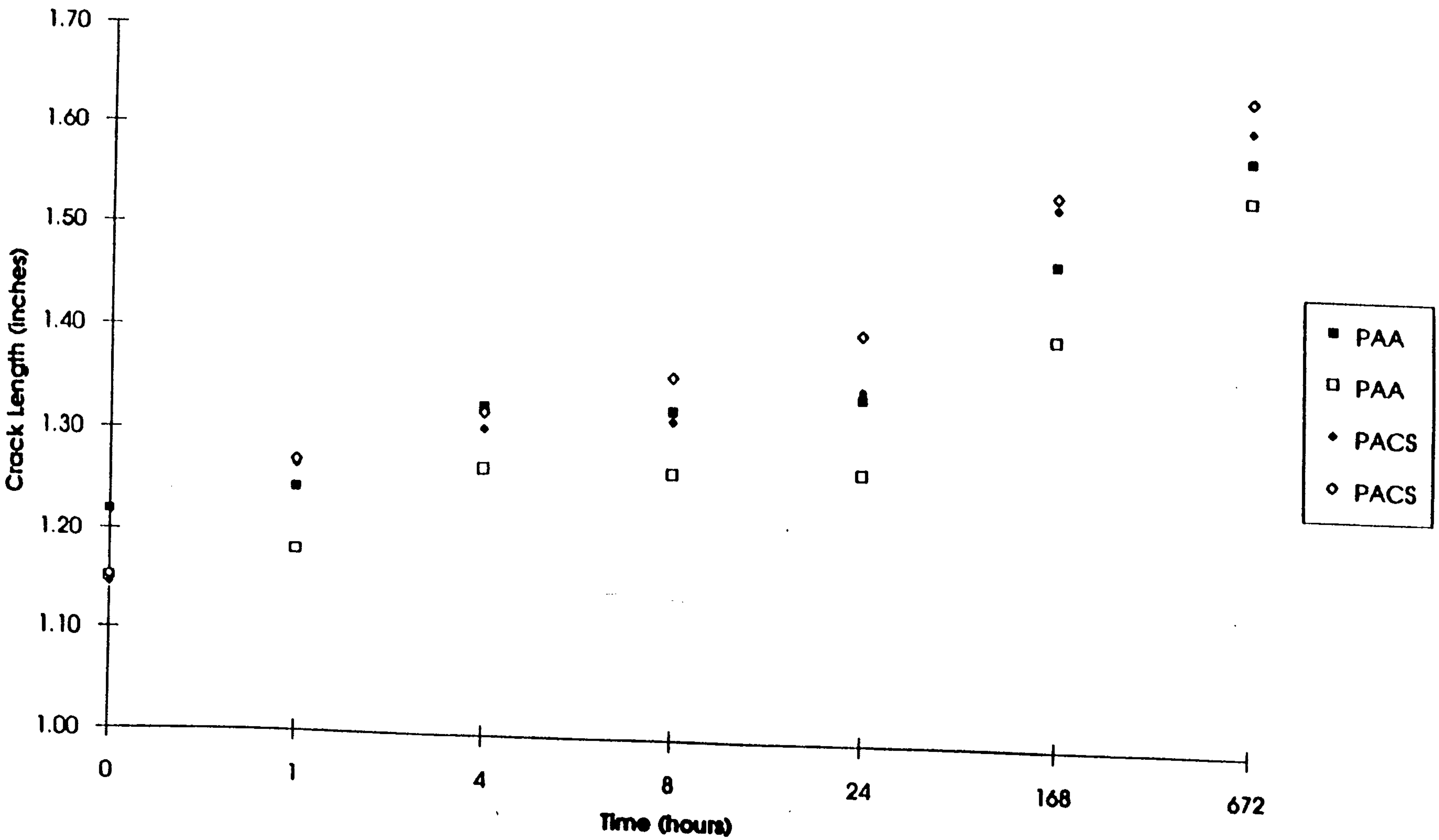
NOTE: (1) All wedge test specimens were aged @ 140°F and 95-100% R.H. Note that all failures were cohesive.

TABLE 3

COMPARISONS OF PAA AND PACS ANODIZED Al 2024-T3 BARE WEDGE TEST PANELS FABRICATED USING BR 127 PRIMER AND AF 163-2 ADHESIVE

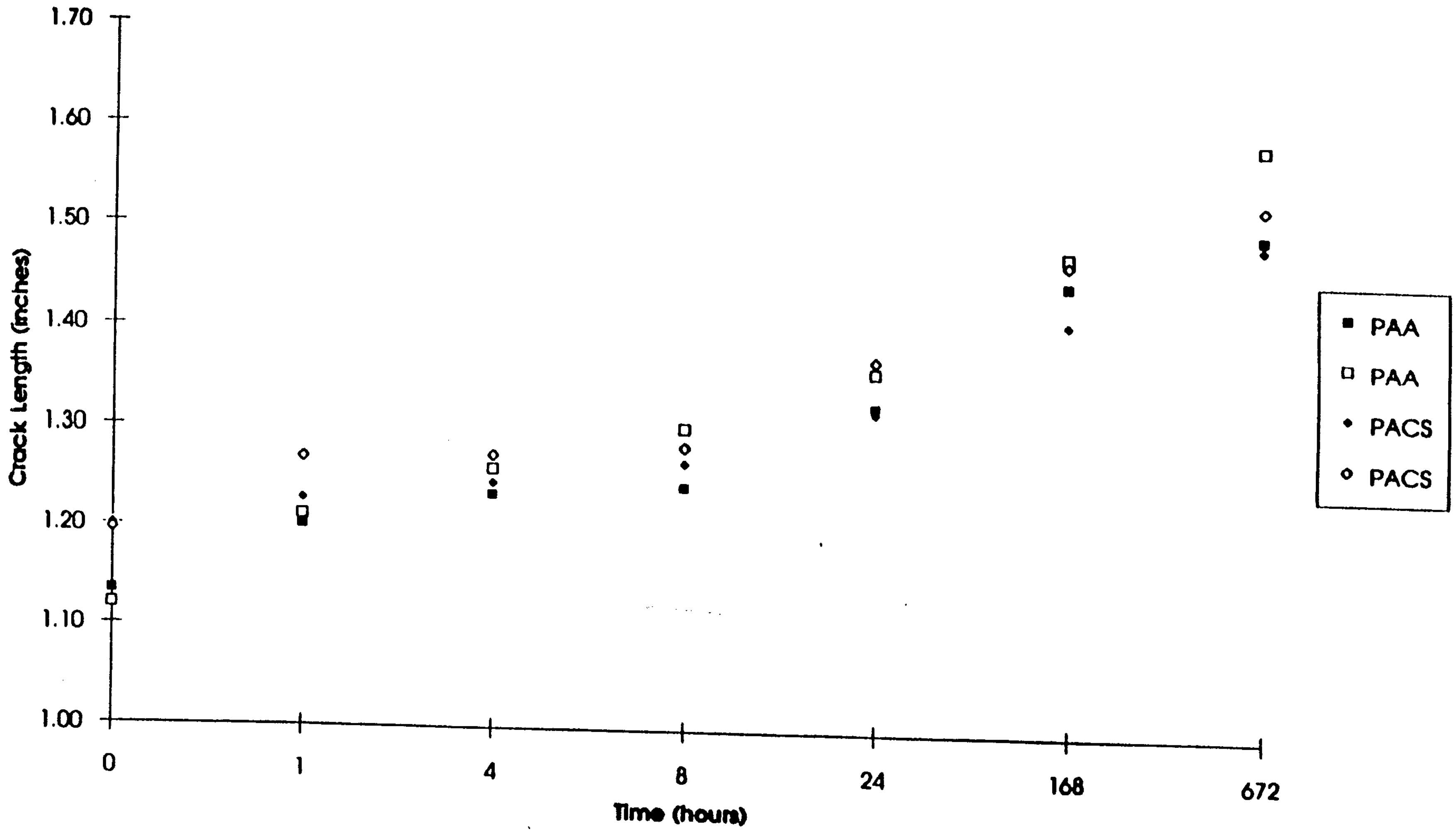
Specimen (1)	Surface Prep.	Adhesive	CUMULATIVE WEDGE TEST (in) Time (hours)						
			0	1	4	8	24	168	672
T3PAAAF1-1	PAA	AF 163-2	1.29	1.29	1.40	1.40	1.40	1.51	1.62
T3PAAAF1-2	PAA	AF 163-2	1.20	1.25	1.30	1.30	1.35	1.48	1.61
T3PAAAF1-3	PAA	AF 163-2	1.25	1.25	1.37	1.37	1.37	1.52	1.60
T3PAAAF1-4	PAA	AF 163-2	1.21	1.24	1.35	1.35	1.38	1.51	1.62
T3PAAAF1-5	PAA	AF 163-2	1.15	1.20	1.22	1.22	1.22	1.38	1.50
		Average	1.22	1.25	1.33	1.33	1.34	1.48	1.59
T3PAAAF2-1	PAA	AF 163-2	1.17	1.17	1.22	1.22	1.22	1.35	1.49
T3PAAAF2-2	PAA	AF 163-2	1.15	1.19	1.27	1.27	1.27	1.42	1.56
T3PAAAF2-3	PAA	AF 163-2	1.10	1.16	1.29	1.29	1.31	1.44	1.57
T3PAAAF2-4	PAA	AF 163-2	1.14	1.20	1.29	1.29	1.29	1.42	1.60
T3PAAAF2-5	PAA	AF 163-2	1.19	1.19	1.27	1.27	1.27	1.40	1.55
		Average	1.15	1.18	1.27	1.27	1.27	1.41	1.55
T3PCSAF1-1	PACS	AF 163-2	1.17	1.32	1.32	1.36	1.39	1.59	1.65
T3PCSAF1-2	PACS	AF 163-2	1.16	1.28	1.33	1.33	1.36	1.50	1.60
T3PCSAF1-3	PACS	AF 163-2	1.16	1.28	1.30	1.32	1.36	1.52	1.58
T3PCSAF1-4	PACS	AF 163-2	1.11	1.19	1.28	1.28	1.32	1.50	1.58
T3PCSAF1-5	PACS	AF 163-2	1.12	1.27	1.30	1.30	1.33	1.57	1.68
		Average	1.14	1.27	1.31	1.32	1.35	1.54	1.62
T3PCSAF2-1	PACS	AF 163-2	1.19	1.30	1.33	1.36	1.42	1.57	1.65
T3PCSAF2-2	PACS	AF 163-2	1.19	1.34	1.37	1.42	1.47	1.63	1.72
T3PCSAF2-3	PACS	AF 163-2	1.15	1.26	1.31	1.35	1.38	1.53	1.66
T3PCSAF2-4	PACS	AF 163-2	1.10	1.22	1.30	1.34	1.39	1.53	1.62
T3PCSAF2-5	PACS	AF 163-2	1.13	1.24	1.30	1.33	1.37	1.48	1.62
		Average	1.15	1.27	1.32	1.36	1.41	1.55	1.65

NOTE: (1) All wedge test specimens were aged @ 140°F and 95-100% R.H. Note that all failures were cohesive.



* All curves are an average of five specimens

Figure 4. Average Crack Growth Curves Comparing PAA and PACS Anodized Al 2024-T3 Fabricated Using BR 127 Primer and AF 163-2 Adhesive



*All curves are an average of five specimens

Figure 5. Average Crack Growth Curves Comparing PAA and PACS Anodized Al 2024-T3 Fabricated Using BR 127 Primer and FM 73 Adhesive.

TABLE 4

COMPARISONS OF PAA AND PACS ANODIZED Al 7075-T6 PANELS FABRICATED USING BR 127 PRIMER AND FM 73 ADHESIVE

Specimen (1)	Surface Prep.	Adhesive	CUMULATIVE WEDGE TEST (in) Time (hours)						
			0	1	4	8	24	168	672
T6PAAFM1-1	PAA	FM 73	1.28	1.28	1.36	1.36	1.42	1.42	1.42
T6PAAFM1-2	PAA	FM 73	1.28	1.28	1.36	1.36	1.43	1.43	1.43
T6PAAFM1-3	PAA	FM 73	1.33	1.40	1.48	1.48	1.55	1.55	1.55
T6PAAFM1-4	PAA	FM 73	1.28	1.34	1.39	1.39	1.43	1.43	1.43
T6PAAFM1-5	PAA	FM 73	1.23	1.23	1.31	1.31	1.40	1.40	1.40
		Average	1.28	1.31	1.38	1.38	1.45	1.45	1.45
T6PAAFM2-1	PAA	FM 73	1.28	1.35	1.41	1.41	1.41	1.41	1.47
T6PAAFM2-2	PAA	FM 73	1.31	1.37	1.43	1.43	1.43	1.43	1.50
T6PAAFM2-3	PAA	FM 73	1.30	1.30	1.34	1.34	1.34	1.34	1.38
T6PAAFM2-4	PAA	FM 73	1.23	1.30	1.38	1.38	1.38	1.38	1.38
T6PAAFM2-5	PAA	FM 73	1.26	1.31	1.37	1.40	1.40	1.40	1.42
		Average	1.28	1.33	1.39	1.39	1.39	1.39	1.43
T6PCSFM1-1	PACS	FM 73	1.24	1.36	1.36	1.36	1.43	1.43	1.52
T6PCSFM1-2	PACS	FM 73	1.23	1.32	1.32	1.38	1.38	1.46	1.50
T6PCSFM1-3	PACS	FM 73	1.28	1.34	1.34	1.34	1.44	1.44	1.54
T6PCSFM1-4	PACS	FM 73	1.26	1.32	1.32	1.32	1.41	1.41	1.53
T6PCSFM1-5	PACS	FM 73	1.26	1.34	1.34	1.34	1.43	1.43	1.50
		Average	1.24	1.34	1.34	1.35	1.42	1.43	1.52
T6PCSFM2-1	PACS	FM 73	1.20	1.32	1.32	1.37	1.42	1.42	1.57
T6PCSFM2-2	PACS	FM 73	1.29	1.37	1.37	1.37	1.43	1.55	1.60
T6PCSFM2-3	PACS	FM 73	1.22	1.30	1.30	1.35	1.45	1.45	1.57
T6PCSFM2-4	PACS	FM 73	1.26	1.32	1.32	1.38	1.45	1.45	1.58
T6PCSFM2-5	PACS	FM 73	1.24	1.42	1.42	1.48	1.57	1.57	1.65
		Average	1.24	1.35	1.35	1.39	1.46	1.49	1.59

NOTE: (1) All wedge test specimens were aged @ 140°F and 95-100% R.H. Note that all failures were cohesive.

TABLE 5

COMPARISONS OF PAA AND PACS ANODIZED Al 7075-T6 PANELS FABRICATED USING BR 127 PRIMER AND AF 163-2 ADHESIVE

Specimen (1)	Surface Prep.	Adhesive	CUMULATIVE WEDGE TEST (in) Time (hours)						
			0	1	4	8	24	168	672
T6PAAAF1-1	PAA	AF 163-2	1.16	1.34	1.41	1.41	1.41	1.47	1.49
T6PAAAF1-2	PAA	AF 163-2	1.19	1.36	1.41	1.41	1.41	1.49	1.49
T6PAAAF1-3	PAA	AF 163-2	1.24	1.35	1.40	1.40	1.40	1.45	1.45
T6PAAAF1-4	PAA	AF 163-2	1.20	1.30	1.32	1.32	1.32	1.37	1.39
T6PAAAF1-5	PAA	AF 163-2	1.17	1.28	1.31	1.31	1.31	1.37	1.39
		Average	1.19	1.33	1.37	1.37	1.37	1.43	1.44
T6PAAAF2-1	PAA	AF 163-2	1.19	1.30	1.35	1.35	1.35	1.46	1.46
T6PAAAF2-2	PAA	AF 163-2	1.25	1.40	1.42	1.42	1.42	1.50	1.50
T6PAAAF2-3	PAA	AF 163-2	1.23	1.34	1.38	1.38	1.38	1.47	1.49
T6PAAAF2-4	PAA	AF 163-2	1.23	1.34	1.37	1.37	1.37	1.47	1.51
T6PAAAF2-5	PAA	AF 163-2	1.22	1.34	1.39	1.39	1.39	1.49	1.52
		Average	1.22	1.34	1.38	1.38	1.38	1.48	1.50
T6PCSAF1-1	PACS	AF 163-2	1.30	1.34	1.40	1.40	1.47	1.47	1.59
T6PCSAF1-2	PACS	AF 163-2	1.23	1.27	1.34	1.34	1.39	1.44	1.52
T6PCSAF1-3	PACS	AF 163-2	1.34	1.34	1.40	1.44	1.49	1.49	1.51
T6PCSAF1-4	PACS	AF 163-2	1.19	1.23	1.33	1.39	1.42	1.45	1.45
T6PCSAF1-5	PACS	AF 163-2	1.20	1.20	1.26	1.34	1.40	1.40	1.42
		Average	1.25	1.28	1.35	1.38	1.43	1.45	1.50

NOTES: (1) All wedge test specimens were aged at 140°F and 95-100% R.H. Note that all failures were cohesive.

(2) Specimens from the second PACS anodized panel exhibited adhesive failures and therefore a replacement panel was fabricated.

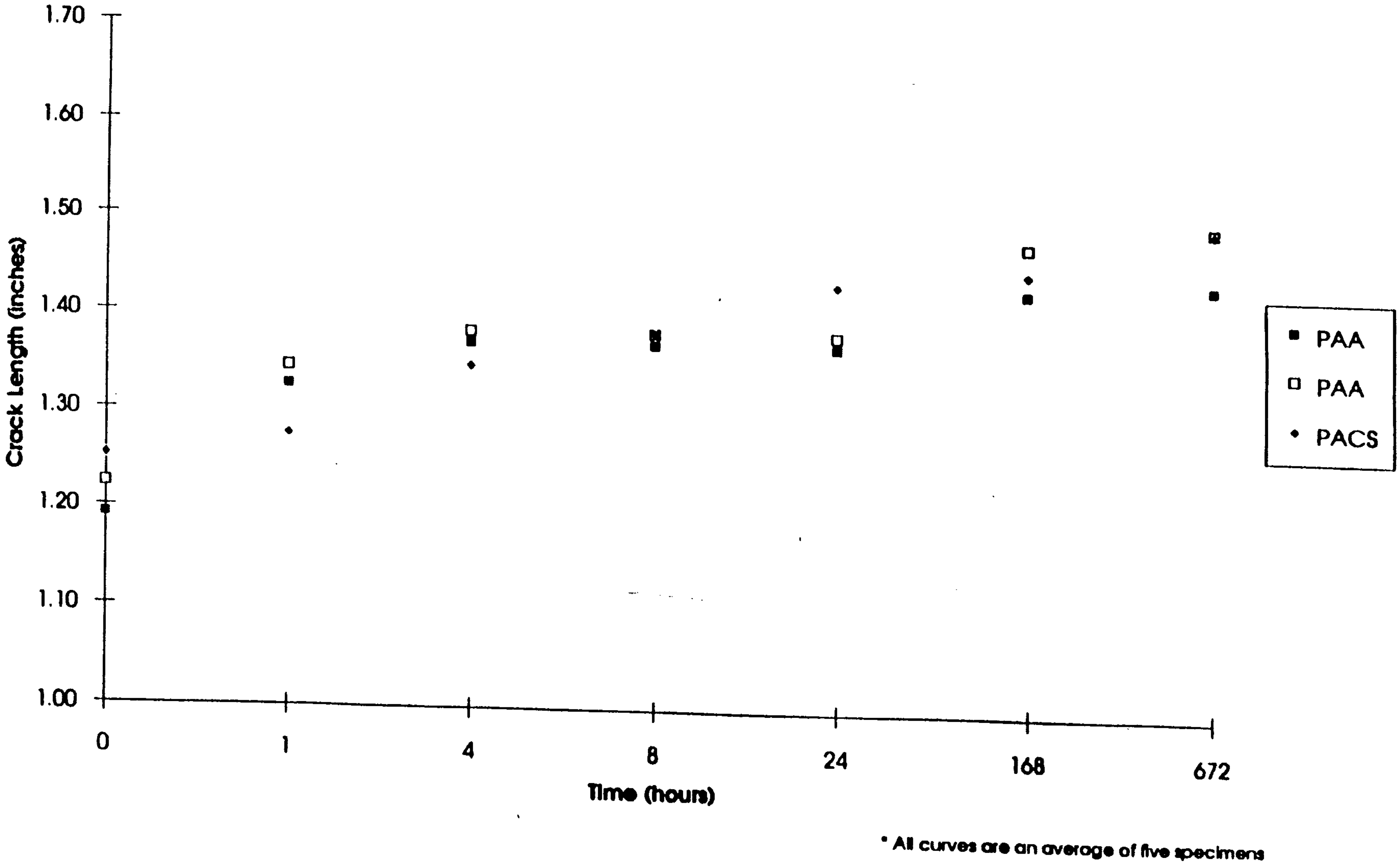


Figure 6. **Average Crack Growth Curves Comparing PAA and PACS Anodized Al 7075-T6 Bare Fabricated Using BR 127 Primer and AF 163-2 Adhesive.**

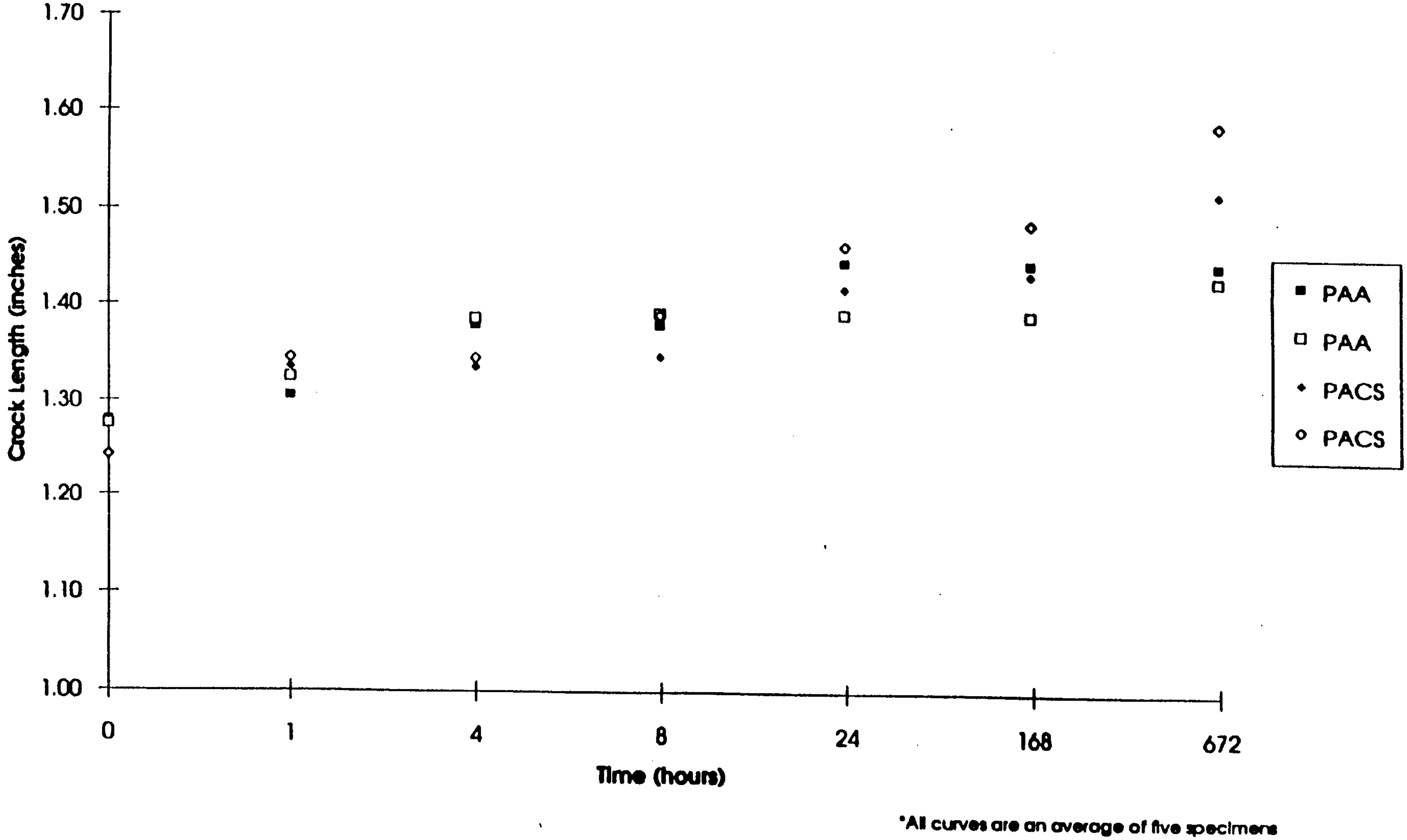


Figure 7. Average Crack Growth Curves Comparing PAA and PACS Anodized Al 7075-T6 Bare Fabricated Using BR 127 Primer and FM 73 Adhesive.

For all of the tests listed above, unless otherwise stated, panels were fabricated using BR 127 primer and FM 73 adhesive on PACS anodized 2024-T3 bare aluminum.

3.1.1.1 Effect of Voltage

The PACS operating manual recommends using a voltage range of 6-10 volts. All of the baseline panels were processed at 6 volts.

Several wedge test panels have been made with nonstandard voltage. Operational limits of the PACS unit ranged from a low of 5 to a high of 10 volts. Figure 8 presents wedge crack growth results for panels anodized at 5V, 8V, and 10V. Results indicate higher crack growth rate for those specimens anodized at 5V, which is out of the 6-10 VDC range recommended in the operating procedure.

3.1.1.2 Effect of Anodization Time/Acid Flow Rate

The operating manual recommends a 25 minute anodization time, and the acid flow rate from a 2-liter acid container is adjusted to last that specified time. When the majority of the experiments were complete, ATACS replaced the original PACS unit with an upgraded unit which included a flowmeter. Consequently, in order to achieve a 25 minute anodization time the flowmeter should be set at 80 cc/min.

Several wedge test panels were made varying the anodization time. Anodization times ranging from 8 minutes to 60 minutes were utilized to anodize panel surfaces with the PACS unit. The acid flow rates for these panels were adjusted appropriately so that the 2-liter supply would last just long enough to complete the anodization. Thus higher flow rates were used for shorter anodization times and lower flow rates for longer times. Figure 9 presents wedge crack growth results for panels anodized for 8 min, 10 min, and 60 min. Figure 9 illustrates that although 25 minutes is recommended, an anodization time of 10 minutes would be sufficient to successfully anodize the surface. Also, extending the anodization time to 60 minutes does not significantly affect the surface quality.

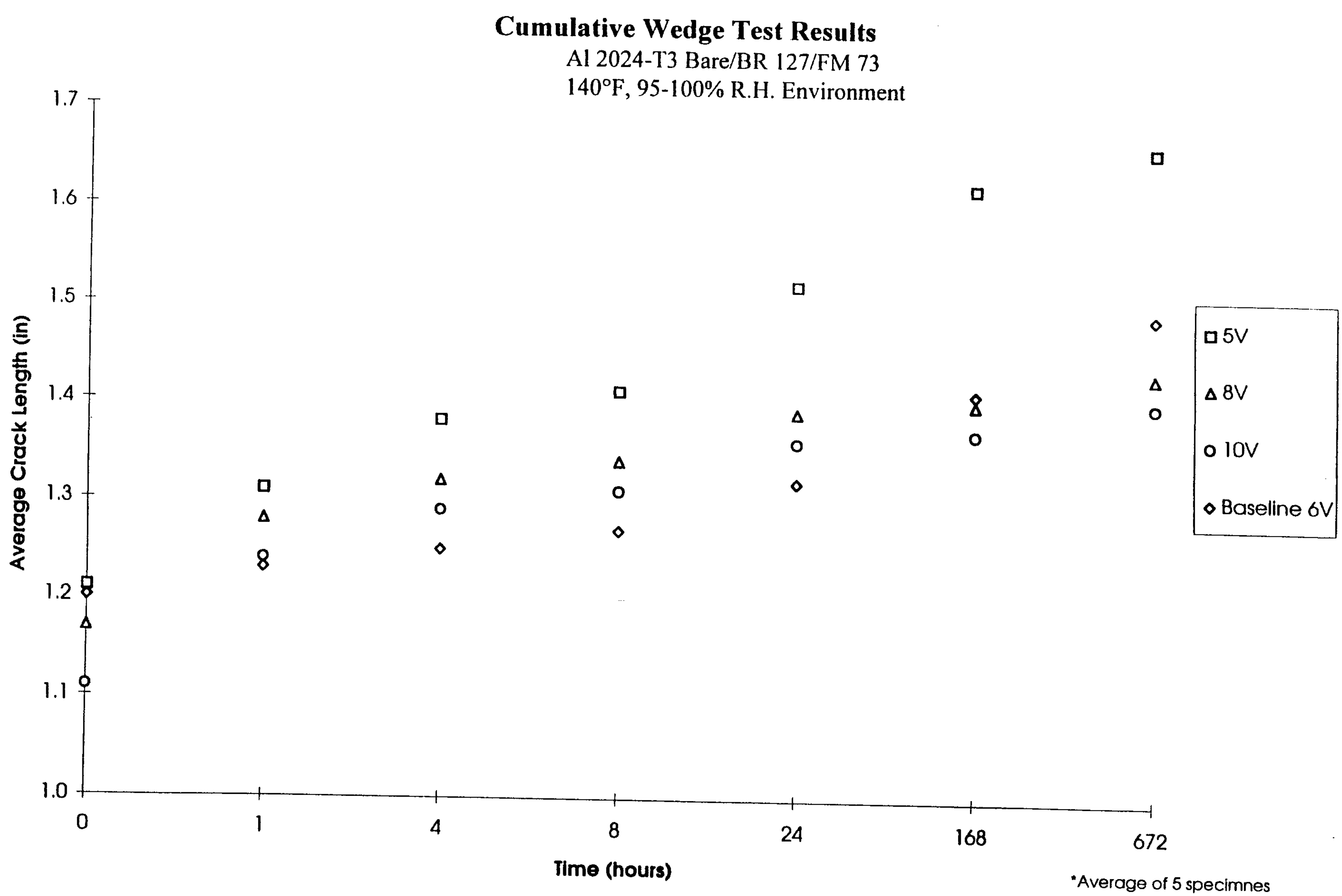


Figure 8. Effect of Voltage on Crack Growth Behavior

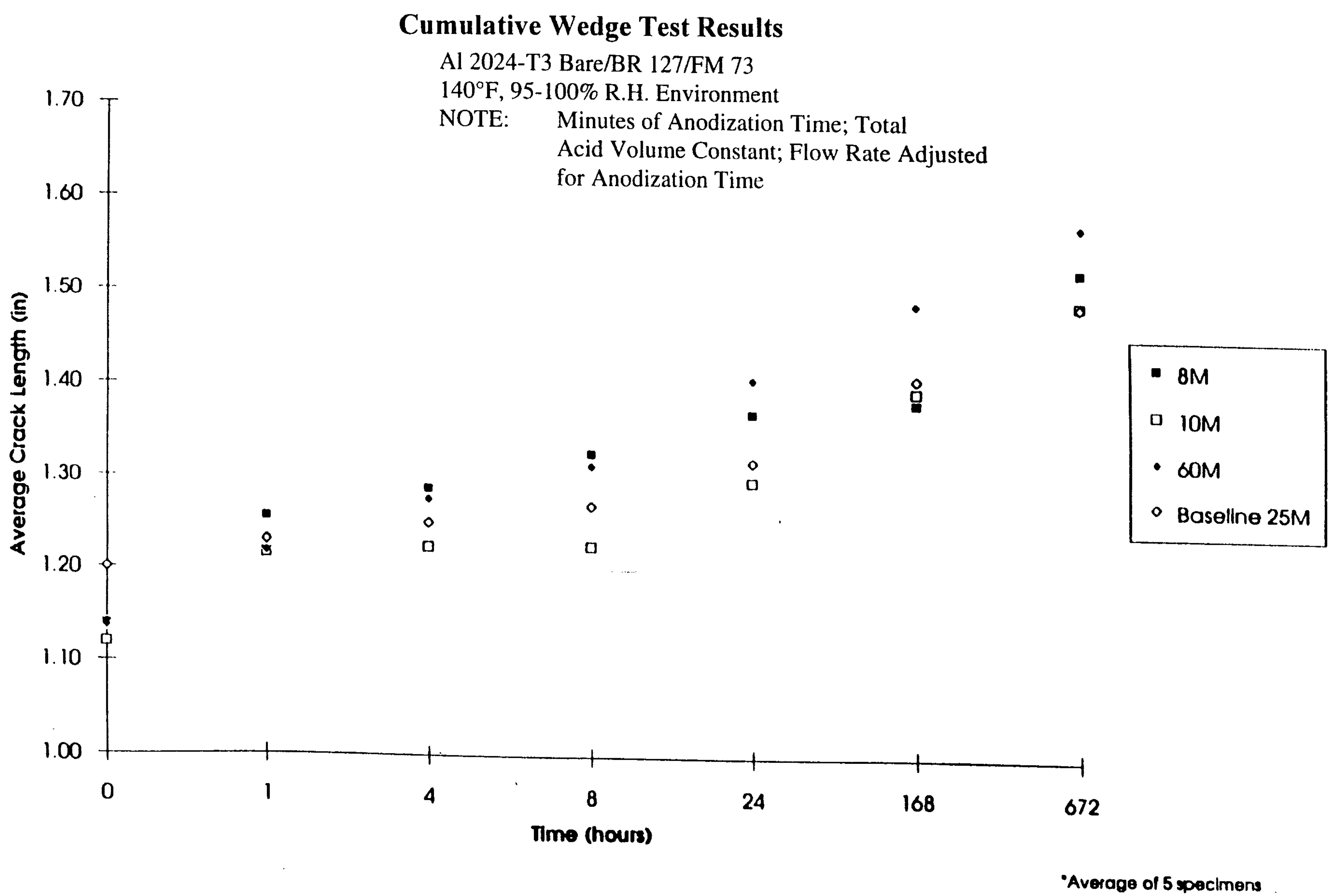


Figure 9. Effect of Anodization Time on Crack Growth Behavior of PACS Prepared Surfaces.

3.1.1.3 Effect of Orientation of the Panel Being Anodized

All baseline data was generated by performing a PACS anodization on a horizontal surface. For comparison purposes, aluminum panels were also anodized in both the vertical and inverted positions. It was observed that in order to achieve good anodization over the entire surface of a vertical panel, the flowrate must be reduced and the acid inlet must be at the bottom of the panel. On a 6" X 6" panel, for example, the flow rate had to be reduced until anodization time lasted for 35 minutes, as compared to the standard 25 minutes on a horizontal surface. The reduced flow rate permits gravity to force acid into all parts of the bagged surface area, and a uniformly anodized surface results. If the flow rate is too fast, lower corners of the bagged surface area will be bypassed as the acid "channels" through only the central region of the bagged surface. Figure 10 illustrates this phenomena. Similarly, a 16" X 16" panel required 45 minutes of anodization time to obtain a uniformly anodized surface. Figure 11 illustrates wedge test results for anodization of a vertical surface. The crack growth for the vertically anodized panels was slightly lower than that for the horizontal panel and both exhibited cohesive failure. Since the crack growth values for the vertical panels are only slightly less than those for the horizontal panels, no significant distinction should be made in terms of anodization effectiveness for each of these orientations.

In order to simulate repair on the underside of a wing, two aluminum (7075-T6) panels were placed on the underside of a flat aluminum plate, bagged, and anodized using the PACS unit. They were then primed with BR127 and bonded with FM 73. MLSE personnel monitored the wedge crack growth for this panel and have indicated that acceptable crack growth rates were obtained.

3.1.1.4 Effect of Temperature

The effect of temperature on the surface being anodized was evaluated. Wedge test panels were anodized at temperatures ranging from 35°F to 100°F using the PACS unit. Figure 12 indicates that although the panel prepared at 50°F resulted in acceptable crack growth, the panel prepared at 100°F resulted in a significantly increased rate of crack growth. Multiple panels were tested at the various temperatures to confirm the upper temperature limits.

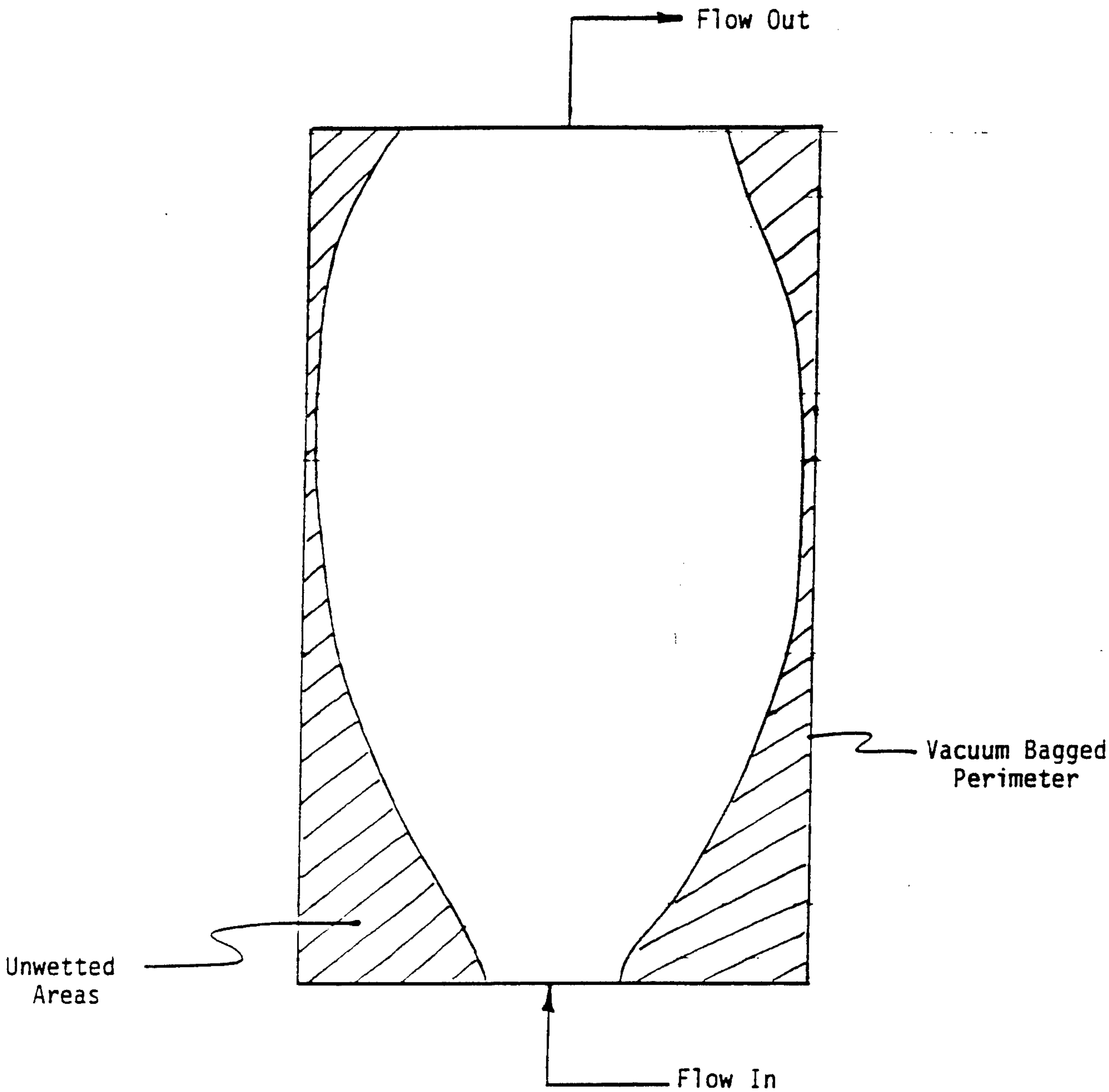


Figure 10. Fluid Channeling on a Vertically Bagged Surface if Flow Rate is Too High

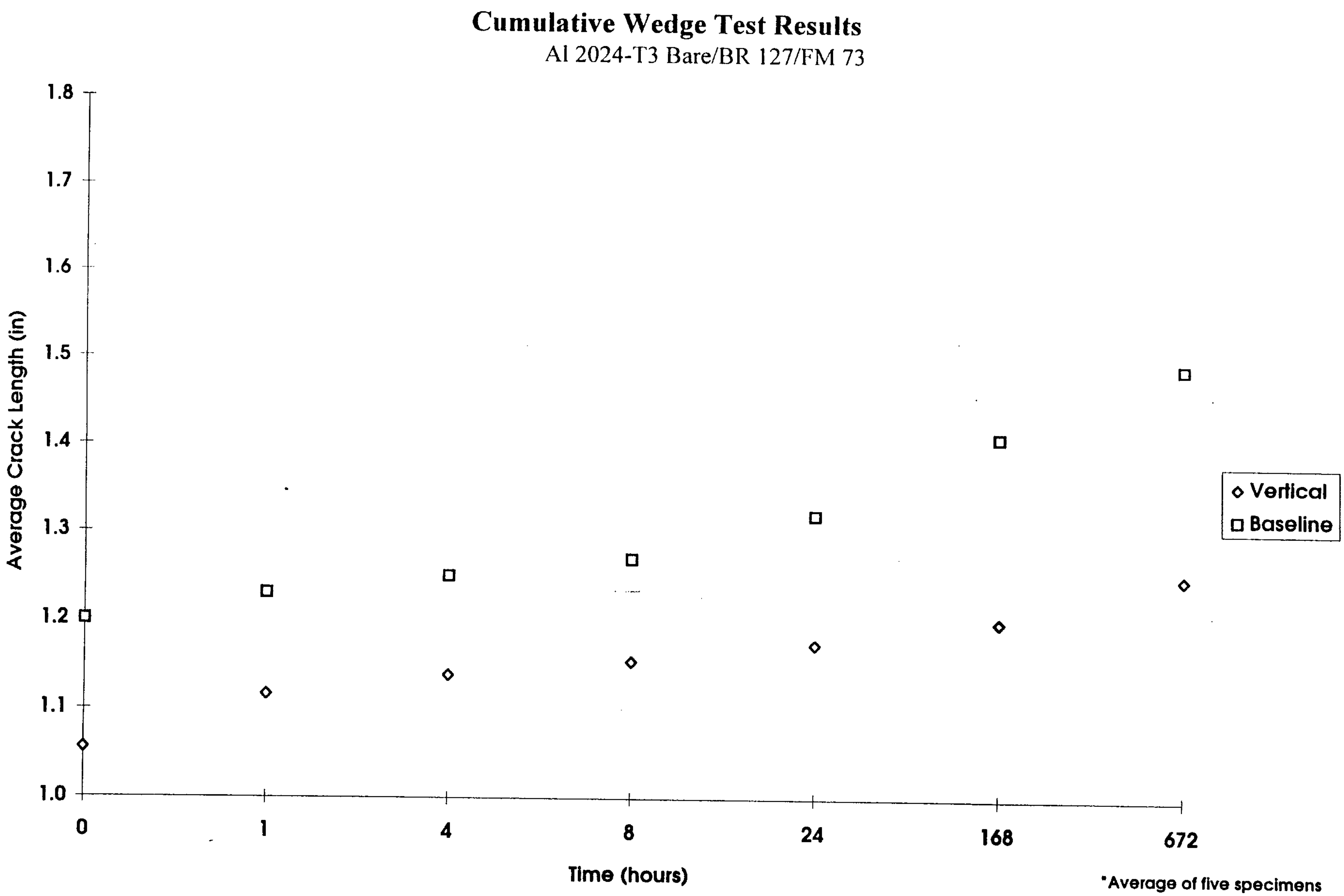


Figure 11. Effect of Panel Position on Crack Growth Behavior of PACS Prepared Surfaces

NOTE: Blackened symbols indicate adhesive failure, while open symbols indicate cohesive failure. Symbols that cannot be blackened indicate cohesive failure.

Al 2024-T3 Bare/BR 127/FM 73
140°F, 95-100% R.H. Environment

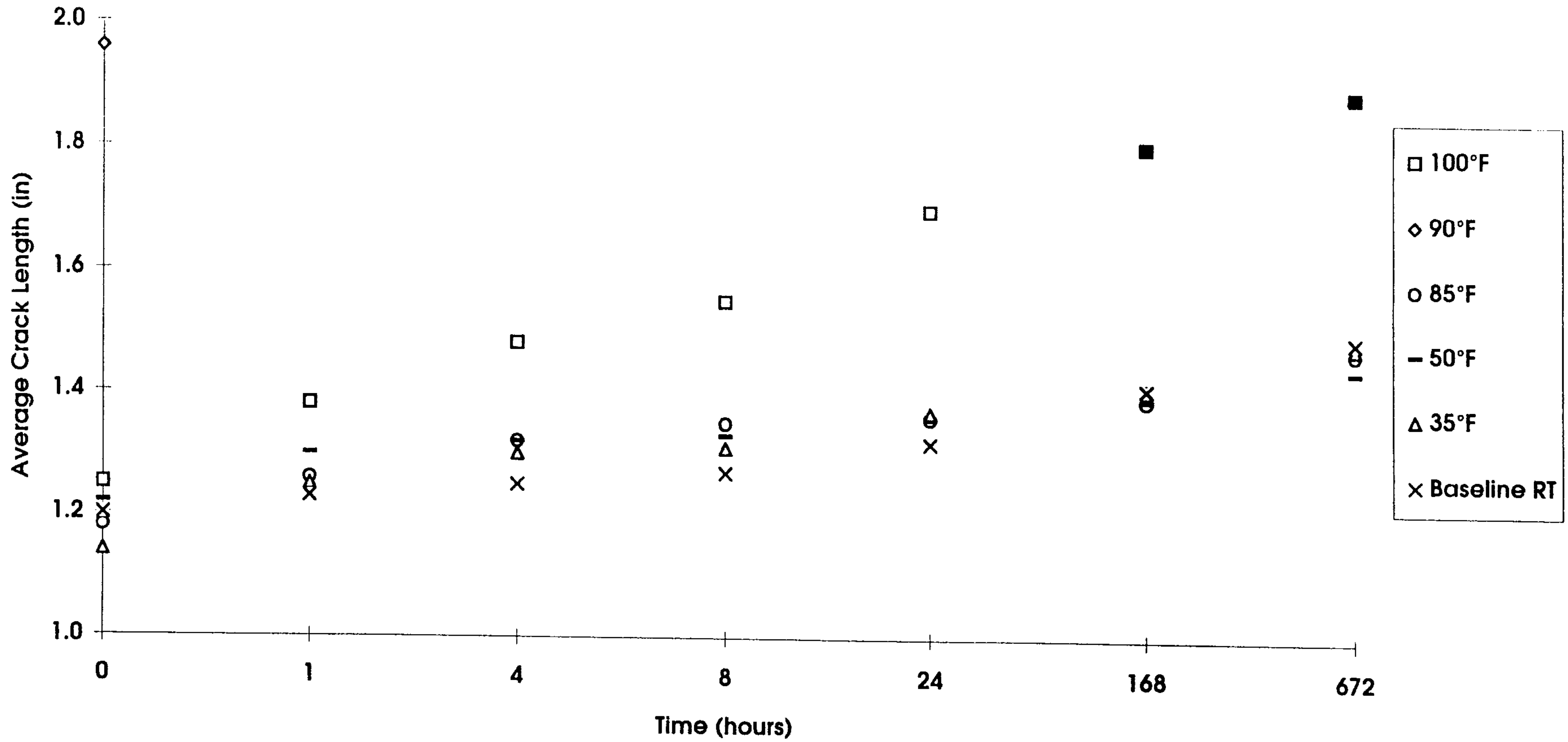


Figure 12. Effect of Processing Temperature on Crack Growth Behavior of PACS Prepared Surfaces

3.1.1.5 Effect of Water Rinse Delay

Figure 13 illustrates the effect of a 5 minute water rinse delay on crack growth behavior of a panel that was at 100°F while being PACS anodized. Adhesive failure occurred almost immediately for all wedge test specimens prepared at 100°F with a 5 minute rinse delay. Figure 14 illustrates the effect of a 5 minute water rinse delay on crack growth behavior of a panel that was anodized at room temperature (RT). Adhesive failure occurred almost immediately for all wedge test specimens prepared at RT with a 5 minute water rinse delay.

3.1.1.6 Effect of Fasteners on Vacuum Integrity

The effect of fasteners on vacuum integrity was illustrated by anodizing an 8" X 8" section of aluminum structure containing numerous fasteners. Two separate experiments were conducted: PACS anodization over uncoated fasteners and PACS anodization over sealed fasteners. Hysol's two-part epoxy, EA 9396, was utilized to seal the fasteners. The goals of this experimentation were to determine if (a) sufficient vacuum could be drawn over an area containing fasteners to permit successful PACS anodization, and (b) any acid leaked around the fasteners during the PACS anodization procedure. The results of the experiment where the fasteners were not coated indicated that full vacuum could be achieved. In addition, visual inspection of the anodized surface indicated successful PACS anodization. Although the results of this experimentation suggested that it was not necessary to coat the fasteners prior to running the PACS procedure, MLSE personnel indicated that current repair procedures over areas containing fasteners often required that the fasteners be sealed prior to any surface preparation procedures. Recognizing this, subsequent experimentation was conducted using EA 9396 to seal the fasteners prior to anodization. As for the uncoated fasteners, full vacuum was achieved and visual inspection of the anodized panel around where the fasteners were sealed indicated successful anodization. Inspection of the backface of the fastener containing structure revealed no acid leakage around the fasteners. It should be noted that only one piece of structure was utilized in this experiment and that further experimentation is recommended to determine the most effective techniques for handling fasteners prior to the PACS anodization. The piece of structure selected for this experimentation contained numerous fasteners, but does not represent the worst case structure that may need to be anodized.

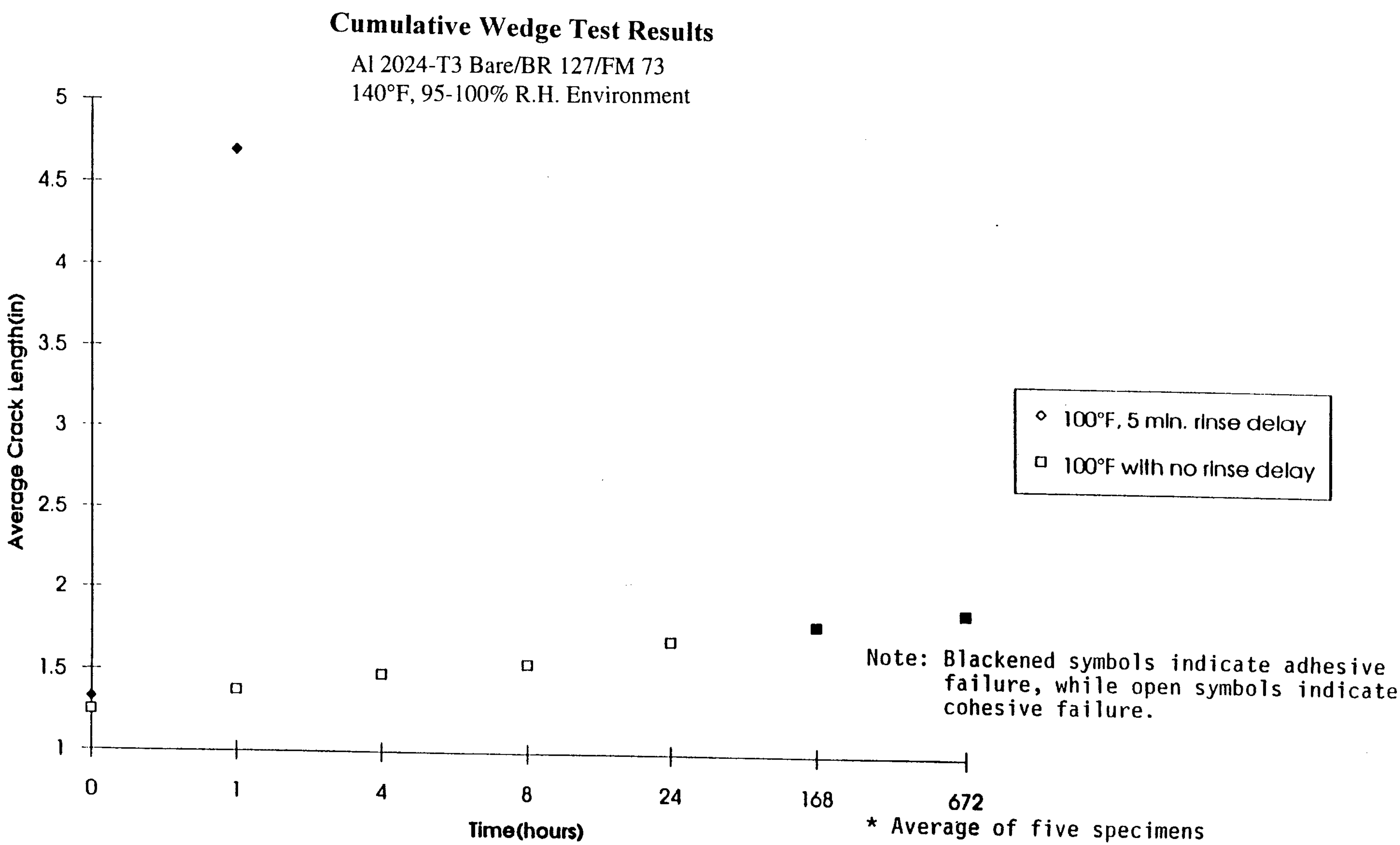


Figure 13. Effect of Five Minute Water Rinse Delay on Crack Growth Behavior of PACS Prepared Surfaces at 100°F

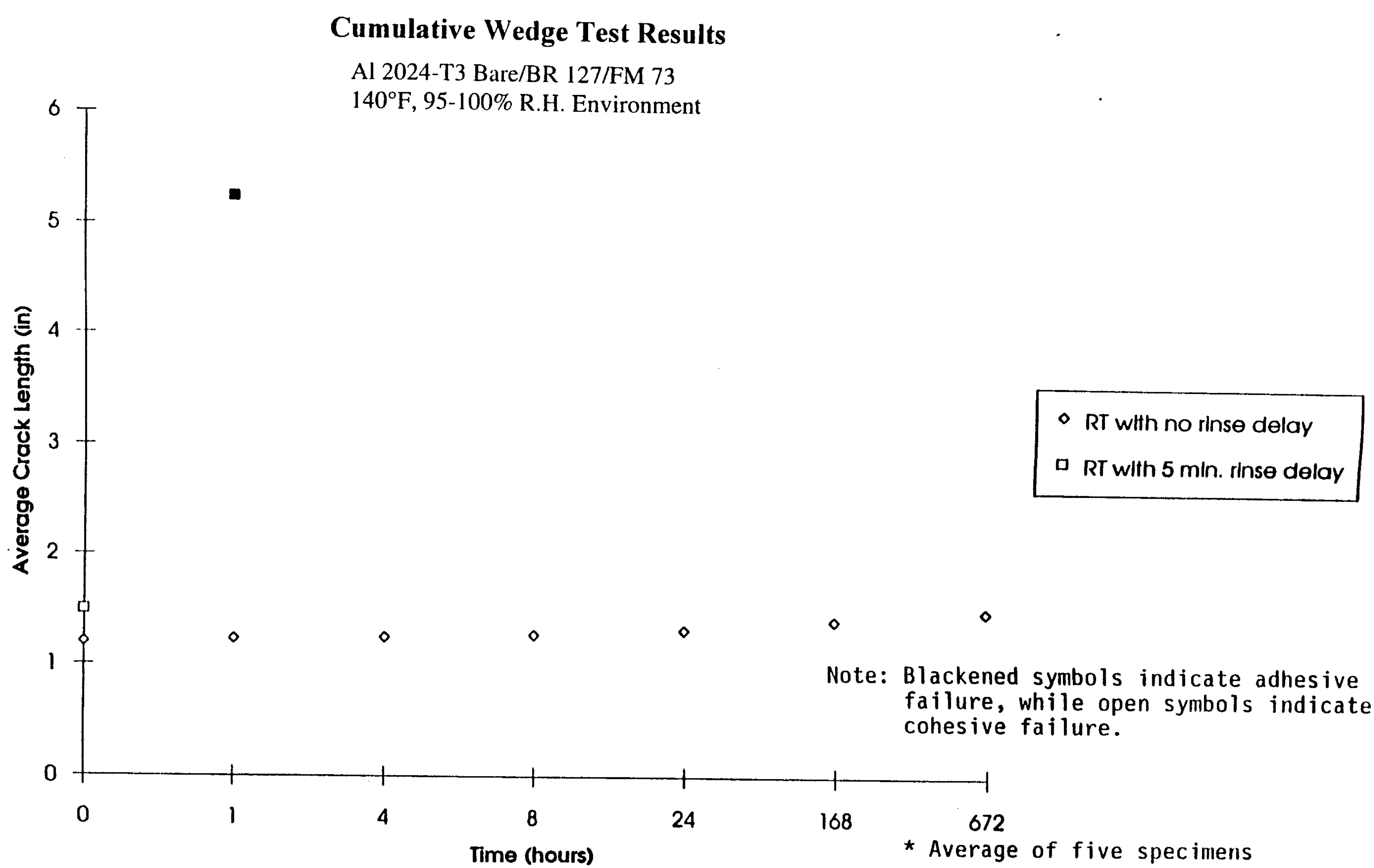


Figure 14. Effect of Five Minute Water Rinse Delay on Crack Growth Behavior of PACS Prepared Surfaces at RT

3.1.1.7 Effect of Screen Type

Figure 15 illustrates the effect of screen type on crack growth behavior of PACS anodized surfaces. The screen supplied with the PACS kit was a stainless steel screen. Two alternative materials were utilized in place of the stainless steel screen: 0.063-inch aluminum sheet and aluminum foil. Although the aluminum foil was securely attached to the electrical lead, no current could be drawn and therefore, anodization was impossible. However, the aluminum sheet is a viable replacement for the stainless steel screen if needed.

3.1.1.8 Effect of Type and Amount of Breather Material

The effect of breather material on the surface being anodized was evaluated. The current layup procedure requires the use of two 10-oz breather plies between the aluminum surface to be anodized and the screen and two 10-oz breather plies on top of the screen. Three 3-oz breather plies were substituted for each of these four 10-oz breather plies. The results presented in Figure 16 indicate essentially equivalent wedge crack growth behavior.

3.1.1.9 Effect of the Addition of Sodium Bicarbonate to the Water Rinse

Figure 17 illustrates the effect of the addition of sodium bicarbonate to the last bottle of rinse water. The addition of sodium bicarbonate to the rinse water cycle resulted in unacceptable crack growth. This was investigated as a means of insuring neutralization of the liquid left in the bagged setup after completion of the process. It has been found that use of water alone for rinsing results in a final pH of 3-4 if one container of water is used and a pH of about 5 if two containers are used. Since a pH level of 5 is not considered hazardous to human contact, the recommended rinse/neutralization procedure is to use two containers of water.

3.1.1.10 Size of the Area Being Anodized

During the examination of the operating and processing variables, the largest area anodized was 12" X 12". Based on discussions with MLSE and Boeing personnel, the maximum area anodized in a repair situation could be a 24" X 24" area. Consequently, tests were conducted to determine if the PACS unit could successfully anodize a 24" X 24" area and, if so, what the process parameters were to achieve good anodization. Results indicate that the maximum size that the PACS unit used in this study is capable of

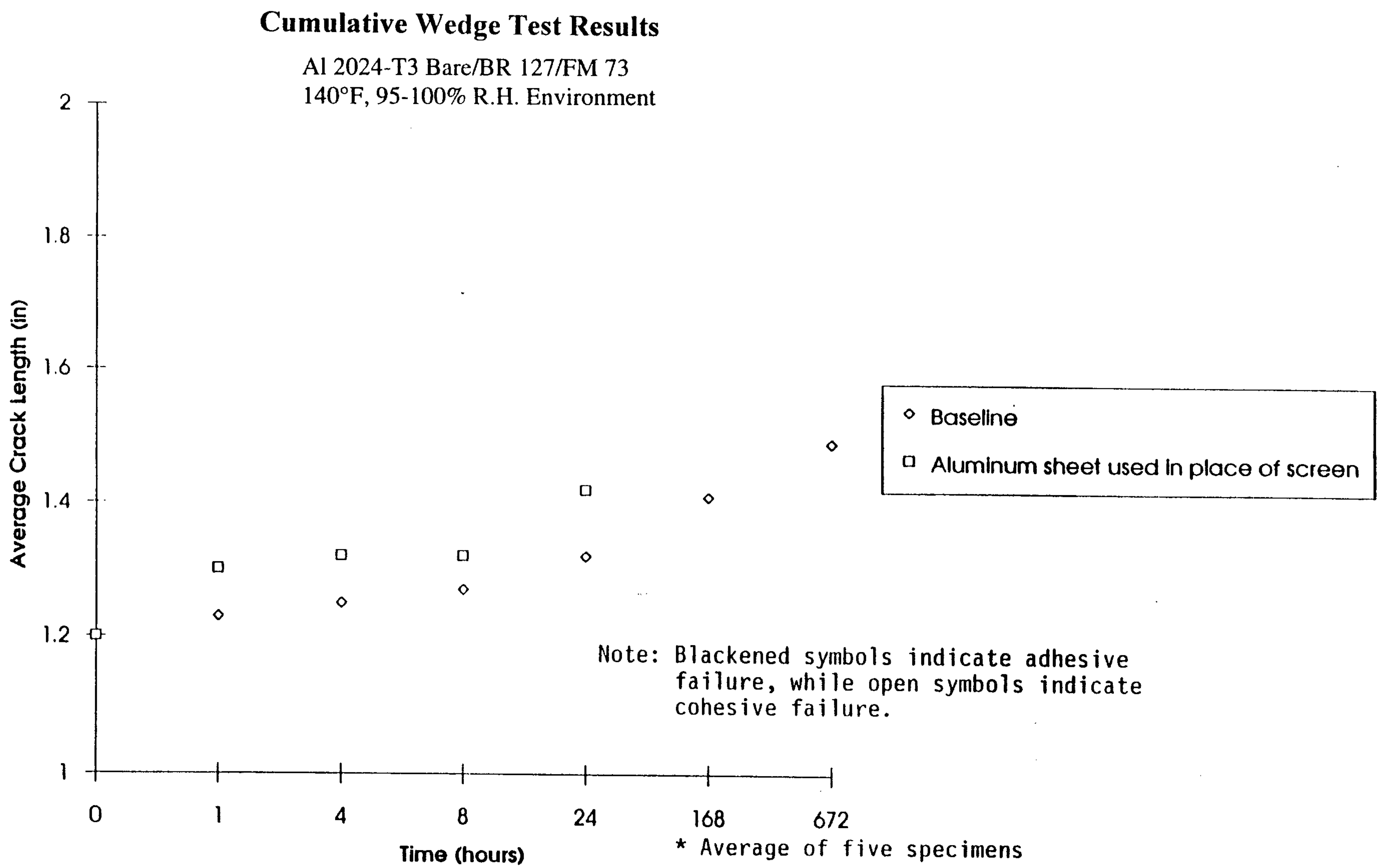


Figure 15. Effect of the Screen Type on Crack Growth Behavior of PACS Prepared Surfaces

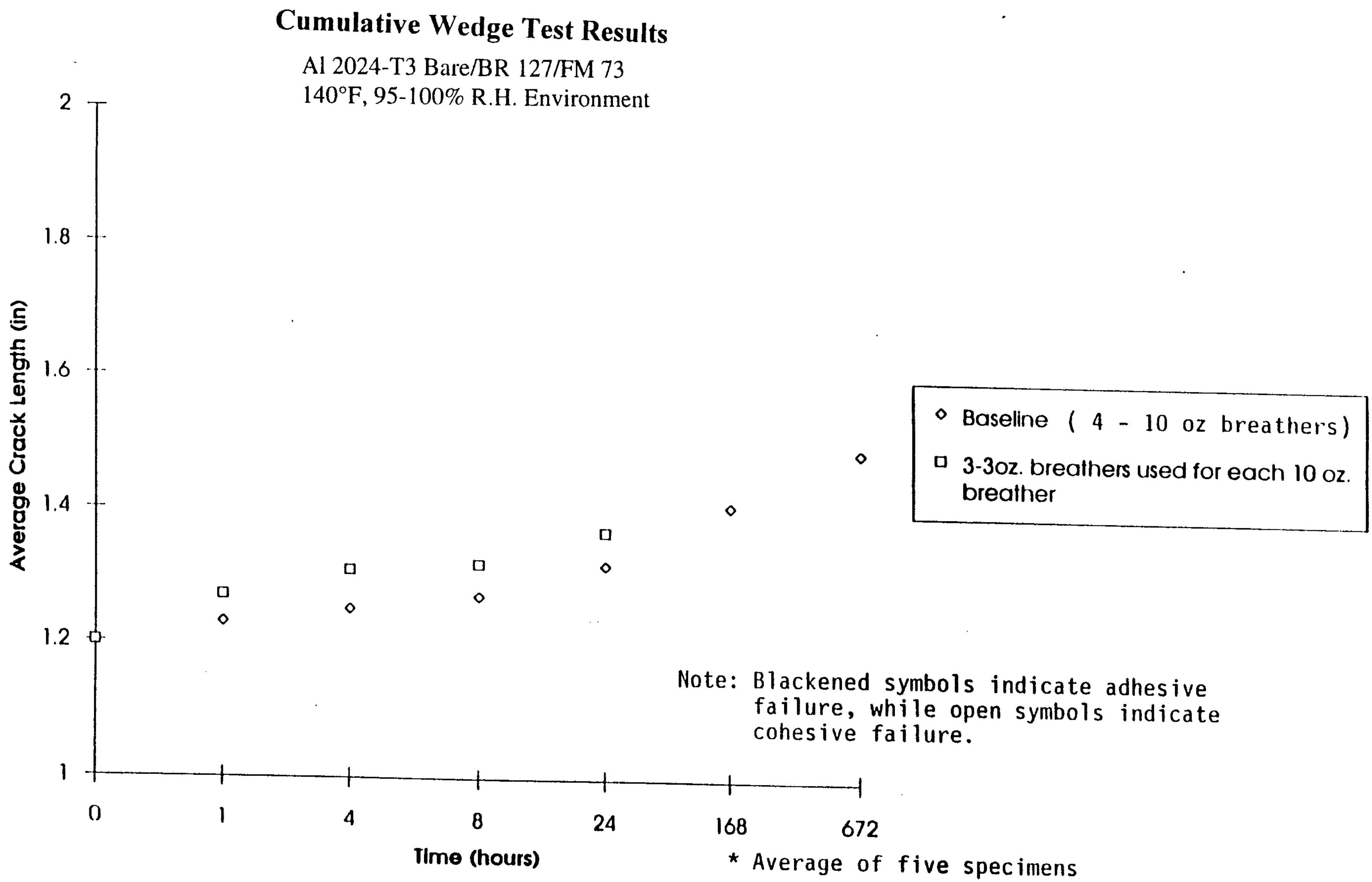


Figure 16. Effect of Type and Amount of Breather Material on Crack Growth Behavior of PACS Prepared Surfaces

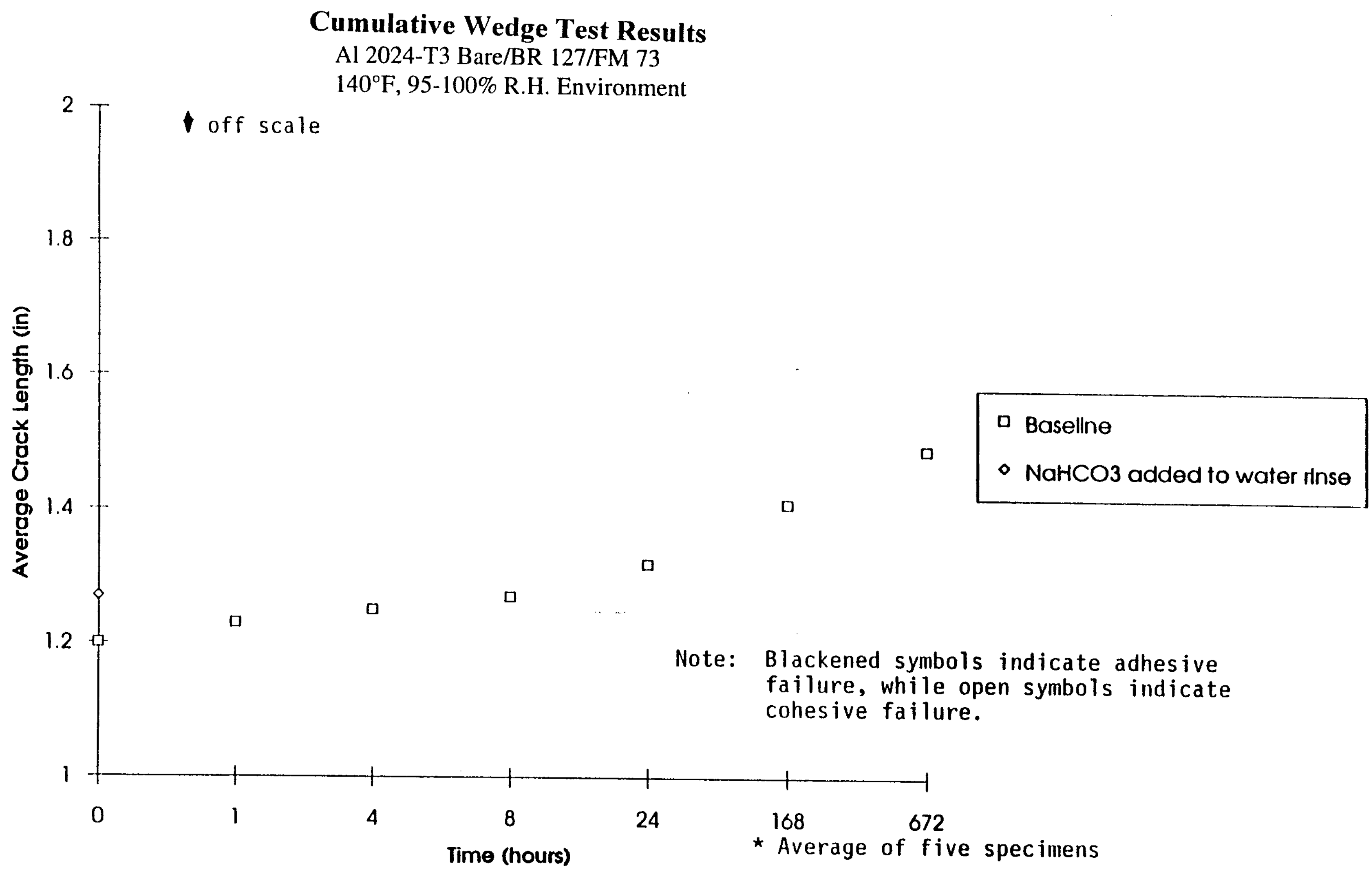


Figure 17. Effect of Sodium Bicarbonate ($NaHCO_3$) Added to Water Rinse on Crack Growth Behavior of PACS Prepared Surfaces

successfully anodizing is a 16" X 16" area. In summary, the results presented in Table 6 indicate recommended procedural variables shown to be acceptable and/or necessary when operating the PACS unit.

3.2 SURFACE MORPHOLOGY

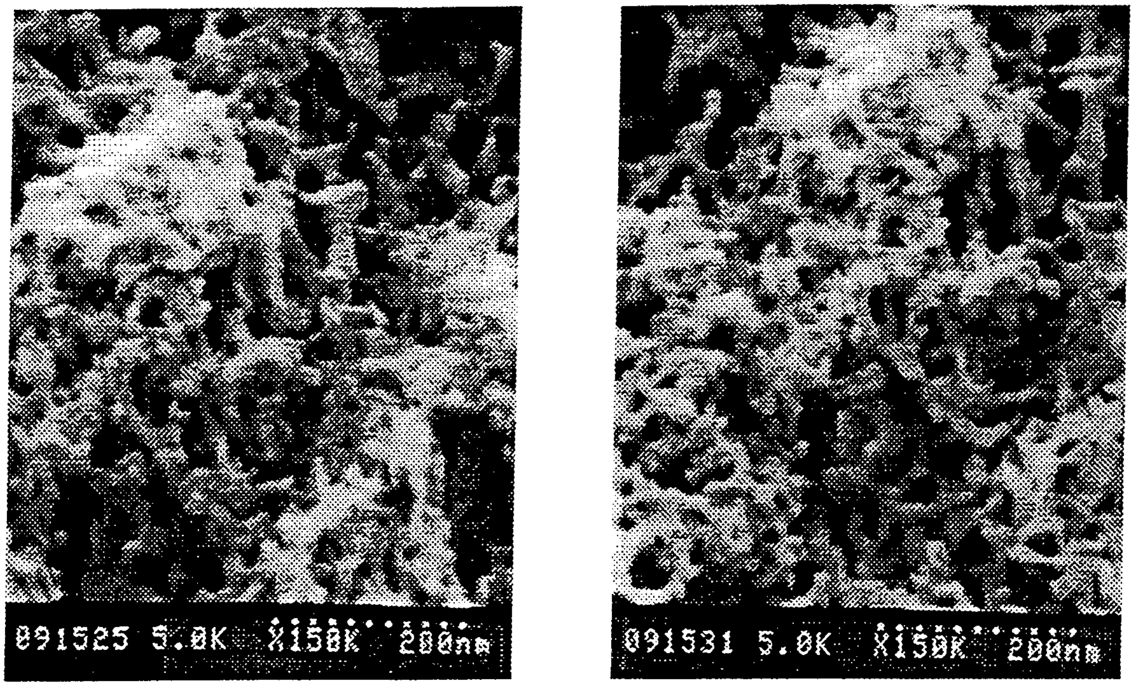
Aluminum panels for surface morphology comparisons were anodized utilizing both the PAA and PACS surface preparation techniques. Stereo pair photographs of the anodized surfaces were obtained to determine and quantify surface morphological features. Comparison of the PAA and PACS oxide structures by this means indicated that while they are similar, the PACS structure exhibits finer features than the PAA prepared surfaces. Stereo pairs of PAA and PACS prepared 2024-T3 clad surfaces are presented in Figure 18. Very similar structures were observed with 7075-T6 bare and 2024-T3 bare. Examination of the oxide layer on both PAA and PACS prepared surfaces indicate a honeycomb structure with finger-like protrusions emanating from the corners of each cell. Visually, the differences seem limited to the diameter of the honeycomb cell. Figure 19 illustrates an isometric drawing of the oxide layer formation for both surface preparation techniques. Similar structures have been reported previously for the PAA surface preparation techniques. Although the structure is similar, the magnitudes of X, Y, and Z are different for the two techniques. Table 7 lists the dimensional measurements of the oxide layer including the values of X (Finger Height), Y (Finger Thickness), and Z (Honeycomb Cell Width) for both the PAA and PACS prepared surfaces. This table includes dimensions for not only the standard PACS and PAA prepared surfaces. but also PACS prepared surfaces where selected processing variables were changed. The results in Table 7 indicate that in general, the finger height is slightly longer for the PAA prepared surfaces, the PAA finger thickness is two times that of the PACS, and the PAA honeycomb cell width is 1.5 times that of the PACS. Two PACS anodized surfaces, 100°F and 100°F with a 5 minute water rinse delay, exhibited alterations of the oxide layer formation on the aluminum surface in addition to poor wedge crack properties previously reported. It was noted that there were significantly fewer honeycomb areas on the specimen anodized at 100°F than the standard specimen. In addition, there were no distinguishable features on the surface of the aluminum anodized at room temperature with a 5 minute water rinse delay.

The overall height of the oxide layer from the top of the aluminum to the top of the finger projections was measured using an Auger Electron Spectroscopy (AES) technique. Figure 20 illustrates the depth profile analysis for a PAA aluminum surface.

TABLE 6

PERMISSIBLE OPERATING WINDOWS FOR PACS

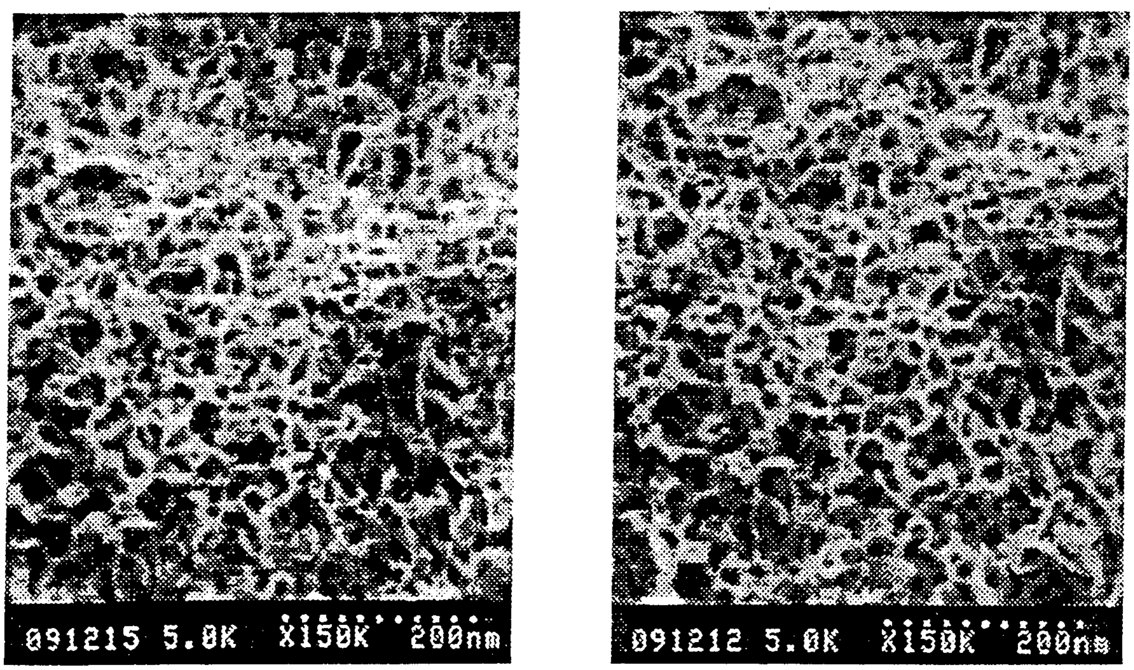
Variable	ATACS Recommended	UDRI Recommended	Permissible Limits or Acceptable Alternates
1. Voltage/Current	6-10V, 1-7 A/ft^2	6V; 2 A/ft^2	6-10V; 1-7 A/ft^2
2. Anodization Time/Acid Flow Rate	25 min; 80 cc/min	25 min; 70 cc/min	10-60 min; adjust flowrate accordingly
3. Surface Orientation	no mention	N.A.	horizontal, vertical, inverted
4. Temperature of Surface Being Anodized	70-85°F	70-75°F	70-85°F
5. Rinse Delay	no mention	None	None
6. Sealing of Fasteners	no mention	EA 9396 or equivalent	N.A.
7. Screen Type	SS screen	Stainless steel screen	Screen, 0.062 Al (not foil)
8. Breather Type/Amount	4 plies of 10 oz.	4 plies of 10 oz.	12 plies of 3 oz.
9. Use of Alkaline Rinse to Neutralize	no mention	Not recommended	N.A.
10. Maximize Anodizable Area	no mention	16" x 16"	16" x 16"



40°

28°

(a) Anodized with Tank PAA Procedure



40°

28°

(b) Anodized with PACS Procedure

Figure 18. SEM Stereo Pairs of Anodized 2024-T3 Clad Aluminum (150,000X)

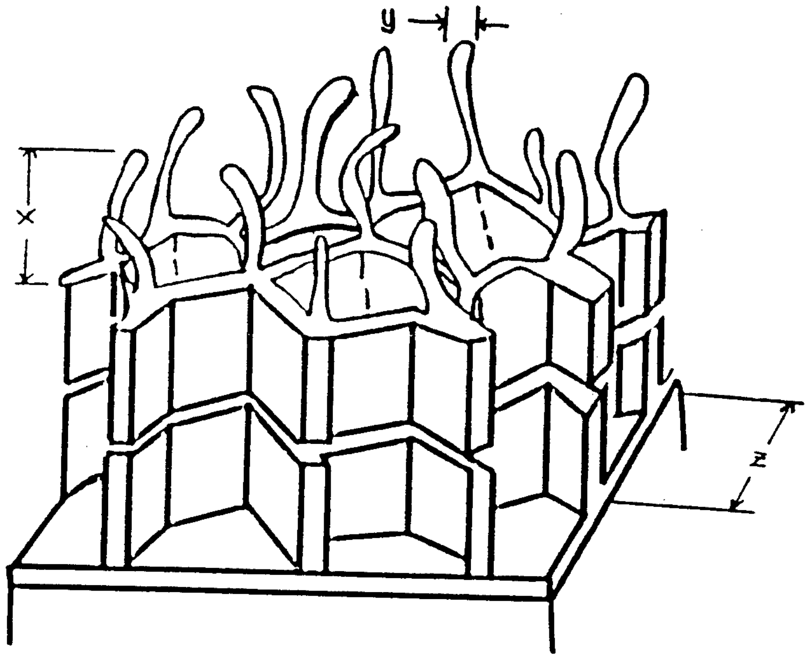


Figure 19. Oxide Layer Structure on a PACS and PAA Anodized Aluminum Surface

(Source: Ref. 5)

TABLE 7

SURFACE MORPHOLOGY OXIDE LAYER DIMENSIONS FOR PACS AND PAA PREPARED ALUMINUM SURFACES

Sample Designation (1)	X Figure Height (Å)	Y Figure Width (Å)	Z Honeycomb Width (Å)
PACS Prepared			
2024-T3 Bare (Standard)	987	99.7	252
2024-T3 Clad (Standard)	1003	89.2	257
7075-T6 Bare (Standard)	994	110	210
2024-T3 Bare with 10 min anodization time	935	110	278
2024-T3 Bare with 60 min anodization time	1192	121	257
2024-T3 Bare at 50°F	733	73.5	304
2024-T3 Bare at 100°F	844	320	289 (2)
2024-T3 Bare at 100°F with 5 min rinse delay	NR (3)	NR	NR
2024-T3 Bare at RT with 5 min rinse delay	NR (3)	NR	NR
PAA Prepared			
2024-T3 Bare	1225	208	387
2024-T3 Clad	1306	205	383
7075-T6 Bare	1215	210	394

(1) All measurements are averages of 9 individual readings.
(2) There were significantly fewer honeycomb areas than in the standard oxide layer formation.
(3) No measurements could be made because there were no distinguishable features on the surface.

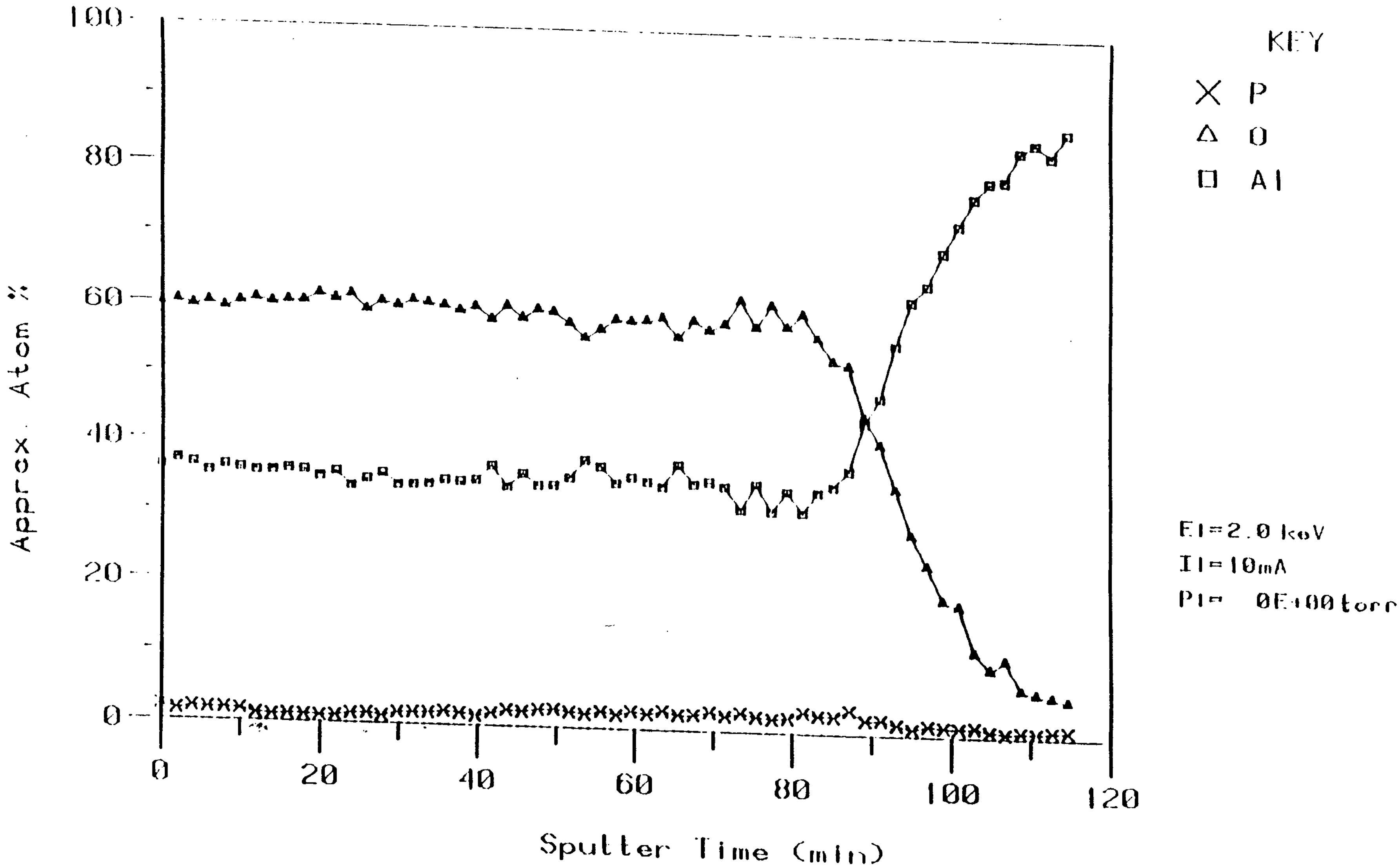


Figure 20. Depth Profile Analysis Using Auger Electron Spectroscopy for PAA Prepared Aluminum Surface

The sputter rate used for this analysis was 5 nm/min. The point at which the curve for aluminum and the curve for the oxygen cross indicates the time required to remove the oxide layer. With a crossover point at 90 minutes, the calculated overall thickness of the oxide layer is 450 nm (≅4500 A). Similarly, Figure 21 illustrates the depth profile analysis for a PACS prepared aluminum surface. With a crossover point at 18.5 minutes and a sputter rate of 5 nm/min, the calculated overall thickness of the oxide layer is 92.5 nm (925 A).

3.3 ROUND ROBIN TESTING

Four additional PACS units were procured for use in a round robin test effort at various repair depots at Kelly, McClellan, Tinker, and Robins AFB. An operating procedure was written and sent with each PACS unit. This procedure was a step-by-step procedure that included specific values for each of the operating parameters/variables outlined above. A kit including Scotchbrite, screen, breather material, bagging material, sealant tape, collapsible bottles, litmus paper, and sodium bicarbonate was assembled at UDRI and included with each of the PACS units.

Each depot was required to anodize and apply primer to both wedge crack and peel adherands. Color chips made at UDRI were included to insure appropriate primer thickness. The primed wedge test and peel adherands were then sent to UDRI for adhesive bonding and testing. Table 8 lists the total number of specimens that were tested in the round robin for each depot. Specimens were received from only two of the four AFBs.

3.3.1 Wedge Test

Wedge test panels were prepared and tested as discussed in Section 2.2. 7075-T6 aluminum was used for all panels. All the panels were primed with BR 127 and bonded with FM 73. The wedge test results are presented in Table 9. Graphical representation of these results is illustrated in Figure 22. With the exception of specimens removed from Panel A, all specimens exhibited cohesive failure.

3.3.2 Peel

Peel panels were prepared and tested as discussed in Section 2.4. 7075-T6 aluminum was used for all panels. All the panels were primed with BR 127 and bonded with FM 73. The peel results from panels prepared at one depot are presented in

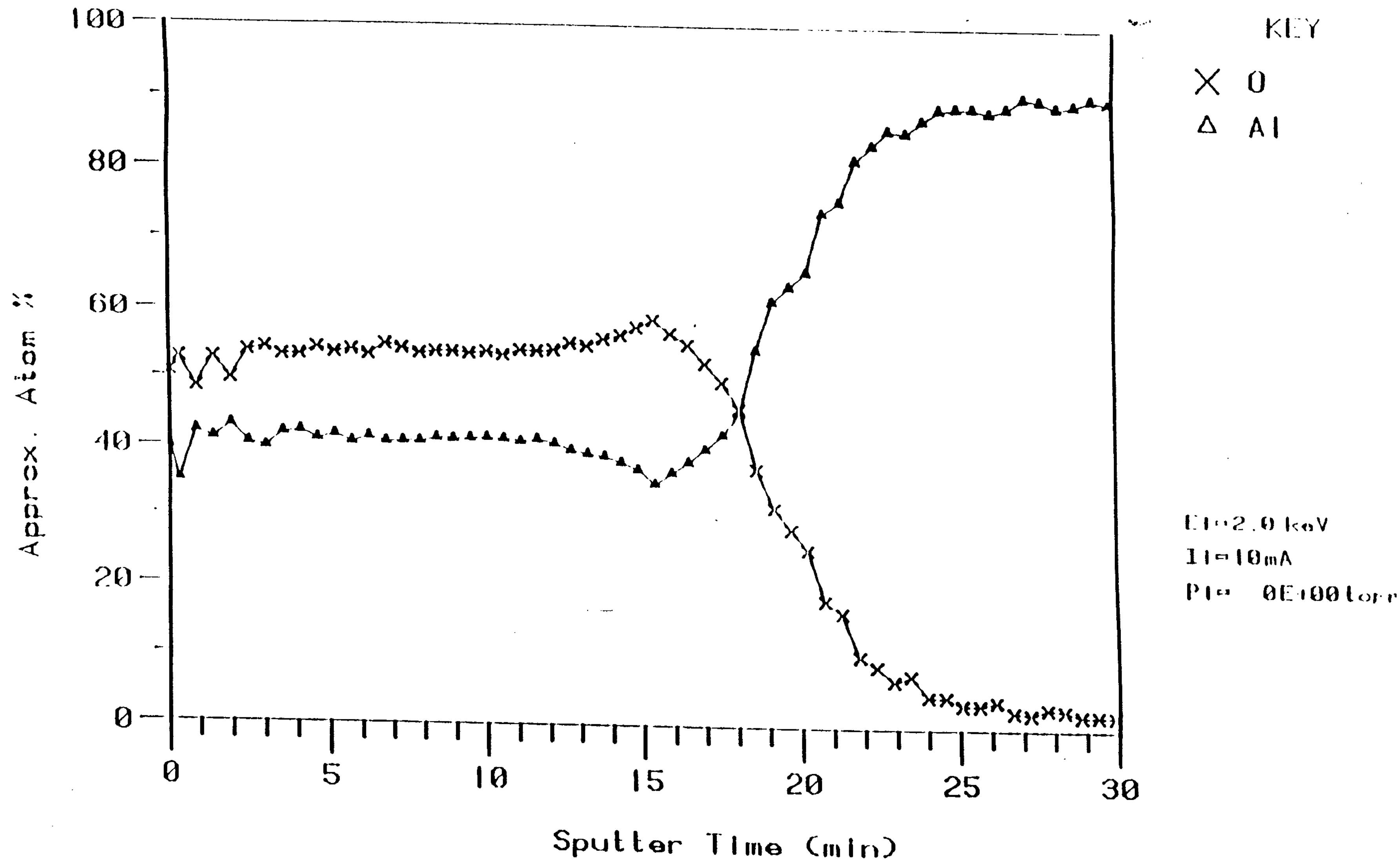


Figure 21. Depth Profile Analysis Using Auger Electron Spectroscopy for PACS Prepared Aluminum Surface

TABLE 8

TEST PLAN FOR DEPOT PREPARED TEST SPECIMENS

Alloy (1)	7075-T6
Surface preparation (1)	PACS
Primer (1)	BR 127
Adhesive (1)	FM 73
Cure Condition (1)	Manufacturer's recommended
Type tests and replicates: Wedge Crack (140°F, 95-100% RH) Wedge Crack (140°F, salt fog) Peel (RT) Peel (-65°F)	 5 5 5 5
TOTAL SPECIMENS Wedge Test Peel	 10 per depot 10 per depot

TABLE 9

WEDGE TEST RESULTS FROM DEPOT PREPARED SPECIMENS

Specimen (1)	CUMULATIVE WEDGE TEST (in) Time (hours)						
	0	**1**	**4**	**8**	**24**	**168**	**672**
A (2)	1.26	4.24	4.31	4.39	4.44	4.46	4.52
B	1.24	1.41	1.49	1.53	1.64	2.01	2.25
C	1.23	1.34	1.41	1.45	1.58	1.93	2.23
D	1.18	1.28	1.36	1.40	1.52	1.88	2.13
Baseline (3)	1.20	1.23	1.25	1.27	1.32	1.41	1.49

(1) All wedge test specimens were anodized using the PACS procedure, primed with BR 127, and bonded with FM 73. They were then aged @ 140°F and 95-100% R.H. Note that all failures were cohesive, unless otherwise noted.

(2) These specimens exhibited adhesive failure.

(3) The baseline specimens were prepared at UDRI.

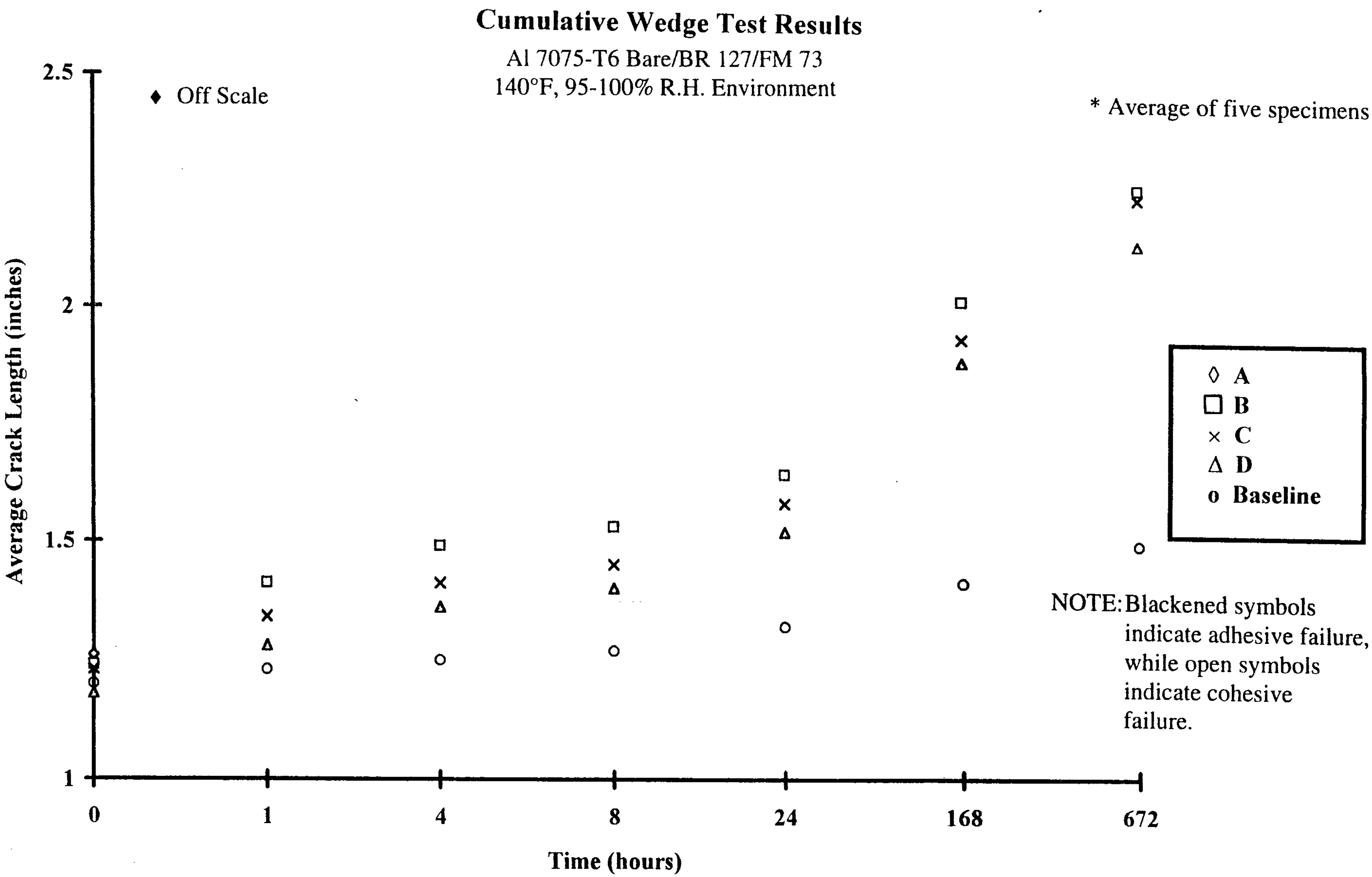


Figure 22. Average Crack Growth Curves Comparing PACS Prepared Surfaces by Specific Depots.

Table 10. It should be noted that although a second depot submitted peel adherends to be bonded, visual observation of the anodized/primed surface indicated that the panels were not properly anodized. Consequently, only the panels supplied by one depot were bonded and subsequently tested. All of the specimens tested exhibited cohesive failure.

TABLE 10

PEEL RESULTS FROM DEPOT PREPARED SPECIMENS

Specimen (1)	Peel (lbs/in) (2)
A	47.99
B	54.88

(1) All specimens were Al 7075-T6, anodized using the PACS procedure, primed with BR 127, and bonded with FM 73. Note that all failures were 100% cohesive.

(2) All specimens were tested in accordance with ASTM D 3167. In addition, the value reported for peel strength is an average value based on five specimens.

SECTION 4
CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

This investigation showed that the phosphoric acid containment system (PACS) can be used to successfully anodize an aluminum surface. In addition, since the phosphoric acid is completely contained during the operation of the PACS unit, potential logistics as well as safety problems which are inherent in the PAA tank surface preparation technique could be eliminated.

Wedge test results indicate that a broad range of voltages/currents as well as anodization times/flowrates can be used to achieve sufficient anodization of the aluminum surface. Operation of the PACS unit at temperatures lower than room temperature was found to be acceptable, although not recommended due to significant reduction in peel properties below RT reported on several other programs. Elevated temperature operation (100°F) of the PACS unit resulted in immediate adhesive failure. In addition, any type of water rinse delay resulted in adhesive failure. The largest area that the ATACS PACS unit can successfully anodize is a 16" X 16" area.

Surface morphology results indicate that surface preparation conducted with the PACS unit yields a similar, although finer, oxide layer than that produced by the phosphoric acid anodization (tank) technique.

4.2 RECOMMENDATIONS

Additional experimentation should be conducted on structures containing fasteners. This work should involve techniques for sealing the fasteners prior to anodization. It should include various types of fasteners such as titanium and high strength steel. In addition, the number and location of fasteners which would require anodization and subsequent bonding should be varied in an effort to simulate current structural requirements.

SECTION 5
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