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DURABILITY OF ADHESIVELY BONDED STRUCTURE

Al E. Hohman
Charles M. Standard
LTV Aerospace and Defense Company
Missiles Division
P.O. Box 650003
Dallas, Texas 75265-0003

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Wright Laboratory
Air Force Systems Command
Wright-Patterson AFB, Ohio 45433-6533

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James J. Mazza

JAMES J. MAZZA, Materials Engineer
Materials Engineering Branch
Systems Support Division
Materials Directorate

Theodore J Reinhart

THEODORE J. REINHART, Chief
Materials Engineering Branch
Systems Support Division
Materials Directorate

THOMAS D. COOPER, Chief
Systems Support Division
Materials Directorate

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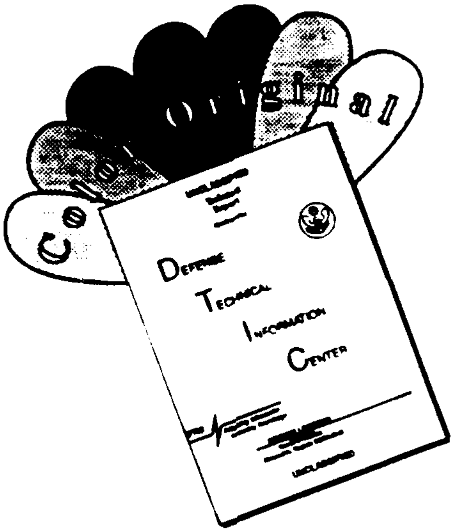

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A. E. Hohman, C. M. Standard

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Missiles Division
P.O. Box 650003
Dallas, TX 75265-0003

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13. ABSTRACT *(Maximum 200 words)*

Two adhesives were exposed to marine atmosphere for a 10-year period. The specimens compared durability of phosphoric acid anodize to sodium dichromate/sulfuric acid (OFPL) surface preparations, each primed with a chromated epoxy primer. Double lap shear specimens were exposed with no load and spring loaded to two stress levels to compare combined corrosion/stress effects. Nondestructive tests were conducted to determine their capability to show delaminations or the presence of corrosion in the adhesive bond line. Specimens were tested for residual mechanical properties after 5 and 10 years. Both room and elevated temperature testing were accomplished. Elevated temperature testing of exposed specimens showed reduced strength significantly below unexposed elevated temperature strengths. Phosphoric acid anodized specimens with the chromated epoxy primer showed markedly superior strength retention to the chromic/sulfuric (OFPL) etch in static stressed specimen in the marine atmosphere. Wedge opened crack extension tests also differentiated between the less and more durable adhesive bonding processes.

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1.0 INTRODUCTION AND BACKGROUND

1.1 Introduction

This is the final report on the research conducted under Air Force Contract F33615-91-C-5624 titled Durability of Adhesively Bonded Structure. This program evaluated adhesively bonded aluminum structural specimens that had been exposed for 10 years to a severe marine atmospheric environment.

A total of 153 specimens were prepared for the test; 1/3 were tested new, 1/3 were tested after 5 years exposure and the final 1/3 were tested after 10 years of exposure. Two adhesives and two substrate surface preparations were among these specimens.

1.2 Background

Adhesive joined structures have been vulnerable to significant losses in strength after aging owing to changes in the adhesives exposed to the environment or corrosion of the substrate. Durability has become a more critical concern, as condition of hardware dominates useful life decisions more frequently. Significant technology improvements have occurred in surface treatment, primers, joint analyses, adhesives and process controls. These have resulted in reliability improvements as measured by initial bond strengths. These improvements facilitated the transition of adhesive bonding into aircraft primary structural application in the PABST (Contract F33615-75-C-3016) advanced development program. This feasibility demonstration program clearly established the initial cost savings potential for adhesive bonding. While this approach addresses the adequacy of joints early in service, there is no basis for extrapolating the test results to long-term service. The most striking lack of information is in the combined effects of corrosive processes with those changes which occur as a result of residual stress or cyclic loading in the adhesive joint.

To fill a small part of this long term durability information gap, two adhesives along with the two widely used surface treatments were exposed both stressed and unstressed, in a marine atmospnere for a period of slightly longer than 10 years. From this exposure, information about the durability of these adhesive systems was documented. Mechanisms of bond degradation in this condition were studied in depth.

The major limitation of this life testing is that the knowledge gained took 10 years to accumulate. An analytical approach, coupled with an accelerated testing program, is more desirable since it provides more timely results which ultimately can become a part of the design decision process so that future systems can be developed to meet specific service life requirements. Lacking, however, are the analytical models and an accelerated test predicting performance under actual service conditions. The results obtained in this program provide valuable strength loss documentation for static stressed specimens. More importantly, the mechanisms of damage for aluminum structure in a marine atmosphere were detected. These specimens showed that an accelerated test must include conditions which accelerate filiform action, found to be the primary damage mode in the test exposures made in this program.

2.0 TECHNICAL APPROACH AND TEST METHODS

At the time of initiation of this program, the chromic/sulfuric acid bath known as Forest Products Laboratory etch (FPL) had been the industry standard for several decades. The bath had also been optimized with increased chromic contents and trace elements from aluminum etching to activate the bath to produce more reliable adhesion, (OFPL). Phosphoric acid anodize, (PAA), developed and introduced by Boeing, had just been thoroughly tested not only by Boeing but in the major Air Force program, PABST.

Long term corrosion durability testing results were not available for either surface treatment. Tests for initial properties in the PABST program were done at moderate temperatures suitable for the American Cyanamid FM 73M adhesive. Thus, in order to obtain long term data on both surface treatments for use at ambient and elevated temperature, American Cyanamid FM 300M adhesive was selected and the 300°F upper use temperature, for which manufacturer's data are available, was utilized in lap shear testing. The substrate material selected was 7075-T6 unclad. This alloy with good strength properties had been shown to have better durability in adhesive bond lines in the unclad condition than the clad alloy. Industry experience indicated however, that 7075 was more subject to bond line degradation than the 2024 alloys, also used in many bonded skin assemblies.

The test time period was set for 10 years. The exposure was made on test racks approximately 270 feet from the Atlantic normal high tide zone. Debris under the racks indicate that sea water may at times have been under the racks. A moist marine atmosphere at the Canaveral Florida site presented an aggressive corrosive and moisture laden air exposure for the 10 year period.

2.1 Specimen Preparation

1. Double lap shear and wedge crack extension specimens for the long-term exposure tests were prepared as shown in Figure 1. An outline of the tests to be performed and the specimens required for each is contained in Table 1.

2. All of the detail parts for the preparation of the test specimens called out in Table 1 were fabricated from 0.125" thick 7075-T6 unclad aluminum alloy and then surface treated as indicated in Table 1.

3. The treated details were then all primed with American Cyanamid BR 127 adhesive primer. The primer was cured 1 hour at 250°F.

4. The primed details were then bonded with the respective adhesives as indicated in Table 1. The autoclave cure cycles used to cure the adhesives are as follows:

   (a) FM 73M cured 90 minutes at 250°F and 40 psi (vented to atmosphere)
   (b) FM 300M cured 90 minutes at 350°F and 40 psi (vented to atmosphere)

   Lap shear specimens were bonded individually; crack extension specimens were saw cut after bonding.

5. After completion of the bonding operations, all of the aluminum surfaces of the test specimens were treated with brush-applied Alodine 1200 (MIL-C-5541) and then spray painted with one coat of MIL-P-23377 primer on all surfaces and edges.

6. After the primer had cured adequately, those double lap shear specimens which were to be stressed at the required loads indicated in Table 1 were loaded into stress fixtures.

7. The ends of all the stress-loaded double lap shear specimens and the spring loading apparatus were then heavily coated with PS-890 B2-1/2 as shown in Figure 3. The springs were wrapped with teflon tape. An empty Semco sealant cartridge was then inverted over the spring and PS-890 B2-1/2 (MIL-S-8802) was injected into the cavity around the spring until the cartridge was completely filled.

8. All surfaces of the stress fixtures and double lap shear specimens excepting the bonded test area were then coated with NAPKO epoxy coal tar to prevent corrosion.

9. Stainless steel wedges as indicated in Figure 1 were then inserted into the crack extension specimens, an initial crack length was measured and remeasured after 81 days of ambient laboratory exposure.

10. Ends of the crack extension specimens were drilled after surface treatment and bonding in order to attach identification tags with corrosion-resistant steel wires. After wire insertion, holes were sealed with MIL-S-8802 polysulfide sealant. Holes were not treated with MIL-C-5541 surface treatment nor primed.

11. The coated stress fixtures containing the double lap shear specimens with the crack extension specimens attached were then taken to the Florida exposure site and set up to begin the long-term salt air environment exposure.

12. Crack lengths were measured on specimens returned from the exposure site after 5 and 10 years. Specimens returned after the 10 year period were also tested by

inserting a wedge on the opposite end of the specimen from the original wedge insertion. The crack resulting from the wedge insertion on the 10-year specimen was measured, the specimen exposed for 24 hours at 95% relative humidity and 120°F temperature prior to measurement to determine any crack length extension.

13. Lap shear specimens were tested at the initiation of the program, at the completion of a 5-year exposure and at the 10-year exposure completion. They were tested on a universal testing machine with a crosshead travel rate of 0.07 inches per minute in accordance with ASTM D 1002.

14. The length of each loading spring was measured before they were released, and again after disassembly. Representative springs from each fixture were compressed in a universal testing machine to the loaded dimensions and the force yielded by each spring was recorded. Several springs were observed to be broken, as noted.

Adhesive, Primer and Surface Treatments Tested

The detailed description of the processing, primers and adhesives used in the three groups of specimens used in this program are:

(1) Unclad 7075-T6 aluminum, .0125 inch thickness, surface treated with a chromic/sulfuric acid bath (OFPL) in accordance with process specification CVA8-51, primed with 0.2- to 0.3- mil BR 127 primer supplied by American Cyanamid Company, Bloomingdale Plant, Havre de Grace, MD. Adhesive was American Cyanamid FM 73M modified epoxy resin film containing a random polyester mat.

(2) Unclad 7075-T6 aluminum, 0.0125 inch thickness, surface treated in accordance with Boeing Process Specification BAC 5555, Phosphoric Acid Anodizing of Aluminum for Structural Bonding, primed with 0.2 to 0.3 mil BR 127 primer supplied by American Cyanamid Company, Bloomingdale Plant, Havre De Grace, Maryland and bonded with American Cyanamid FM 300M modified epoxy resin film adhesive containing random polyester fiber mat.

(3) Unclad 7075-T6 aluminum alloy, surface treated with OFPL etch in accordance with CVA 8-51, aluminum, cleaning and etching for bonding, primed with 0.2 to 0.3 mil BR 127 primer and bonded with FM 300M adhesive.

2.2 Characterization of Bonds Using Nondestructive Techniques

Neutron Radiography

Neutron radiography was used on the double lap shear and crack extension specimens using the three million volt Van de Graaff accelerator neutron radiography source with an HVEC Neutrocoll I target/moderator/collimator assembly. An L/D ratio of approximately 25 was used in order to bring a sharper definition of the bond lines which are at some distance from the image plane. The techniques used were selected to be useful in full scale part or aircraft inspection to find corrosion in the adhesive bond.

Ultrasonic/X-Ray

Specimens were inspected using a thru-transmission ultrasonic technique on the Computerized Advanced Data Acquisition System (ADIS) manufactured by McDonnell Douglas to establish a base line comparison of the specimens. The specimens were then evaluated in greater detail using pulse echo ultrasonic techniques, eddy current and real time microfocus X-ray. The detailed nondestructive inspection results were used to characterize the extent of corrosion and determine which bond line(s) have corrosion. The severely corroded specimens were not evaluated because of the probable damage which would have resulted from water contact with the friable corrosion product.

2.3 Characterization of Specimen Condition

Specimens were examined visually and magnified to 50 times actual size, using the binocular microscope. Surface chemical analysis techniques which have the capability of determining the outer several molecular layers in the surface (ESCA) was performed on surface treatments (OFPL and PAA) within 24 hours of initial processing. These surfaces were analyzed with the intent of finding ion species which would indicate the presence of thin layers of the surface treatment on both the adherend and the opposing surface of primer and adhesive which was mechanically separated from the adherend. It was intended to use phosphorous or chromium ion indications to study the possibility of cohesive or adhesive failure within the surface treatment. Electron microscopy was used to search for features which would contribute to understanding the degradation mechanisms. Color photomicrography of features magnified 140 times real size was used extensively to record surface phenomena.

3.0 RESULTS

3.1 Lap Shear Strength and Crack Extension Results

Initial unexposed strength values at ambient and 180°F for the FM 73M specimens and ambient and 300°F for the FM 300M specimens are shown in Table 2. All failures occurred cohesively within the adhesive layer.

Crack extensions for the three adhesive systems are shown in Table 3 and Figure 2. Table 4 shows the crack extension failure modes. Table 5, 6, and 7 show the lap shear strengths and modes of failure occurring after 5-year exposures for specimens exposed with no tensile load, 800 pounds and 1200 pounds nominal spring loads. Tables 8, 9, and 10 compile shear strengths over the 10-year exposure period.

3.2 Exposure Stress Levels on Specimens

Specimens were initially loaded to 0, 800 and 1200 psi stress levels for each surface treatment/adhesive configuration. These stress levels changed over the 10-year exposure duration to lesser stresses. Protection provided for the springs failed in many instances allowing stress corrosion cracking. Specimen degradation also resulted in tension release. At the end of 5 years, most springs were intact. Broken springs noted on the 5-year specimens are noted in Table 6 and 7. Average stress value of the unbroken springs for the 5-year specimens is shown in Table 11. Table 12 shows the condition of the springs after 10 years and the final exposure stress.

3.3 Nondestructive Inspection Results

The neutron radiography was able to show corrosion products in the presence of the organic adhesive through the aluminum adherends. Significant filiform which had not progressed into the secondary buildup of aluminum hydroxide was not detected. Both through transmission and pulse echo ultrasonics did an excellent job of showing the complete delaminated areas. Areas of filiform, either tightly held in a debonded condition or bonded with such a damaged adhesion that the specimens parted on disassembly, were not detectable with either ultrasonic technique. X-ray was excellent in showing adhesive anomalies and thickness but gave no indication of filiform. Eddy current was used to look for aluminum cracks but none were found. Table 13 summarizes nondestructive characterization and comments.

3.4 Adhesive Thickness Anomalies

FM 73M and FM 300M are adhesives with short polyester fiber additions. These adhesives can be reduced to cured film thickness of 0.003 inch as was demonstrated in the x-ray measurements of these films after exposure. These films in the higher polyester contents also indicated a lower density than the films at the other thickness extreme, 0.025 inches. Since such a wide thickness variation occurred in specimen manufacture, Table 14 was used to see if any correlation to durability or mechanical property was evident. No correlation was evident.

3.5 Chemical Analysis Results

Surface chemical analysis of new treatments did not provide useful atomic indicators which could be used to show traces of OFPL or PAA on cohesively or adhesively separated specimens. Aluminum, oxides were so prevalent as to not be helpful. Chlorides found in exposed specimens were not unexpected but chlorides were also found in newly processed OFPL specimens. Small traces of chlorides during initial processing could have deleterious effects on bond line durability.

4.0 DISCUSSION OF RESULTS

4.1 Nondestructive Inspection

Nondestructive Inspection - Inspection of the partially or completely disassembled specimens was made after mechanical property testing was completed. Comparison of 50 power microscopic examination with the results obtained by nondestructive inspection prior to intentional disassembly or mechanical property testing was made in the "Comments" column of Table 13. The good correlation of those examinations was encouraging. Neutron radiography consistently found buildups of aluminum hydroxide and aluminum oxide products in the presence of adhesive. Both ultrasonic techniques showed delamination clearly. X-ray inspection showed corrosion products and showed variations in adhesive thicknesses (See Table 14).

A "red flag" should be waved to emphasize that there was no detection of filiform damage, however. Unless the initial filiform has progressed to a buildup of a significant amount of "white powder," filiform adhesion damage was undetected by any of these techniques. Based on these specimens, bondlines can lose essentially all strengths for several inches from a panel edge or a fastener hole penetration without being detected by any of these techniques.

4.2 Phosphoric Acid Anodize vs. Optimized Forest Product Laboratory Etch

Strength durability of phosphoric acid anodize was markedly superior to the OFPL in this 10-year exposure. After 5 years, lap shear tests of both FM 73M and FM 300M bonded with BR 127 primer to phosphoric acid anodize had retained essentially all initial strength, and continued to part cohesively in the adhesive layer. At this time the OFPL specimens were showing distinct strength losses, significant change of failure mode from cohesive to the adhesive/primer interface and evidence of corrosion.

One important phenomenon that was seen in the 5-year specimens was the strong correlation between sustained stress exposure levels and strength loss in the OFPL specimens. This was apparently not true for one nominally-stressed 1200 psi specimen. On further examination we saw essentially no stress because of a broken spring. The 5-year specimens were not examined to determine if the corrosion damage was the filiform type. Based on the highly damaging results of filiform seen in the 10-year OFPL specimens, we believe it is the same mechanism in the 5-year specimens. This leads to the speculation that stress accelerates the filiform actions in an OFPL treated specimen. This possibility is corroborated by the much faster growth of filiform in the OFPL wedge tests than in phosphoric acid anodized specimens bonded with FM 300M adhesive. In this case stress and the corrosive atmosphere were also potential degrading influences.

10-year lap shear specimen characterization showed the continued trends seen at 5 years. OFPL specimens were degraded past the point of meaningful mechanical tests. FM 300M adhesive applied to phosphoric acid anodize began to suffer from filiform action, but there was not an accelerated damage caused by exposure stress levels. FM 73M applied to phosphoric acid anodize demonstrated remarkable retention of properties in ambient temperature tests over the 10-year period with no loss because of corrosion or the higher exposure stress levels. See Figures 3 through 18 for condition of specimens returned from the exposure site.

4.3 Elevated Temperature Testing of Exposed Specimens

FM 73M showed a trend towards decreased strength at all exposure stress levels as the 10-year exposure progressed. The final strengths at 180°F suffered a loss of 5% in 5 years and 23% in 10 years.

FM 300M was tested at a more severe temperature, 300°F. In addition, the PAA/BR 127/FM 300M system is more subject to filiform damage. These two factors along with degrading effects long term exposure had on the adhesive itself, resulted in significant long term degradation to this system tested at 300°F. Five year loss of 30% of initial 300°F strength and 60% of initial strength after 10 years makes this system questionable for use at 300°F after long term exposure in a severe environment. The rate of heating of the specimens to 300°F after long term exposure provides the potential of steam pressure providing a significant strength loss. A reduction of the glass transition temperature below the test temperature is significant. Chemical changes within the adhesive may have occurred but were not detected.

The program did not have specimens which could be used to determine if this phenomenon is reversible with a low temperature drying. The specimens had been stored in a laboratory environment, with approximate 80±10°F temperatures and relative humidity of 25 to 60 percent for 75 days prior to test which would have provided a reasonable drying opportunity. A typical surface of the FM 300M lap shear tested at 300°F is shown in Figure 19.

4.4 Mechanisms of Bond Strength Degradation at Ambient Temperature

Initial reduction in strength is a result of moisture ingress into the primer and adhesive. This is shown by the wedge specimens in which the crack progresses as a cohesive failure to a lengthened crack after moisture conditioning. This shows the lower crack resistance within the adhesive to the constant stress in the wet condition. The crack generally remained as a cohesive separation in both adhesives, applied over phosphoric acid anodize (Figure 20). This reduction in strength is accompanied by a reduction in the modulus of elasticity as shown by the neat film measurements of torsional modulus in Figures 21, 22 and 23.

The mode of separation changes when corrosion becomes a factor. This is shown in Figure 24 where filiform has initiated bond line strength loss in the Phosphoric Acid Anodize, BR 127/ FM 300M crack extension specimens shown in Figure 2. Figure 25 shows most of the features which can be used to understand the filiform action in reducing the adhesion. An initiation site is seen at the notch which was used to mark the initial crack extension. This also provided an unprotected corrosion initiation site at the specimen edge. The dark area adjacent to the initiation site is a mature filiform. The shadow is filiform in a less developed condition to a point near the FM 300M adhesive edge. An aluminum hydroxide eruption is located slightly to the left of the V shape area of missing adhesive. This eruption is like the more translucent eruption adjacent to it and the eruption next to the smaller filiform initiation on the right hand upper portion of the figure. The adhesive has been lifted from this bond by hydrogen and the first aluminum hydroxide jelly emanating from these eruptions. The flow chart showing the sequence of this activity is shown in Figure 26.

4.5 Other Filiform Evidence

Figure 27 shows the initiation of filiform at a drilled hole in a phosphoric acid anodized specimen adhered with FM 300M. This was typical of initiations in PAA which were limited to damaged areas which exposed the aluminum/anodize interface with no corrosion protection. Traces of aluminum hydroxide are seen; these emanated from an eruption not shown. Figure 28 shows an eruption, at the arrow, in a filiform near the adhesive edge. Figure 29 shows the filiform head progressing towards the adhesive edge. A small area of phosphoric acid anodize has been lifted from the center of the area. Figure 30 shows the filiform progressing under the FM 300M film, and aluminum hydroxide on the surfaces adjacent to the adhesive film. Figure 31 shows a mature corroded area from under the adhesive film. The massive aluminum hydroxide corrosion products effectively mask all prior filiform action. Figures 19, 20 and 24 through 30 were magnified about 140 times. A higher magnification in Figure 32 is an electron microscope magnification to 1110X. It appears to be a filament network on the surface of an OFPL specimen which forms the filiform paths seen at the lower magnification. An aluminum hydroxide eruption at this higher magnification is shown in one corner. The grooves may be etched grain boundaries which could provide galvanic guidance for the filiform growth. Figure 33 shows an oxygen depleted zone detected by energy dispersive x-ray analysis adjacent to filiform shown in Figure 32. The oxygen layer developed by the Optimized Forest Products Laboratory Etch process has been removed from this area. This is a secondary damage mechanism resulting from the hydraulic lifting action of the aluminum hydroxide gel and hydrogen gas emanating from the filiform corrosion site.

4.6 Rheological Properties

Rheological properties of the two adhesives in the "dry" and "wet" condition are shown in Figures 21 through 23. Both FM 73M and FM 300M show a broad peak in the G", loss modulus, demonstrating a significant elastomeric property throughout the ranges of measurement. The G', modulus of elasticity, is reduced for both adhesives after moisture impregnation at ambient temperatures and shows a greater drop-off as the temperatures approach the glass transition temperature, Tg. A significant reduction in Tg, 36°F, is shown for both adhesives after moisture ingress. Appearance of failure modes in which corrosion is present show uncorroded areas surrounding corrosion penetration sites. These sites initiate from corrosion beneath the surface treatment. This may be a step necessary for further filiform growth. Providing penetration resistance to the surface treatment along with overall adhesion of the surface treatment to aluminum offers an opportunity for durability improvement. Lower modulus of elasticity in the wet condition shown by the FM 73M may have contributed to its superior resistance to rupture due to better stress distribution of aluminum hydroxide gel and hydrogen pressures from beneath the surface treatment (PAA) at the penetration site. Surrounding this eruption is an area in which the adhesive, primer or surface treatment appears to have been mechanically lifted from the adherend. This program provided a direct comparison of this aluminum hydroxide/hydrogen hydraulic lifting for specimens exposed in the same environment with the same surface treatment processing (PAA) and primer. Of the two adhesives in this program, the FM 300M had a slightly lower adhesion prior to corrosion becoming a factor in joint strength. A better understanding of how the surface treatment, primer and adhesive properties affect the corrosion rate of the metal under the surface treatment is a critical step in producing more durable adhesive bonds.

5.0 CONCLUSIONS

5.1 Nondestructive Characterization of Bondlines

5.1.1 - Neutron radiography detected significant aluminum hydroxide corrosion products in the presence of FM 73M or FM 300M adhesives through aluminum adherends.

5.1.2 - Both through transmission and pulse echo ultrasonics were excellent techniques to show true delaminations.

5.1.3 - Large areas of filiform degradation not resulting in significant aluminum hydroxide or in separated laminations were not detectable using neutron radiography, ultrasonic, x-ray or eddy current techniques.

5.2 Durability Comparison of OFPL and PAA Surface Treatment

5.2.1 - Phosphoric acid anodized 7075-T6 aluminum primed with BR 127 and bonded with FM 300M was markedly more durable than OFPL surface treated 7075-T6 primed with BR 127 and bonded with FM 300M.

5.2.2 - Filiform corrosion progressed 5 inches in 10 years under OFPL; progression was only 1.5 inches in 10 years under PAA.

5.2.3 - Residual stress accelerated the rate of lap shear strength loss in OFPL specimens but not PAA specimens when both were bonded to 7075-T6 aluminum with the BR 127/FM 300M system.

5.2.4 - OFPL treated double lap shear specimens showed a progressive loss of strength with none remaining after 10 years.

5.3 Degradation of Strength Within the Adhesive

5.3.1 - Phosphoric acid anodized 7075-T6 aluminum primed with BR 127, adhered with FM 73M, exposed ten years under a stress of 1016 psi, retained a remarkable 95% of its initial ambient lap shear strength.

5.3.2 - FM 73M bonded with BR 127 to PAA treated 7075-T6 aluminum and tested as double lap shear at 180°F lost strength progressively over the 10-year period with maximum loss of 25 percent.

5.3.3 - FM 300M adhered to BR 127 primed phosphoric acid anodized 7075-T6 retained 97% of ambient temperature strength in shear for the 10-year period.

5.3.4 - PAA/BR 127/FM 300M tested at 300°F showed a 30% strength loss after 5-years, and a 60% loss after 10 years.

5.4 Filiform Effects

5.4.1 - Filiform corrosion began at specimen edges, file notches used for crack marking and drilled holes.

5.4.2 - Filiform progressed 5 inches in 10 years under OFPL and 1.5 inches in 10 years under PAA in crack extension specimens.

5.4.3 - Filiform eruptions result in adhesive separation from primed surface treatment, primer lifting from the surface treatment and surface treatment separating from the adherend.

5.4.4 - Filiform initiates under the primed surface treatment in the aluminum adherend but anode progress is affected by the adhesive properties as well as the surface treatment.

5.4.5 - Adhesion of the primer to the surface treatment, adhesive to primer adhesion, surface treatment coherent strength and adhesive modulus all may be critical to resisting aluminum hydroxide eruptions and, therefore, producing durable adhesive bonds.

5.4.6 - Primer and adhesive mechanical properties contributed to prevention of filiform eruptions. Edge sealing and chemical resistance may be more important than primer corrosion inhibitors in bond durability optimization.

6.0 RECOMMENDED FOLLOW-ON

6.1 Develop a Valid Accelerated Test

6.1.1 - Reproduce specimens in accelerated tests which reproduce 10-year natural exposure results.

6.1.2 - Modify test conditions to produce filiform in addition to valid changes in modulus, and strength at ambient and elevated temperatures.

6.1.3 - Calibrate test conditions with results from 10-year exposure to develop realistic degradation rates for the adhesive systems.

6.1.4 - Develop better understanding of filiform and elevated temperature strength loss mechanisms.

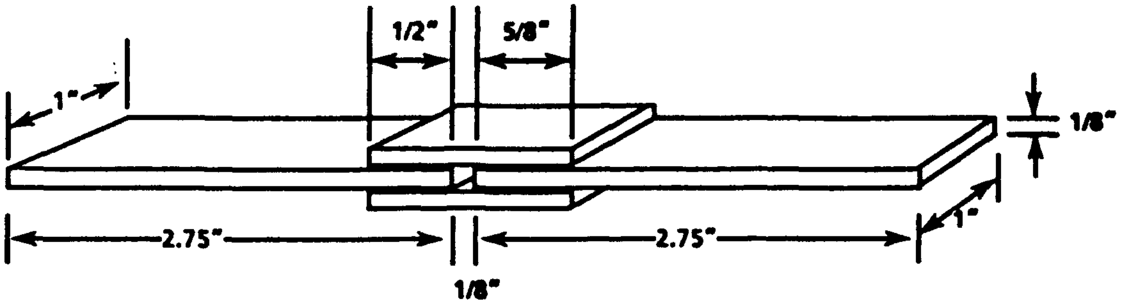
6.2 Long Term Natural Exposure

6.2.1 - Expose other aluminum alloys, steel, magnesium and composite adherends with appropriate surface treatment primers and adhesives presently in use into long term durability exposures.

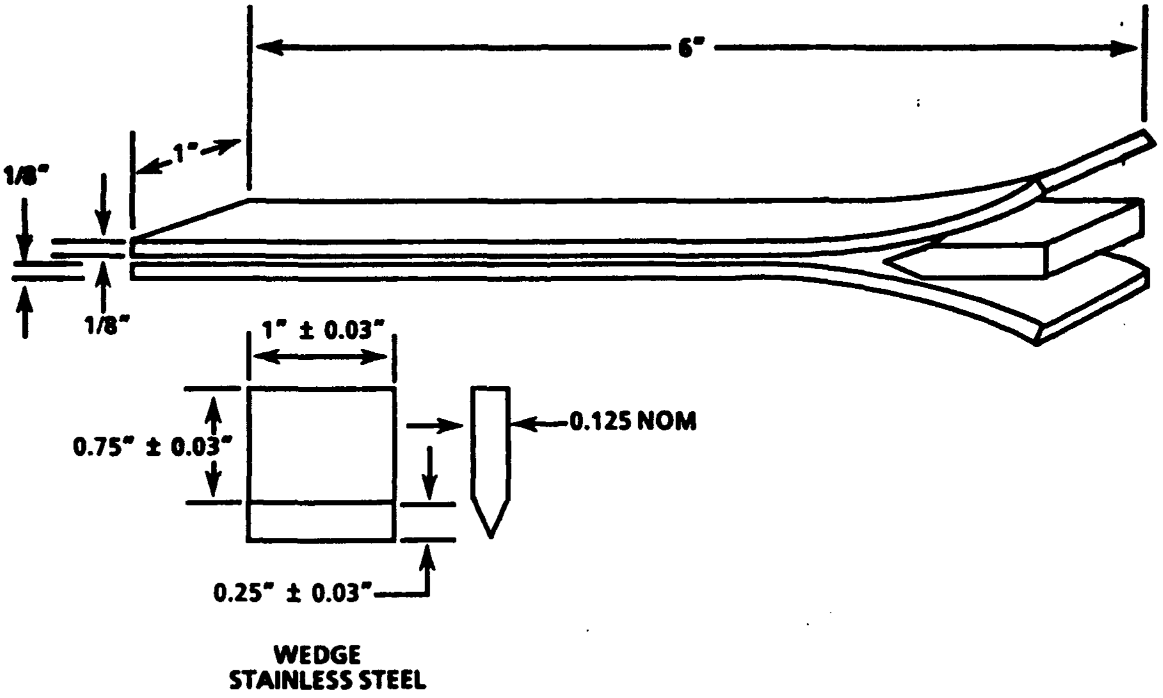
6.2.2 - Select promising nonchromated and water based primers with environmentally acceptable surface treatments for long-term exposures.

6.2.3 - Predict long-term results with accelerated test methods.

6.2.4 - Correlate intermediate and long-term results with accelerated test performance.



DOUBLE LAP SHEAR SPECIMEN



WEDGE CRACK EXTENSION SPECIMEN

Figure 1: Test Specimen Configurations

TABLE 1
SUMMARY OF SPECIMENS

Structural Film Adhesive	Substrate Surface Treatment	Outdoor Exposure Period	Double Lap Shear Sustained Load, Psi	Specimens Required			
				*Double Lap Shear			Crack Extension (CETA)
				R.T.	180°F	300°F	
FM 73M	Phosphoric Acid Anodize	None	0	3	3	-	3
FM 300M	Phosphoric Acid Anodize	None	0	3	-	3	3
	FPL Etch	None	0	3	-	3	3
FM 73M	Phosphoric Acid Anodize	5 Years	0	3	3	-	3
			800	3	3	-	-
			1200	3	3	-	-
FM 300M	Phosphoric Acid Anodize	5 Years	0	3	-	3	3
			800	3	-	3	-
			1200	3	-	3	-
FM 300M	OFPL Etch	5 Years	0	3	-	3	3
			800	3	-	3	-
			1200	3	-	3	-
FM 73M	Phosphoric Acid Anodize	10 Years	0	3	3	-	3
			800	3	3	-	-
			1200	3	3	-	-
FM 300M	Phosphoric Acid Anodize	10 Years	0	3	-	3	3
			800	3	-	3	-
			1200	3	-	3	-
FM 300M	FPL - Etch	10 Years	0	3	-	3	3
			800	3	-	3	-
			1200	3	-	3	-
		TOTAL SPECIMENS		63	21	42	27

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TABLE 2
CONTROL SHEAR TEST RESULTS OBTAINED ON UNEXPOSED DOUBLE LAP SHEAR TEST SPECIMENS

Adhesive and Surface Preparation	Test Conditions	Specimen No.	Shear Strength, PSI	Mode of Failure	
				% Cohesive	% Adhesive
FM 73M Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	5,520	100	-
		2	5,580	100	-
		3	-		
		Avg	5,550	100	-
	180°F	1	3,940	100	-
		2	3,750	100	-
		3	3,640	100	-
		Avg	3,776	100	
FM 300 Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	4,400	100	-
		2	5,470	100	-
		3	5,200	100	-
		Avg	5,023	100	
	300°F	1	1,520	100	-
		2	1,800	100	-
		3	1,675	100	-
		Avg	1,665	100	-
FM 300 FPL Etch with BR 127 Primer	Room Temperature	1	5,660	100	-
		2	5,700	100	-
		3	5,380	100	-
		Avg	5,580	100	
	300°F	1	2,000	100	-
		2	1,975	100	-
		3	-		
		Avg	1,987	100	

TABLE 3
COMPARISON OF WEDGE CRACK EXTENSION SPECIMENS TESTED UNDER FOUR DIFFERENT CONDITIONS

	Newly Bonded Specimens Tested in Laboratory		Specimens Tested for 5 Years in Sea-Side Environment		Specimens Tested for 10 Years in Sea-Side Environment		Specimens Aged for 10 Years in Sea-Side Environment Then Tested (2)	
	a	Δa (1)	a	Δa	a	Δa (5)	a	Δa
PAA/BR 127/ FM 73M (3)	2.09	0	2.16	.14	2.14	.20	2.18	.09
PAA/BR 127/ FM 300M (3)	2.40	.09	2.48	.25	2.48	.21	2.48	.05
OFPL/BR 127/ FM 300 (4)	2.32	.02	2.52	.23	2.51	1.89	2.75	.01

(1) 81 Days in Laboratory Environment
(2) 24 Hours at 95% Relative Humidity
(3) 3 Specimens tested at each time interval
(4) 3 Specimens tested unexposed and after 5 years, and 2 specimens tested after 10 years aging
(5) Crack length does not include unseparated low adhesion areas
a - Initial crack resulting from wedge insertion
Δa - Crack extension resulting from environmental exposure

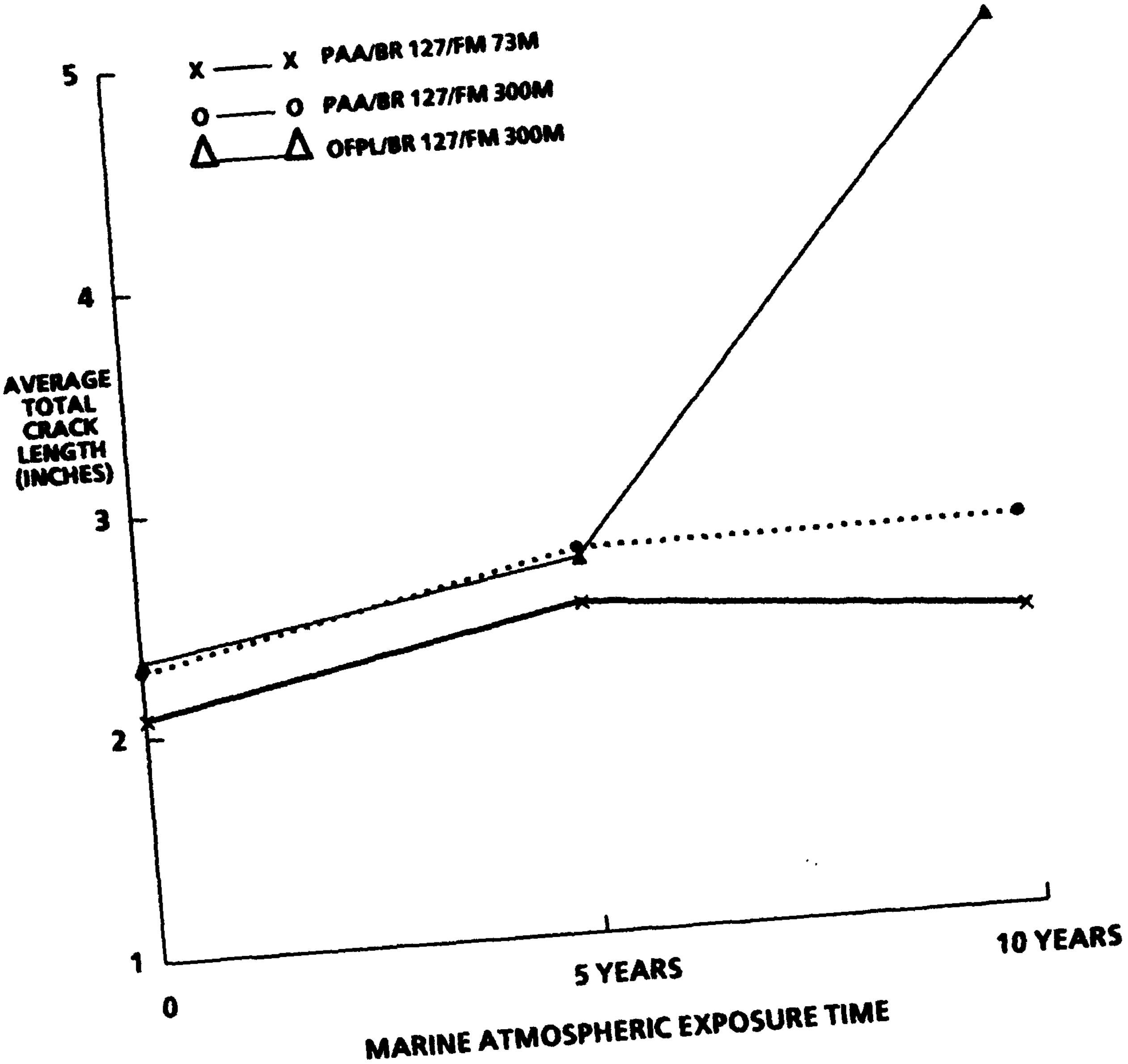

Figure 2: Crack Extension Specimens Total Length of Damaged Bond

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TABLE 4

FAILURE MODES OF 10-YEAR CRACK EXTENSION SPECIMENS

Adhesive System	Failure Mode of Specimens Stressed during 10-year Marine Exposure	Failure Mode of Specimens Exposed 10 Years, Wedge Inserted After 10-year Exposure
PAA/BR 127/FM 73M	Cohesive in FM 73M adhesive	Cohesive in FM 73M adhesive
PAA/BR 127/FM 300M	95 percent cohesive in FM 300M adhesive; 5 percent adhesive to primed PAA at filiform edge initiation	Cohesive in FM 300M adhesive
OFPL/BR 127/FM 300M	Adhesive to filiform damaged OFPL surface	No test because of specimen delamination at OFPL surface

TABLE 5

TEST RESULTS OBTAINED ON DOUBLE LAP SHEAR TEST SPECIMENS AFTER 5 YEARS WITH NO TENSILE LOAD

Adhesive and Surface Preparation	Test Conditions	Specimen No.	Shear Strength psi	Mode of Failure (%)		
				Cohesive	Adhesive	Primer
FM 73M Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	5,958	100	-	-
		2	6,061	100	-	-
		3	5,857	100	-	-
		Avg	5,959			
	180°F	1	3,563	100	-	-
		2	3,915	100	-	-
		3	4,133	100	-	-
		Avg	3,870			
FM 300M Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	4,500	100	-	-
		2	5,302	100	-	-
		3	6,047	100	-	-
		Avg	5,283			
	300°F	1	812	50	50	-
		2	1,408	50	50	-
		3	1,088	50	50	-
		Avg	1,103			
FM 300M OFPL Etch with BR 127 Primer	Room Temperature	1	4,940	90	-	10 (1)
		2	5,426	95	-	5 (1)
		3	1,883	50	-	50 (1)
		Avg	4,083			
	300°F	1	979	30	50	20 (1)
		2	876	30	60	10 (1)
		3	1,342	15	15	70 (1)
		Avg	1,066			

Note: (1) Corrosion observed on substrate metal under bond

TABLE 6

TEST RESULTS OBTAINED ON DOUBLE LAP SHEAR TEST SPECIMENS AFTER 5 YEARS AT 800 LBS. TENSILE LOAD

Adhesive and Surface Preparation	Test Conditions	Specimen No.	Shear Strength psi	Mode of Failure (%)		
				Cohesive	Adhesive	Primer
FM 73M Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	5,768	100	-	-
		2	6,305	100	-	-
		3	5,732	100	-	-
		Avg	5,935			
	180°F	1	3,088	100	-	-
		2	3,174	100	-	-
		3	3,787	100	-	-
		Avg	3,353			
FM 300M Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	5,317	100	-	-
		2	5,017 (2)	100	-	-
		3	5,726	100	-	-
		Avg	5,353			
	300°F	1	1,299	80	20	-
		2	1,392	80	20	-
		3	900	85	15	-
		Avg	1,197			
FM 300M FPL Etch with BR 127 Primer	Room Temperature	1	4,665	95	0	5 (1)
		2	1,569	60	0	40 (1)
		3	1,375	20	0	80 (1)
		Avg	2,536			
	300°F	1	932	35	45	20 (1)
		2	1,136 (2)	20	60	10 (1)
		3	1,053 (2)	30	30	50 (1)
		Avg	1,040			

Note: (1) Corrosion observed on substrate metal under bond
(2) Springs applying tension to the samples were broken prior to disassembly of the stress fixture.

TABLE 7

TEST RESULTS OBTAINED ON DOUBLE LAP SHEAR TEST SPECIMENS AFTER 5 YEARS EXPOSURE AT 1200 LBS TENSILE LOAD

Adhesive and Surface Preparation	Test Conditions	Specimen No.	Shear Strength psi	Mode of Failure (%)		
				Cohesive	Adhesive	Primer
FM 73M Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	6,401	100	-	-
		2	6,144	100	-	-
		3	5,536	100	-	-
		Avg	6,027			
	180°F	1	3,370	100	-	-
		2	3,847	100	-	-
		3	3,289	100	-	-
		Avg	3,502			
FM 300M Phosphoric Acid Anodize with BR 127 Primer	Room Temperature	1	5,398	100	-	-
		2	6,261	100	-	-
		3	5,000 (2)	100	-	-
		Avg	5,553			
	300°F	1	1,292 (2)	40	60	-
		2	1,432 (2)	50	50	-
		3	867 (2)	50	50	-
		Avg	1,197			
FM 300M FPL Etch with BR 127 Primer	Room Temperature	1	(3) (4)	-	-	(1)
		2	(3)	-	-	(1)
		3	3,545 (4)	100	-	-
		Avg	1,182			
	300°F	1	1,302	20	60	20 (1)
		2	1,197	20	40	40 (1)
		3	1,215 (4)	45	45	10 (1)
		Avg	1,238			

NOTE:
(1) Corrosion observed on substrate metal under bond.
(2) Springs applying tension to the samples were broken prior to disassembly of the stress fixture.
(3) Samples were broken before removal from the test fixtures.
(4) Springs applied no load on the test samples at the end of the 5 year period.

TABLE 8

LAP SHEAR VALUES OF PHOSPHORIC ACID ANODIZED 7075-T6 ADHEREND WITH BR 127/FM 300M ADHESIVE IN 10-YEAR MARINE EXPOSURE

Exposure Prior to Test	Ambient Laboratory Temperature UTS	Ambient Laboratory Temperature Mode	300°F Test Temperature UTS	300°F Test Temperature Mode
			1520	100C
	4400	100C	1800	100C
	5440	100C	1675	100C
None	5020	100C	Avg. 1665	
	Avg. 5023			

	Ambient Laboratory Temperature						300°F Test Temperature					
	Exposure Stress - 0		Exposure Stress - 800		Exposure Stress - 1200		Exposure Stress - 0		Exposure Stress - 800		Exposure Stress - 1200	
	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode
5 Years	4500	100C	5317	100C	5398	100C	812	50C	1299	80C 20A	1292	40C 60A
	5302	100C	5017	100C	6261	100C		50A	1392	80C 20A	1432	50C 50A
	6047	100C	5726		5000	100C	1408	50C	900	85C 15A	867	50C 50A
	5283 Avg.		5353 Avg.		5553 Avg.			50A	1197 Avg.		1197 Avg.	
							1088	50 50A				
							1103 Avg.					
10 Years	4448	85C 15A	3116	50C 50M	4702	95C 5A			1006	50C 50A	451	20C 80A
	5190	85C 15A	3412	35C 65M	5190	95C 5A			609	20C 80A	743	20 70A
	4979	85C 15A	5517	30C 65A	4384	95C 5A	606	60A	485	5C 95A		10M
	4872 Avg.			5M	4758 Avg.			40C	700 Avg.		655	50C 50A
			4015 Avg.				673	60A			616 Avg.	
								40C				
							649	60A				
								40C				
							643 Avg.					

Mode Abbreviations
C = Cohesive
A = Adhesive
M = Metal surface indicating corrosion

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TABLE 9

LAP SHEAR VALUES OF PHOSPHORIC ACID ANODIZED 7075-T6 ADHEREND WITH BR 127/FM 73M ADHESIVE IN 10 YEAR MARINE EXPOSURE

Exposure Time	Ambient Laboratory Temperature						180°F Test Temperature					
	UTS	Mode					UTS	Mode				
None	5520 5580 5550 Avg.	100C 100C					3940 3750 3640 Avg. 3776	100C 100C 100C				
	Exposure Stress - 0		Exposure Stress - 800		Exposure Stress - 1200		Exposure Stress - 0		Exposure Stress - 800		Exposure Stress - 1200	
	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode
5 Years	5958 6061 5857 5959 Avg.	100C 100C 100C	5768 6305 5732 5935 Avg.	100C 100C	6401 6144 5536 6027 Avg.	100C 100C 100C	3563 3915 4133 3870 Avg.	100C 100C 100C	3086 3174 3787 3353 Avg.	100C 100C 100C	3370 3847 3289 3502 Avg.	100C 100C 100C
10 Years	5478 5297 5463 5413 Avg.	98C 2M 100C 100C	4847 5337 5563 5249 Avg.	100C 100C 100C	5243 5198 5634 5358 Avg.	100C 100C 100C	2579 3075 2836 2830 Avg.	100C 100C 100C	3056 2970 3025 3017 Avg.	100C 98C 2M 100C	2778 3092 2574 2814 Avg.	98C 2A 98C 2A 98C 2M

TABLE 10

LAP SHEAR VALUES OF CHROMIC ACID/SULFURIC ACID (OFPL) ETCHED 7075-T6 ALUMINUM ADHEREND WITH BR 127/FM 300M IN 10 YEAR MARINE EXPOSURE

Exposure Time	Ambient Laboratory Temperature						300°F Test Temperature					
	UTS	Mode					UTS	Mode				
None	5660	100C					2000	100C				
	5700	100C					1975	100C				
	5380	100C					3776 Avg.					
	5580 Avg.											
	Exposure Stress - 0		Exposure Stress - 800		Exposure Stress - 1200		Exposure Stress - 0		Exposure Stress - 800		Exposure Stress - 1200	
5 Years	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode	UTS	Mode
	4940	90C	4665	95C 5A	Delam.	100M	979	30C 50A	932	35C 45A	1302	20C 50A
		10M	1569	60C 40A	Delam.	1100M		20M		20M		20M
	5426	95C 5M	1375		3545	100C*	876	30C 60A	1136	20C 60A	1197	20C 40A
	1883	50C	2536 Avg.		1181 Avg.			10M		10M	40M	
		50M					1342	15C 15A	1053	30C 30A	1215	45C 45A
	4083 Avg.							70M		50M		10M
							1066 Avg.		1040 Avg.		1238 Avg.	
10 Years	Specimens Debonded		Specimens Debonded		Specimens Debonded		Specimens Debonded		Specimens Debonded		Specimens Debonded	

* Spring Broken

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TABLE 11

FORCE (LBS) EXERTED BY SPRINGS COMPRESSED TO LOADED DIMENSION ON SPECIMENS REMOVED AFTER 5 YEARS

1200 LB FIXTURES	800 LB FIXTURES
1030	725
1055	770
890	682
1095	720
1155	705
1085	-
1052 (AVG.)	720 (AVG)

TABLE 12

SPRING TENSION ON LAP SHEAR SPECIMENS AFTER TEN YEAR EXPOSURES

Specimen #	Adhesive	Surface Treatment	Nominal Stress psi	Measured Stress psi	Spring Condition	Specimen Condition
1	FM 73M	PAA	800	706	-	-
2	FM 73M	PAA	800	741	-	-
3	FM 73M	PAA	800	758	-	-
4	FM 73M	PAA	800	646	-	-
5	FM 73M	PAA	800	-	Broken	-
6	FM 73M	PAA	800	695	-	-
7	FM 73M	PAA	1200	1082	-	-
8	FM 73M	PAA	1200	-	Broken	-
9	FM 73M	PAA	1200	1015	-	-
10	FM 73M	PAA	1200	1017	-	-
11	FM 73M	PAA	1200	-	Broken	-
12	FM 73M	PAA	1200	-	Broken	-
13	FM 300M	FPL	800	608	-	Partial Delam.
14	FM 300M	FPL	800	616	-	"
15	FM 300M	FPL	800	500	-	"
16	FM 300M	FPL	800	588	-	"
17	FM 300M	FPL	800	525	-	"
18	FM 300M	FPL	800	481	-	"
19	FM 300M	PAA	800	748	-	-
20	FM 300M	PAA	800	836	-	-
21	FM 300M	PAA	800	796	-	-
22	FM 300M	PAA	800	-	Broken	-
23	FM 300M	PAA	800	695	-	-
24	FM 300M	PAA	800	753	-	-
25	FM 300M	FPL	1200	-	-	Delaminated
26	FM 300M	FPL	1200	-	-	"
27	FM 300M	FPL	1200	-	-	"
28	FM 300M	FPL	1200	-	-	"
29	FM 300M	FPL	1200	-	-	"
30	FM 300M	FPL	1200	986	-	Partial Delam.
49	FM 300M	PAA	1200	-	Broken	-
50	FM 300M	PAA	1200	1091	-	-
51	FM 300M	PAA	1200	1050	-	-
52	FM 300M	PAA	1200	1077	-	-
53	FM 300M	PAA	1200	-	-	End Corroded
54	FM 300M	PAA	1200	1009	-	-

TABLE 13

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
Double Lap Shear #1	PAA BR 127 FM 73M 706	No Corrosion Indication	Adhesive Recessed at Specimen Edge. 0.015" Adhesive Thickness 0.010". Typical Attenuation	No Indication of Delamination	No Al Cracks	No Indication	No Corrosion Indication
#2 Lap Shear	PAA BR 127 FM 73M 741	No Corrosion Indication	Low Density of Adhesive at Lap Shear Edge. Adhesive Thickness 0.003" one side, 0.005" other. Typical attenuation	No Indication of Delamination	No Al Cracks	No Indication	No Indication of corrosion
#3 Lap Shear	PAA BR 127 FM 73M 758	No Corrosion Indication	Low density at lap shear edge. 0.003" adhesive thickness, .0005" adhesive attenuation normal.	No Indication of Delamination	No Al Cracks	No Indication	No Indication of corrosion
#4 Lap Shear	PAA BR 127 FM 73M 646	No Corrosion Indication	Low density of adhesive at specimen edges. Thickness 0.007", 0.010"	No Indication of Delamination	No Al Cracks	No Indication	100% cohesive. No corrosion Indication

TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#5	PAA BR 127 FM 73M Broken Spring	No indication of Corrosion	No debond evident. Adhesive density low at specimen edge on two faces. Two faces normal thickness 0.010", 0.005".	No disbond detected	No cracks in Al	No disbond indication	100% cohesive. No corrosion indication
#6	PAA BR 127 FM 73M 695	No indication of corrosion	No debond evident. Attenuation typical. Thickness 0.007" and 0.010"	No debond detected	No cracks in Al	No debonds detected	No indication of corrosion
#7	PAA BR 127 FM 73M 1082	No indication of corrosion	Attenuation typical. Adhesive recessed in two places. Bond line adhesive thickness 0.015"	No debonds	No cracks in Al	No debonds	No indication of corrosion
#8	PAA BR 127 FM 73M Spring Broken	No indication of corrosion in bond line	Adhesive recessed in three edges. Density normal. 0.015" Adhesive thickness	No disbonds	No cracks in Al	No disbonds	No indication of corrosion

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#9	PAA BR 127 FM 73M 1015 psi	No bondline corrosion	Attenuation normal. 0.025" thickness, 0.020"	No disbonds	No cracks in Al	No disbonds	100% cohesive. No corrosion indication
#10	PAA BR 127 FM 73M 1017	No indication of bond line corrosion	Adhesive recessed in two edges. Thickness 0.020", 0.025"	No disbonds	No cracks in Al	No disbonds	No indication of corrosion
#11	PAA BR 127 FM 73A Spring Broken	No indication of corrosion in bond line	Adhesive recessed at all edges. Thickness 0.005", 0.007"	No disbonds	No cracks in Al	No disbonds	Cohesive 100%. No corrosion indication
#12	PAA BR 127 FM 73M Spring Broken	No indication of bond line corrosion	Adhesive recessed density low. Thickness 0.005"	No disbonds	No cracks in Al	No disbonds	No corrosion indication

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#13	FPL BR 127 FM 300M 608		-	-	-	-	Specimen delaminated as it was removed from fixture
#14	FPL BR 127 FM 300M 616	Corrosion clouds indicate bond line corrosion	-	-	-	-	3 of 4 faces delaminated when removed from fixture
#15	FPL BR 127 FM 300M 500	-	-	-	-	-	Specimen debonded in 3 of 4 faces when removed from fixture
#16	FPL BR 127 FM 300M 588	Corrosion indication in bondline	-	-	-	-	Two faces on 0.5" lap debonded at specimen retrieval. Corrosion found in bond line

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#17	FPL BR 127 FM 300M 525	Corrosion indication in bondline	-	-	-	-	Specimen debonded on 3 of 4 faces when removed from fixture
#18	FPL BR 127 FM 300M 481	Corrosion indication in bondline	Density of adhesive appears normal 0.010" thickness	Delamination on 0.5". Specimen end attenuation normal	No cracks in Al	Delamination on 0.5"	Corrosion found in bond lines
#19	PAA BR 127 FM 300M 748	No indication of corrosion	Density normal. Thickness 0.010", 0.015"	No delamination Attenuation normal	No cracks in Al	No disbonds	Filiform on 50% of one 0.5" face
#20	PAA BR 127 FM 300M 836	No corrosion indicated	Density normal. 0.020" thickness	No indication of disbonds. Attenuation normal	No cracks in Al	No disbonds	Filiform on 75% of one 0.5" face

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#21	PAA BR 127 FM 300M 796 psi	No corrosion indicated	Bond line thickness 0.010", 0.005" adhesive has very low density on 0.005" side	No disbonds Attenuation normal	No cracks in Al	No indication of disbonds	100% cohesive, 1% filiform
#22	PAA BR 127 FM 300M Spring Broken	No corrosion indicated	Bond line thickness 0.010", 0.005" adhesive density normal	No indications of disbonds. Attenuation normal	No cracks in Al	No disbonds	Corrosion spots at edge. 100% cohesive
#23	PAA BR 127 FM 300M 695	No corrosion indicated	Thickness 0.020" one side, 0.025" other side. Density of adhesive normal	No disbonds	No cracks in Al	No disbonds	Corrosion spots and edge discoloration. Cohesive 40%, 59% adhesive to primer
#24	PAA BR 127 FM 300M 753	No corrosion indicated	Thickness 0.003" one side, 0.005" other side. Density of adhesive is very low	No disbonds	No cracks in Al	No disbonds	No corrosion 100%, 40% cohesive, 60% adhesive to primer. Excellent fillet

TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#25	FPL BR 127 FM 300M 986	-	-	-	-	-	Specimen debonded on all bond faces when removed from stress fixture
#26	FPL BR 127 FM 300M 1091	-	-	-	-	-	Specimen debonded on all faces when removed from stress fixture
#27	FPL BR 127 FM 300M 1200	-	-	-	-	-	Specimen debonded on all faces when removed from stress fixture
#28	FPL BR 127 FM 300M 1200	-	-	-	-	-	Specimen debonded on all faces when removed from stress fixture
#29	FPL BR 127 FM 300M 1200	-	-	-	-	-	Specimen debonded on 3 of 4 faces when removed from stress fixture

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#30	FPL BR 127 FM 300M 986	-	-	-	-	-	Specimen debonded when removed from stress fixture
#31	FPL BR 127 FM 300M 0	Corrosion indicated on reassembled specimen	-	-	-	-	Specimen debonded on all faces when disassembled from fixture
#32	FPL BR 127 FM 300M 0	Corrosion indications shown on reassembled specimen	-	-	-	-	Specimen debonded at disassembly from stress fixture
#33	FPL BR 127 FM 300M 0	-	-	-	-	-	Specimen debonded on all faces when removed from stress fixture

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#34	FPL BR 127 FM 300M 0	-	-	-	-	-	Debonded on all faces when removed from stress fixture
#35	FPL BR 127 FM 300M 0	Corrosion indications shown on reassembled specimen	-	-	-	-	Debonded on 2 of 4 faces at disassembly
#36	FPL BR 127 FM 300M	-	-	-	-	-	Debonded on all 4 faces at disassembly
#37	PAA BR 127 FM 73M	No corrosion indication	Adhesive density normal. 0.010" one side, 0.015" one side. Adhesive recessed at two edges	No disbonds	No cracks in Al	No disbonds	No corrosion indication

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#38	PAA BR 127 FM 73M 0 LOAD	No corrosion indications	Bond line thickness 0.015". Edges recessed from 3 edges	No disbonds. Attenuation normal	No cracks in Al	No disbonds	Cohesive 100%. No corrosion indication
#39	PAA BR 127 FM 73M 0 LOAD	No indication of corrosion in bondline	Bondline thickness is 0.010". Adhesive is recessed in 3 areas. Density of adhesive is normal	No delamination indications	No cracks in Al	No disbonds	100% cohesive. No corrosion indication
#40	PAA BR 127 FM 73M 0 LOAD	Corrosion indications inbond line	Bond line thickness is 0.020". Adhesive is recessed in 3 edges. Density appears normal	No delamination Attenuation is typical	No cracks in Al	No disbonds	100% cohesive. No corrosion indications
#41	PAA BR 127 FM 73M 0 LOAD	No corrosion indicated	0.005" adhesive thickness. Density of one bond line is low.	No indication of delamination Attenuation normal	No cracks in Al	No disbonds	100% cohesive. No corrosion indications

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#42	PAA BR 127 FM 83M O	No corrosion indicated	Bondline thickness 0.005" one face, 0.003". Density of adhesive is low, recessed at all edges	No disbonds	No cracks in Al	No disbonds	100% cohesive. No corrosion indications
#43	PAA BR 127 FM 73M O	No corrosion indicated	Bondline thickness 0.005", one face 0.003". Adhesive recessed at all areas	No disbonds	No cracks in Al	No disbonds	Filiform initiating at gap between lap bonds and from one edge; 50% cohesive, 50% adhesive to primer
#44	PAA BR 127 FM 300M 0 LOAD	No corrosion indicated	Bondline thickness 0.005" one side, 0.003" on the other. Density low	No disbonds	No cracks in Al	No disbonds	Filiform initiating at edge and center gap 5%, 80% cohesive, 15% adhesive to primer
#45	PAA BR 127 FM 300M 0	No corrosion indicated	Bondline thickness 0.005" one side, 0.003" other. Density low both sides	No disbonds Indications. Attenuation normal	No cracks in Al	No disbonds	100% cohesive. No corrosion except edge spots

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#46	PAA BR 127 FM 300M 0	No corrosion indications	Bondline thickness 0.005" one side, 0.003" other. Density of both bondlines very low	No delamination indications. Attenuation typical	No cracks in Al	No disbond indications	1% filiform initiating at edge, 75% adhesive to primer, 24% cohesive
#47	PAA BR 127 FM 300M 0	No corrosions indicated	Bondline thickness 0.005" one side, 0.003" other. Density very low	No disbonds	No cracks in Al	No disbonds	No corrosion. 50% adhesive to primer, 50% cohesive
#48	PAA BR 127 FM 300M 0	No corrosion indication	Bondline thickness 0.005" one side, 0.003" other. Density of all bond lines very low	No disbonds indications	No cracks in Al	No disbonds	No corrosion. 60% adhesive to primer, 35% cohesive
#49	PAA BR 127 FM 300M 0	No corrosion indication	Bondline thickness 0.020" both faces. Densities of bond lines apear normal	No disbonds indication	No cracks in Al	No disbonds	No corrosion. 100% cohesive

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#50	PAA BR 127 FM 300M 1091	No corrosion indications	Bondline thickness 0.020" one face, 0.015" other. Density appears normal	No disbond indications	No cracks in Al	No disbond indication	Filiform on 3%, 97% cohesive
#51	PAA BR 127 FM 300M 1050	No corrosion indications	Bondline thickness 0.005" one face, 0.003" other. Density of both bonds very low	No disbond indications	No cracks in Al	No disbond indications	100% cohesive. No corrosion indications
#52	PAA BR 127 FM 300M 1077	No corrosion indication	0.010" adhesive thickness. Adhesive density normal	No disbond indications	No cracks in Al	No disbond indications	No corrosion. 70% adhesive to primer, 30% cohesive
#53	PAA BR 127 FM 300M String Broken	No corrosion indication	Thickness 0.010" one side, 0.015" other side. Density normal	No disbond indications	No cracks in Al	No disbond indications	Filiform 10%, 80% adhesive to primer, 10% cohesive

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TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
#54	PAA BR 127 FM 300M 1009	No corrosion indications	Bondline thickness 0.015". Density normal	No disbond indications	No cracks in Al	No disbond indications	1% filiform, 49% adhesive to primer. 50% cohesive
A - Crack Extension Specimen	FPL BR 127 FM 300M	Corrosion shown at wedge insertion end of specimen	Corrosion shown on wedge end of specimen	41% of specimen has delamination indication	No cracks in Al	Approx. 40% of specimen delaminated	Heavy corrosion at wedge end, filiform film over remaining area
B - Crack Extension Specimen	FPL BR 127 FM 300M	No corrosion indicated in bondline	Specimen shows evenly distributed corrosion, pitting (surface or internal)	65% of specimen delaminated, 5% partially bonded, 30% bonded	No cracks in Al	Approx. 65% delaminated	White aluminum oxide on wedge end of specimen. Filiform over 60% of specimen
C - Crack Extension Specimen	PAA BR 127 FM 73M	No corrosion indicated in bondline	Specimen has small amounts of evenly distributed corrosion (surface or internal)	35% delaminated, 5% partially bonded, 60% bonded	No cracks in Al	Approx. 35% delaminated	Significant filiform in wedge end of specimen. 35% cohesive delamination

TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
D - Crack Extension Specimen	PAA BR 127 FM 73M	No corrosion indication in bondline	Small amounts of evenly distributed corrosion (surface or internal)	35% delaminated, 10% partially bonded, 60% bonded	No cracks in Al	30% delaminated, 10% partially bonded, 60% bonded.	No corrosion in bondline. Corrosion on surface only. 35% discolored adhesive indicating delamination prior to specimen disassembly
E - Crack Extension Specimen	PAA BR 127 FM 73M	Corrosion shown in wedge end of specimen	Surface or internal corrosion	40% delaminated, 5% partially bonded, 55% delaminated	No cracks in Al	Approx. 40% debonded	Small amounts of corrosion in wedge end of specimen. 40% unbonded area
F - Crack Extension Specimen	PAA BR 127 FM 300M	Corrosion shown at crack tip	Surface or internal corrosion	30% delaminated, 10% partially bonded, 60% bonded	No cracks in Al	Approx. 30% delaminated	Small amount of corrosion at crack tip. Significant filiform over 25% of opposite end undetected

TABLE 13 (continued)

NONDESTRUCTIVE CHARACTERIZATION OF SPECIMENS

Specimen Identification	Processing Final Exposure Stress (psi)	Neutron Radiography	X-Ray	Thru Transmission Ultrasonics	Eddy Current	Pulse Echo Ultrasonics	Comments After Disassembly
G - Crack Extension Specimen	PAA BR 127 FM 300M	Three corrosion striations shown	Small amounts of evenly distributed corrosion on surface	40% delaminated, 5% partially bonded, 55% bonded	No cracks in Al	Approx. 40% delaminated	Slight corrosion at crevice end. 40% delaminated cohesively
H - Crack Extension Specimen	PAA BR 127 FM 300M	No corrosion indicated	Small amounts of evenly distributed corrosion on surface	40% delaminated, 5% partially bonded, 55% bonded	No cracks in Al	Approx. 40% delaminated	Filiform corrosion on edge of wedge end

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TABLE 14

VARIATION IN PROPERTIES WITH ADHESIVE FILM THICKNESS

Adhesive System Stress, Specimen #	Lap Shear Adhesive Thickness	Lap Shear	Average Lap Shear for this System	Failure Mode Corrosion Indication
PAA/BR 127/FM 73M 741 psi final stress #2	0.003" 0.005"	5337	77°F	100% cohesive
PAA/BR 127/FM 73M 706 psi final stress #5	0.010" 0.015"	4847	77°F	100% cohesive
PAA/BR 127/FM 73M 0 Stress #40	0.020" 0.020"	4448	180°F	100% cohesive
PAA/BR 127/FM 73M Spring Broken #12	0.005" 0.005"	2574	180°F	98% cohesive 2% filiform
PAA/BR 127/FM 73 1073 psi final stress #10	0.025" 0.025"	2778	180°F	98% cohesive 2% adhesive
PAA/BR 127/FM 300 796 psi final stress #21	0.005" 0.010"	5517	77°F	100% cohesive failure 1% filiform
PAA/BR 127/FM 300M 695 psi final stress #23	0.020" 0.025"	609	300°F	Corrosion spots 24% cohesive 75% adhesive to primer
PAA/BR 127/FM 73M #46	0.003" 0.005"	606	300°F	24% cohesive, 75% adhesive to primer, 1% filiform
PAA/BR 127/FM 73M 0 stress #39	0.010" 0.010"	5463	77°F	100% cohesive
PAA/BR 127/FM 300M 0 stress #43	0.005" 0.003"	4448	77°F	85% cohesive 15% adhesive
PAA/BR 127/FM 300M 0 stress #49	0.020" 0.020"	4560	77°F	100% cohesive
PAA/BR 127/FM 300M 1050 psi #5	0.005" 0.003"	4384	77°F	100% cohesive

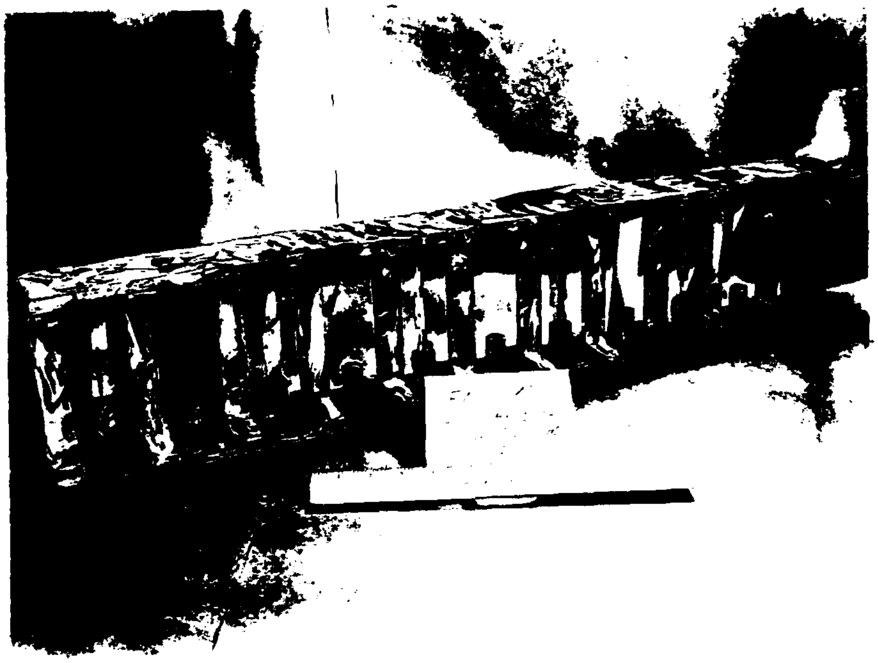


Figure 3: PAA, BR 127/FM 73M Exposed 10 years with No Stress

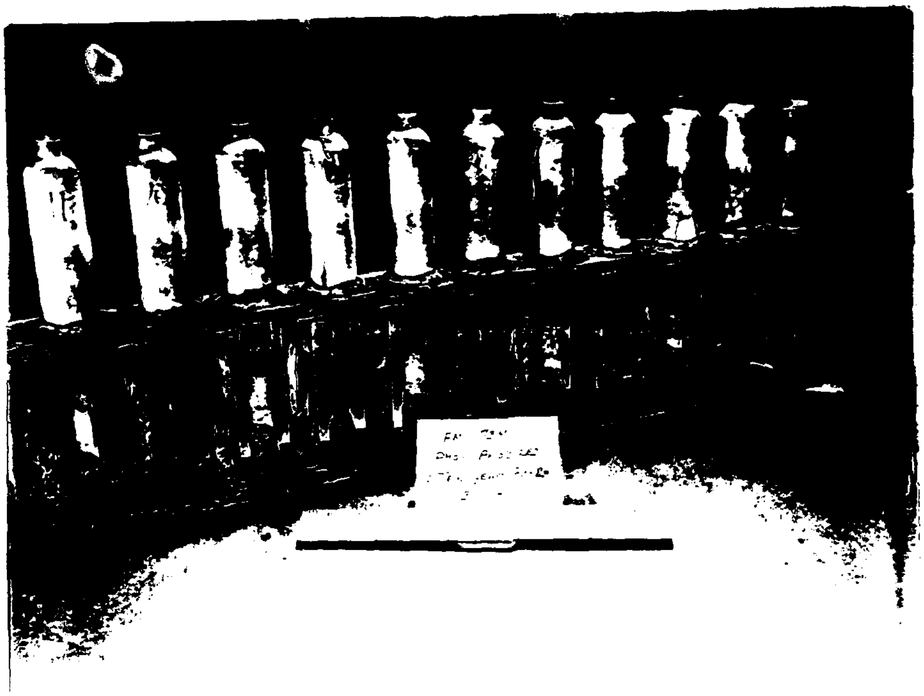


Figure 4: PAA/BR 127/FM 73M Specimens in Racks at Nominal 800 psi after 10 years

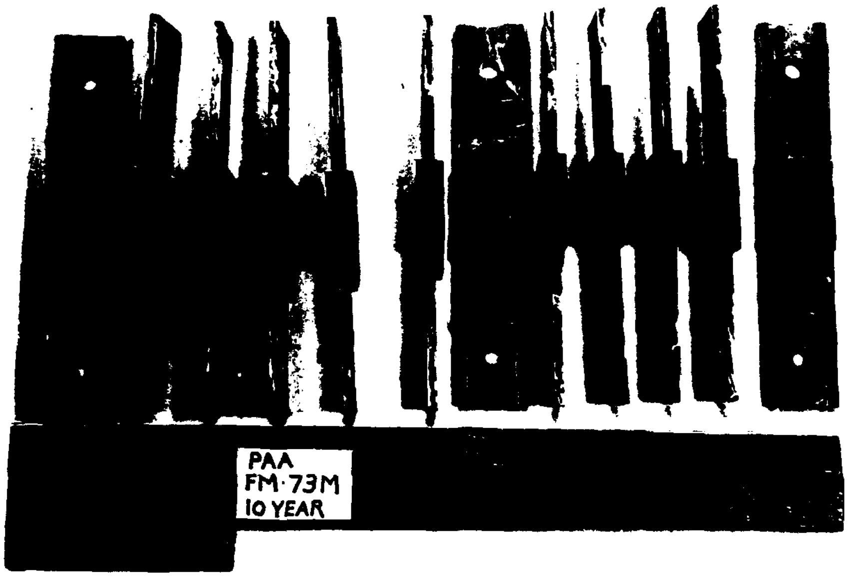


Figure 5: PAA/BR 127/FM 73M Specimens Stressed 800 psi and 1200 psi for 10 years

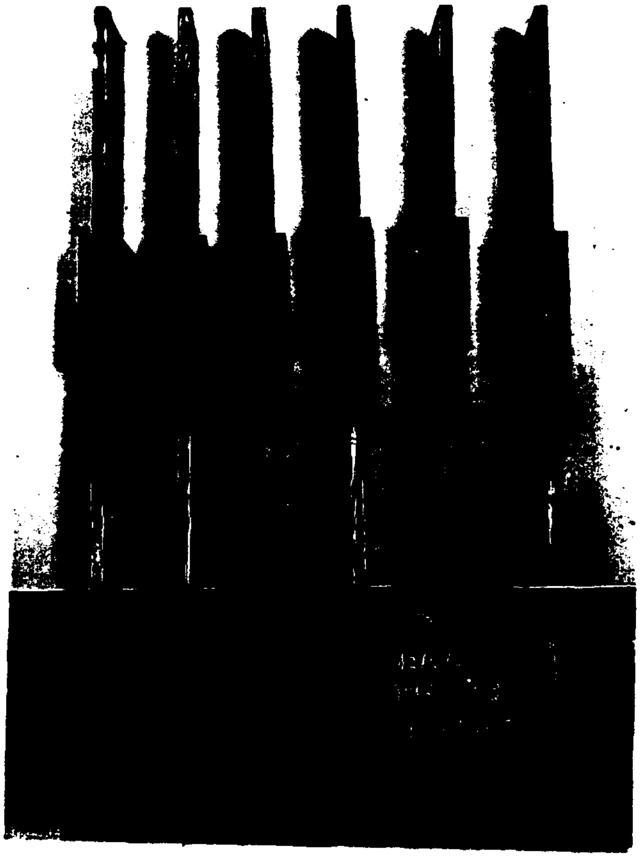


Figure 6: PAA/BR 127/FM 73M Exposed with No Applied Stress for 10 years

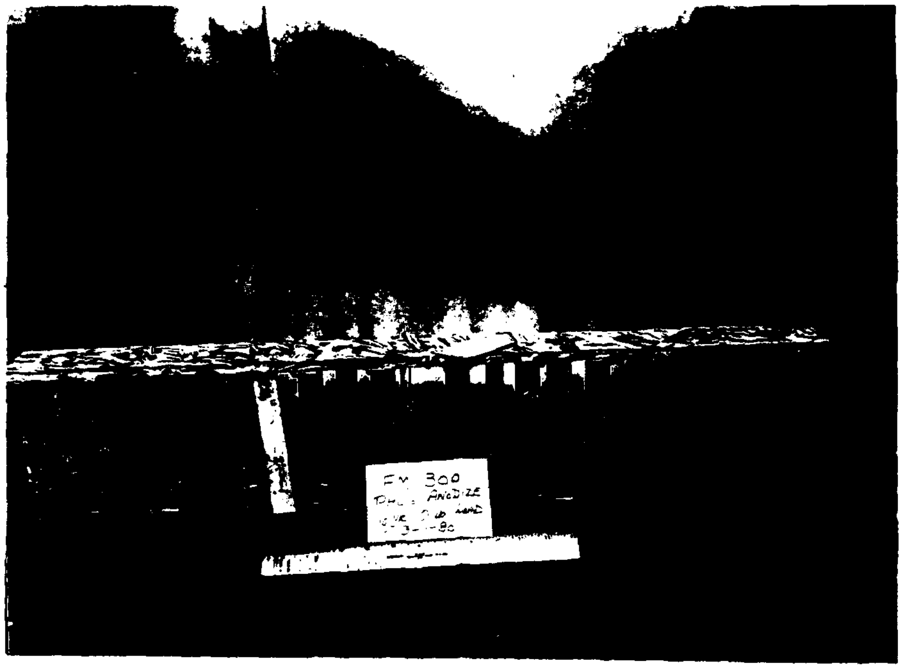


Figure 7: PAA/BR 127/FM 300 Exposed 10 years with No Load

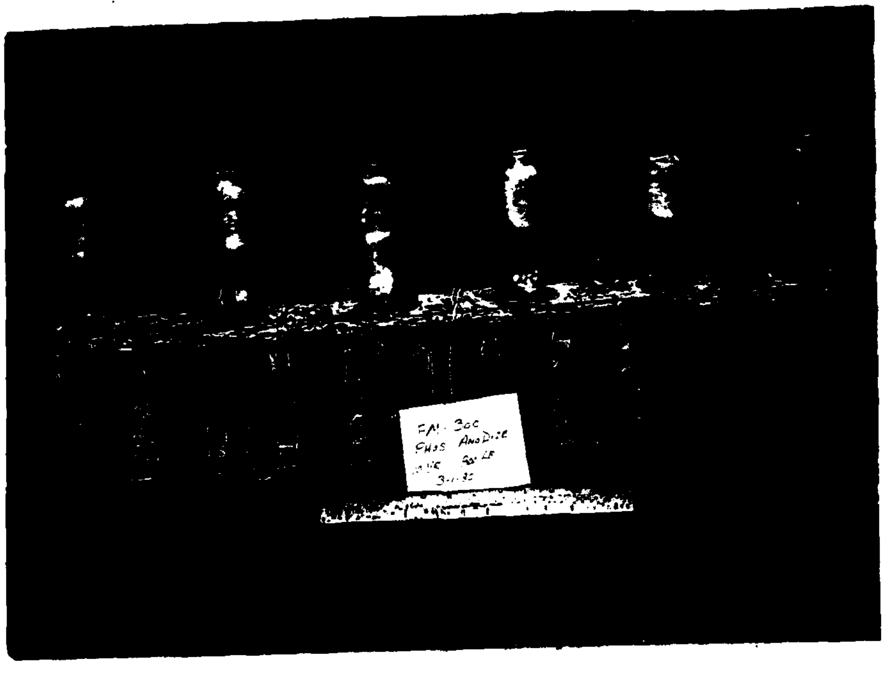


Figure 8: PAA/BR 127/FM 300M 10-year Exposure at 800 psi Nominal Stress

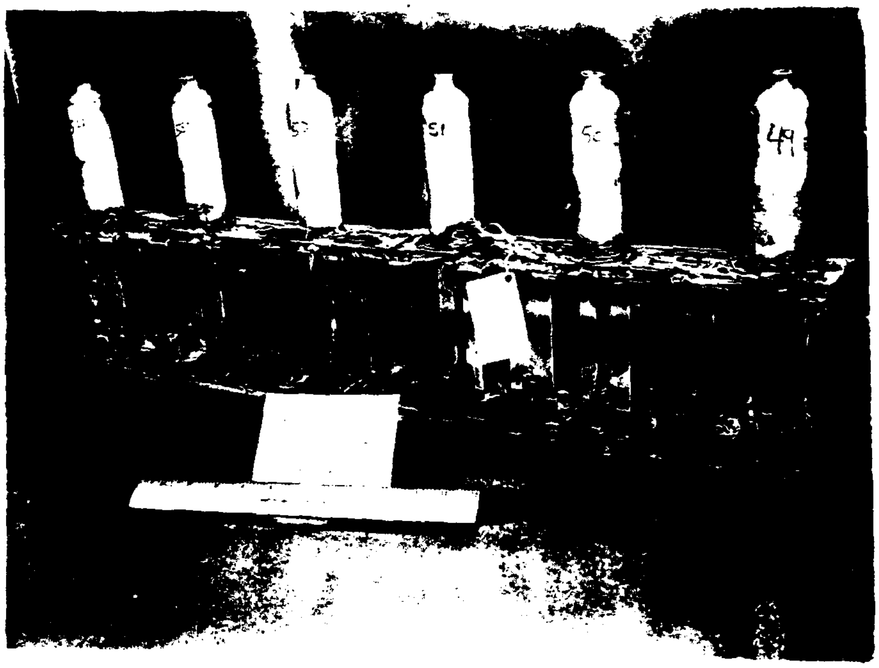


Figure 9: PAA/BR 127/FM 300M in Racks After 10 years Exposure Stressed at a Nominal 1200 psi

Figure 10: PAA/BR 127/FM 300M No Load Specimens After 10 Years Exposure

Figure 11: PAA/BR 127/FM 300M Specimens Exposed 10 years at 800 psi Nominal Stress

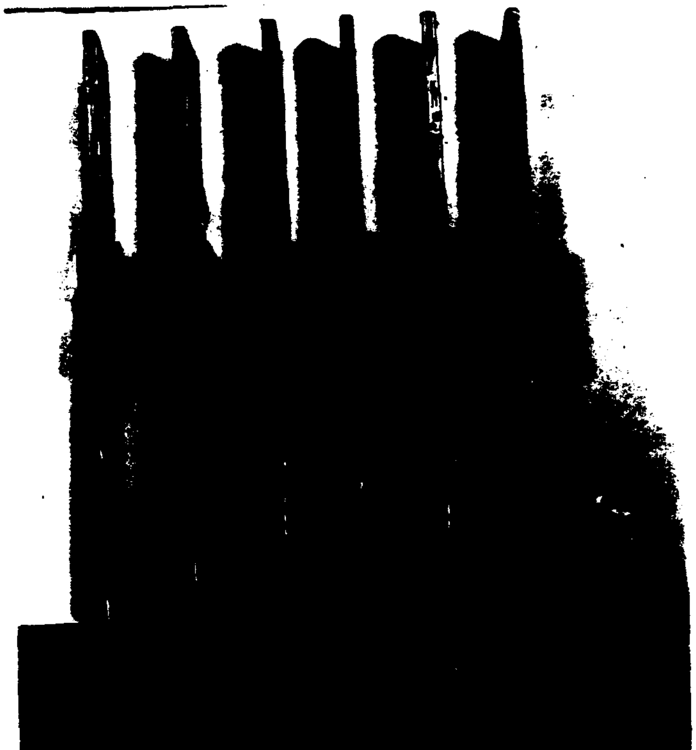


Figure 12: PAA/BR 127/FM 300M Specimens After 10 years 1200 psi Nominal Stress Exposure

Figure 13: OFPL/BR 127/FM 300M in Rack Exposed Under No Load for 10 years

Figure 14: OFPL/BR 127/FM 300M in Rack following 10 years Exposure at Nominal 1200 psi Stress

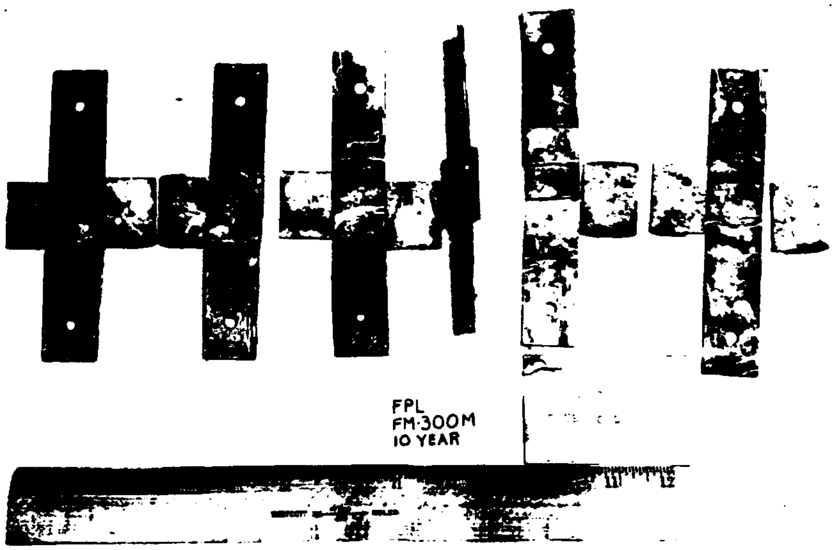


Figure 15: OFPL Specimens Delaminated During Removal from Rack

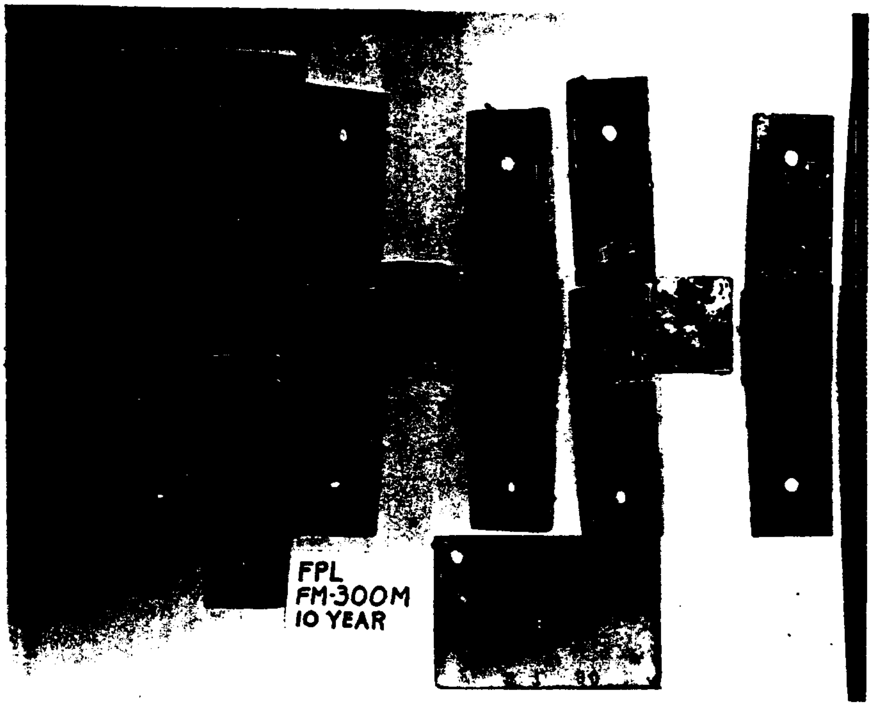


Figure 16: OFPL Specimens Exposed at 800 psi for 10 years Which Delaminated During Removal from Rack

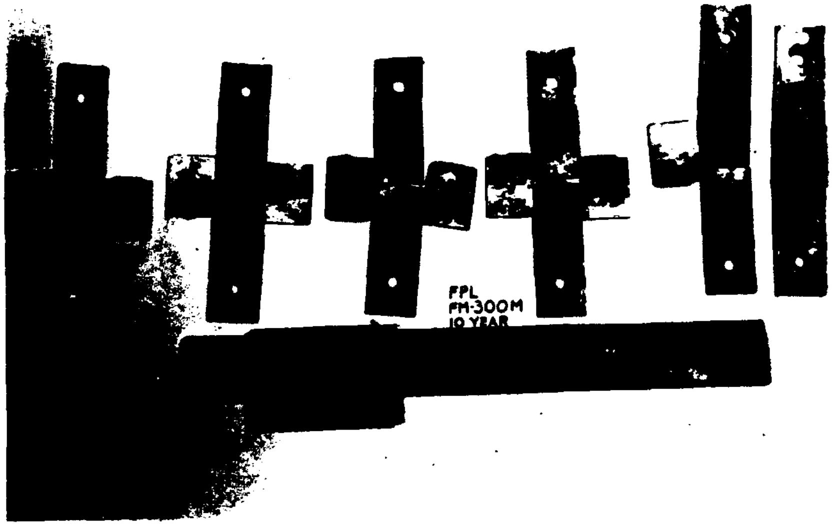


Figure 17: OFPL/BR 127/FM 300M Stressed at 1200 psi Nominal for 10 years Delaminated During Removal from Rack

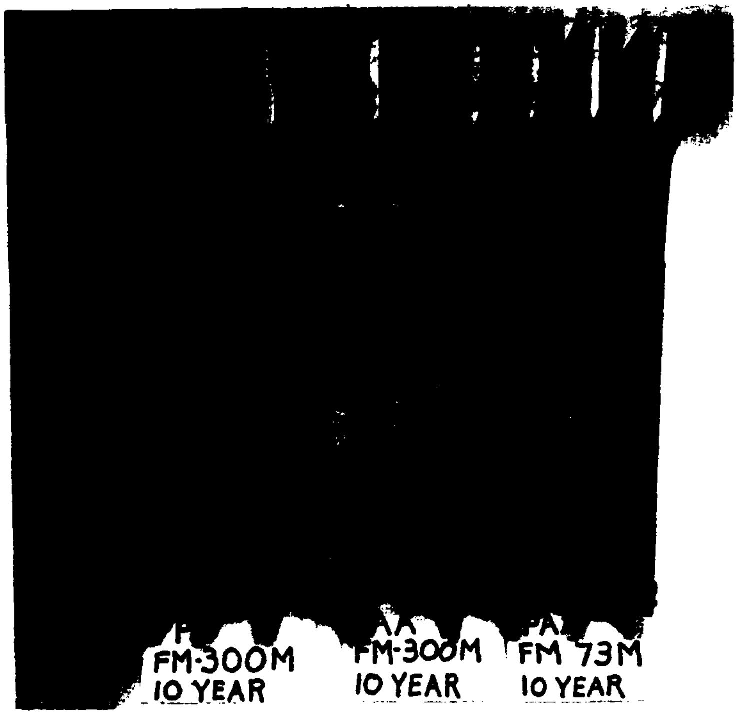


Figure 18: Crack Extension Specimens Showing Wide Differences in Crack Lengths after 10 years in Marine Atmosphere

Figure 19: Typical Separation Appearance of FM 300M Lap Shear Tested at 300° F

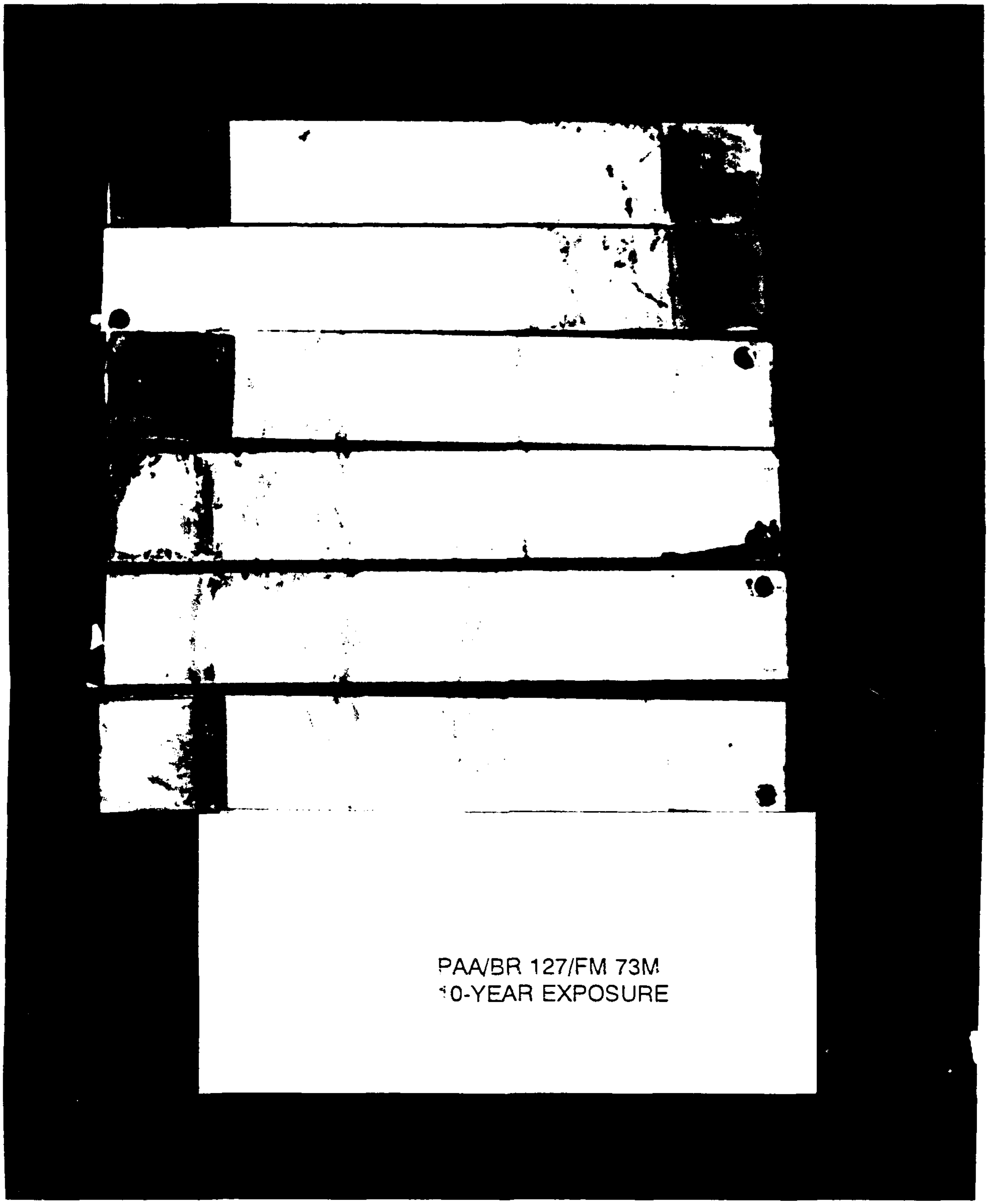
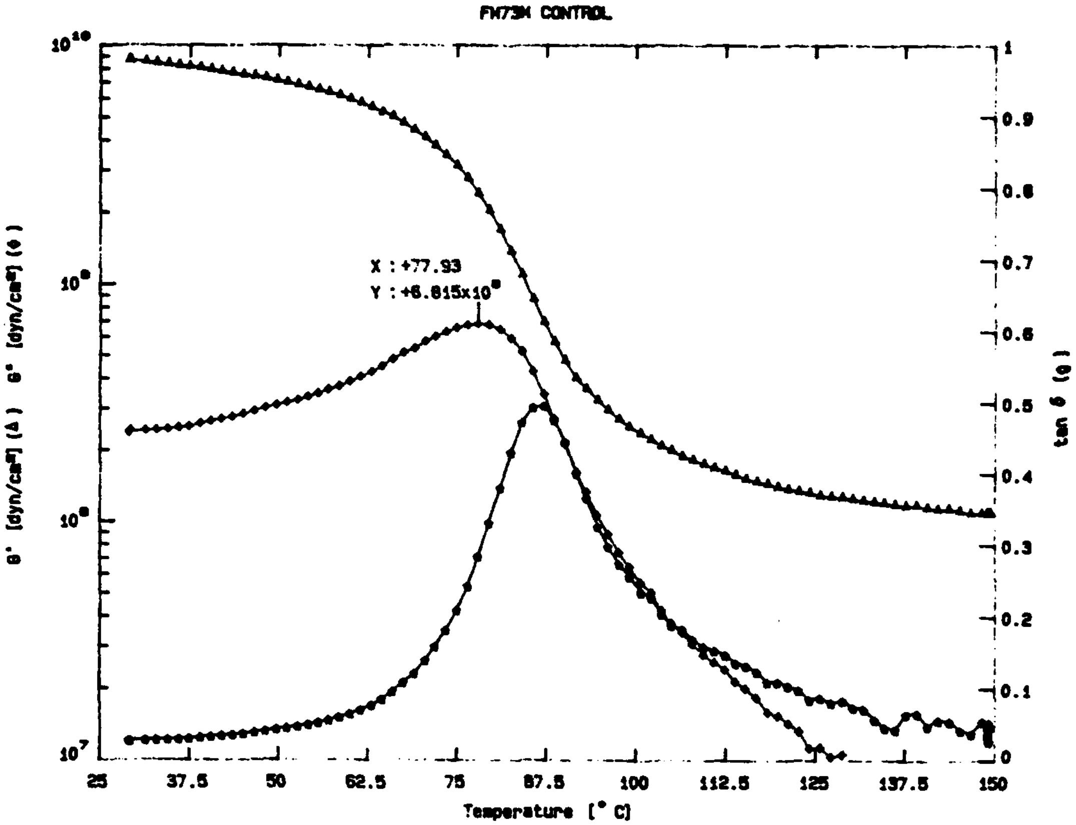


Figure 20: PAA/BR 127/FM 73M Crack Extension Specimens Exposed 10 years in Marine Atmosphere



FM 73M Control for Elastic Modulus, Loss Modulus and Glass Transition

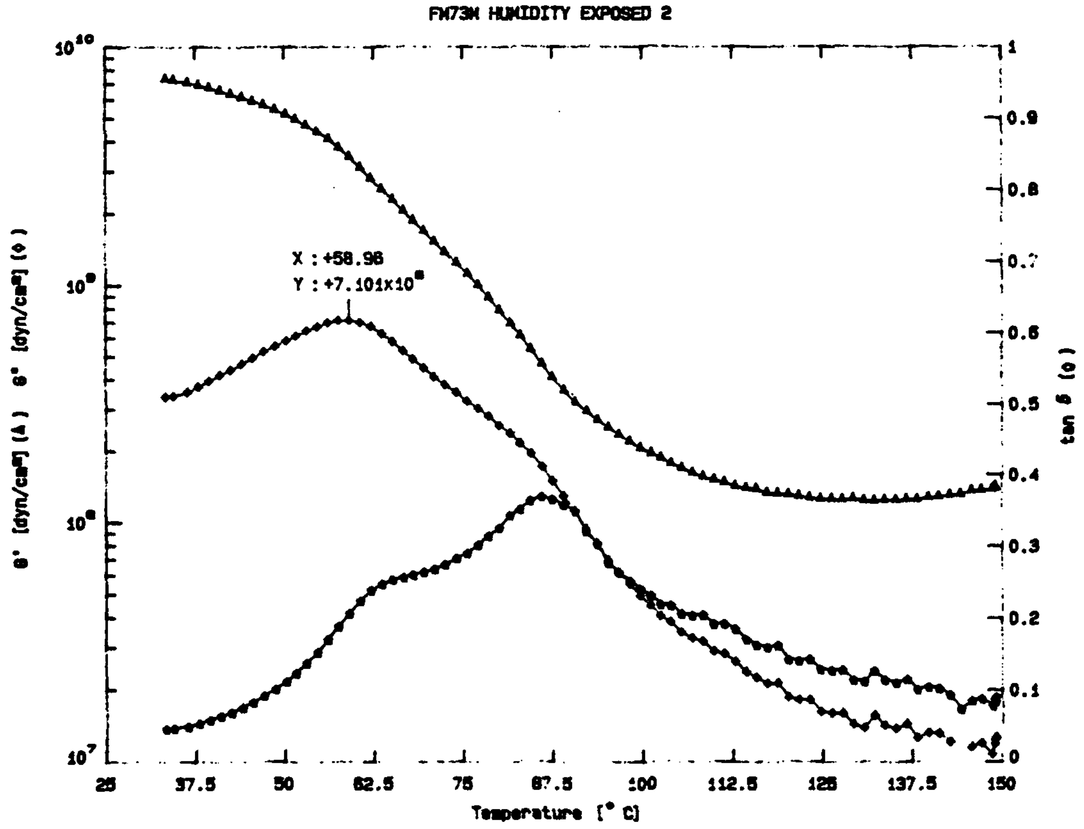


Figure 21: Moisture Conditioned FM 73M Elastic, Loss Modulus and Glass Transition

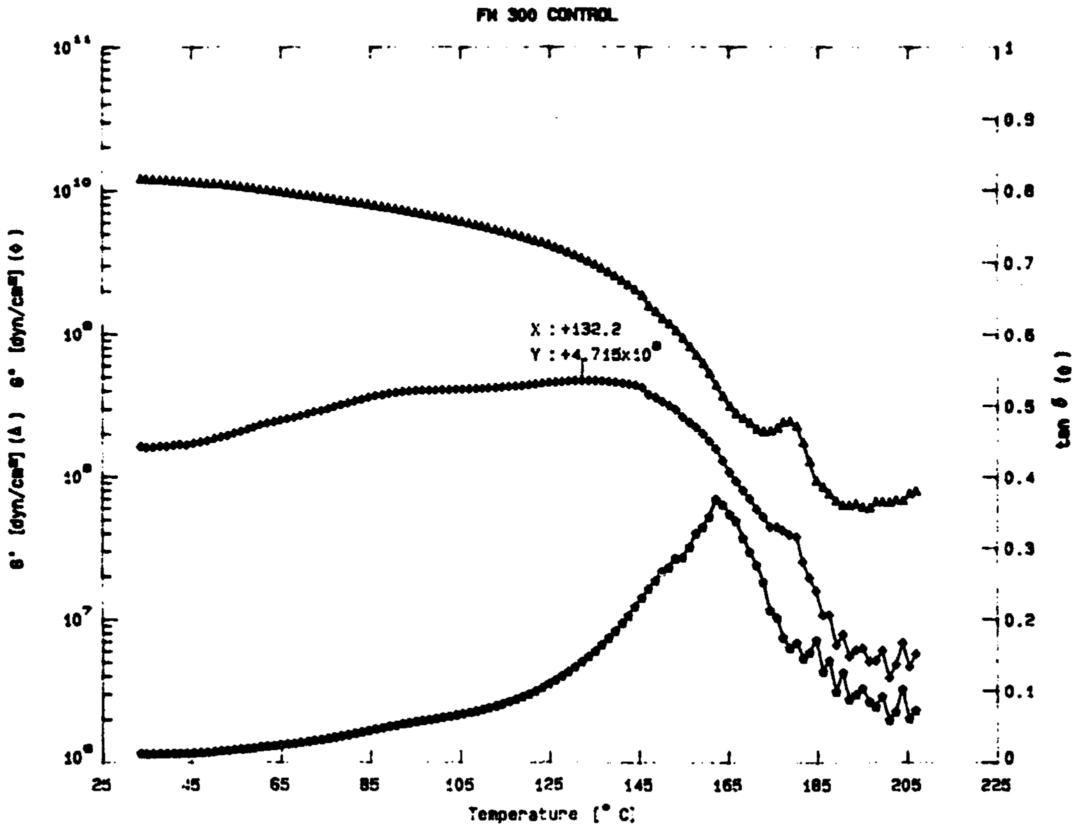


Figure 22: FM 300M Adhesive Elastic, Loss Modulus and Glass Transition

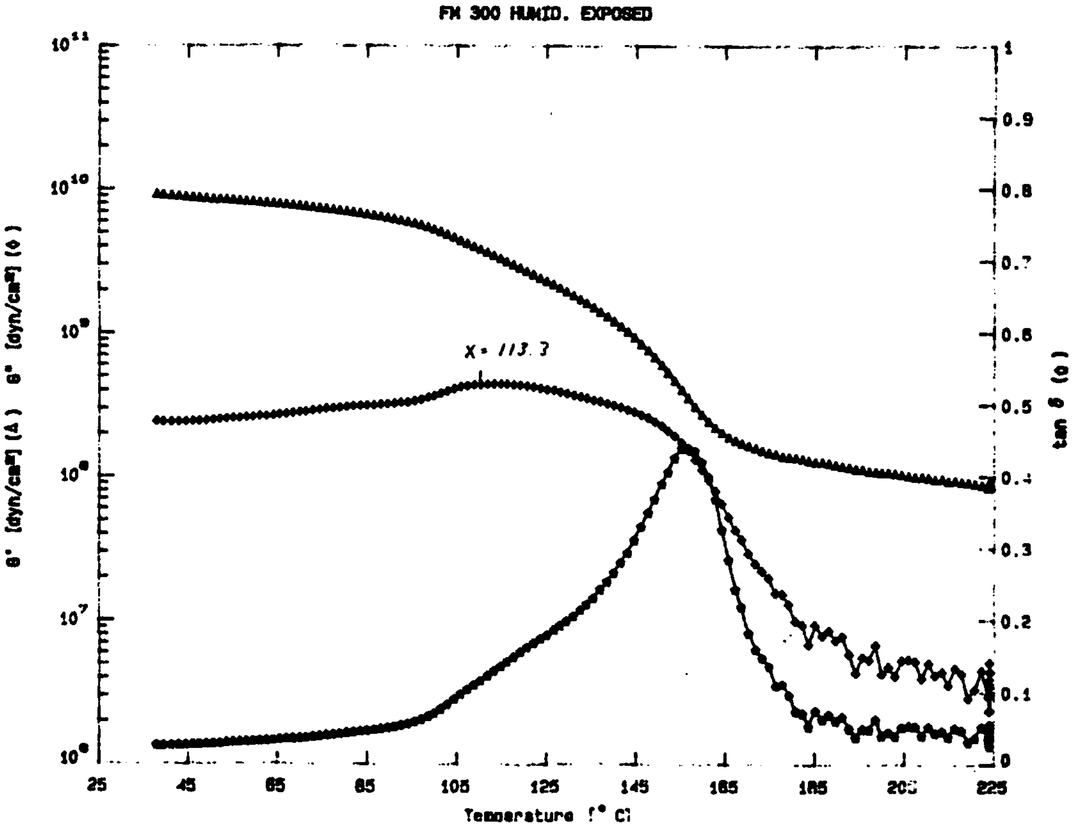


Figure 23: Moisture Conditioned FM 300M Adhesive Elastic, Loss Modulus and Glass Transition

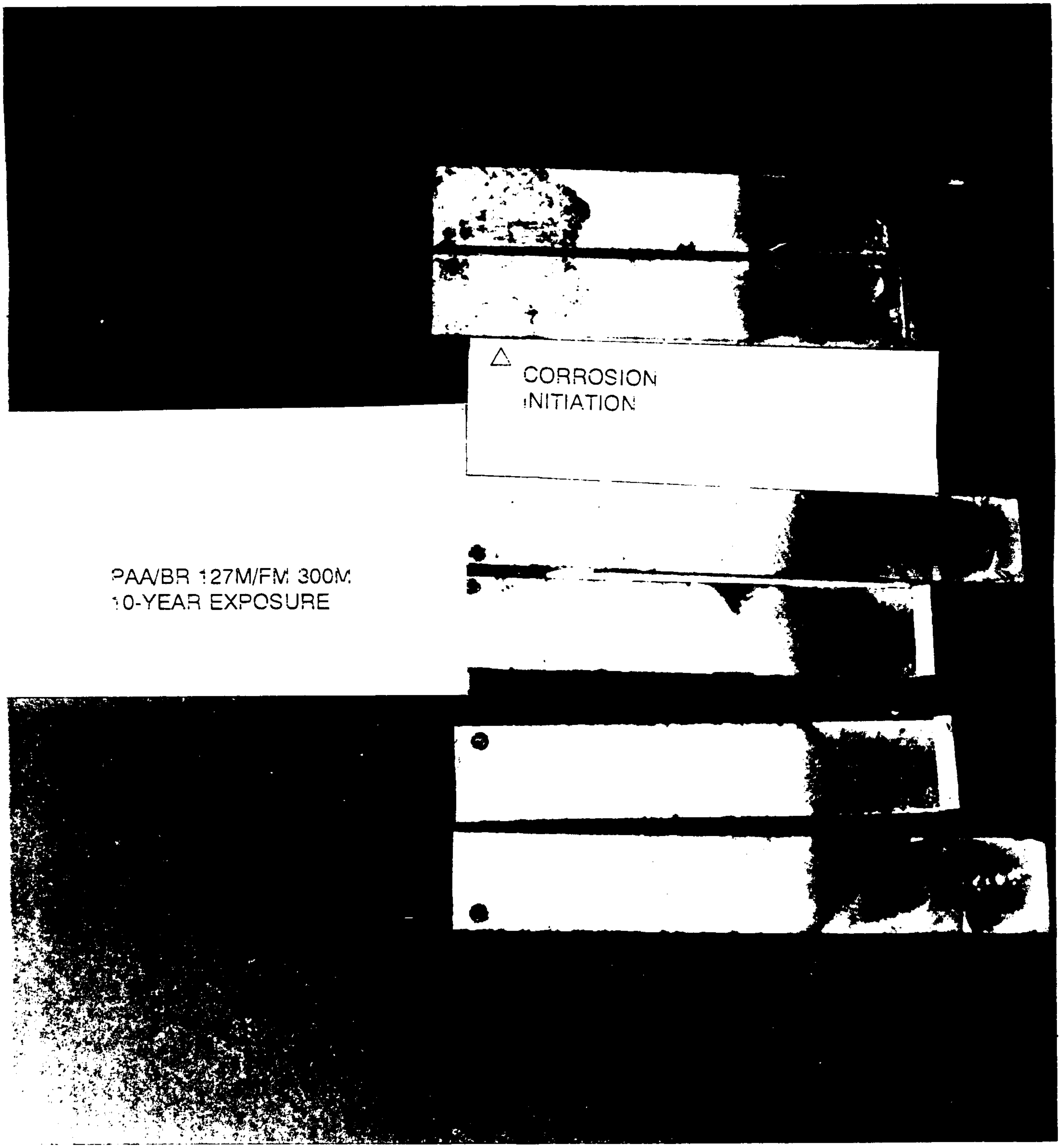
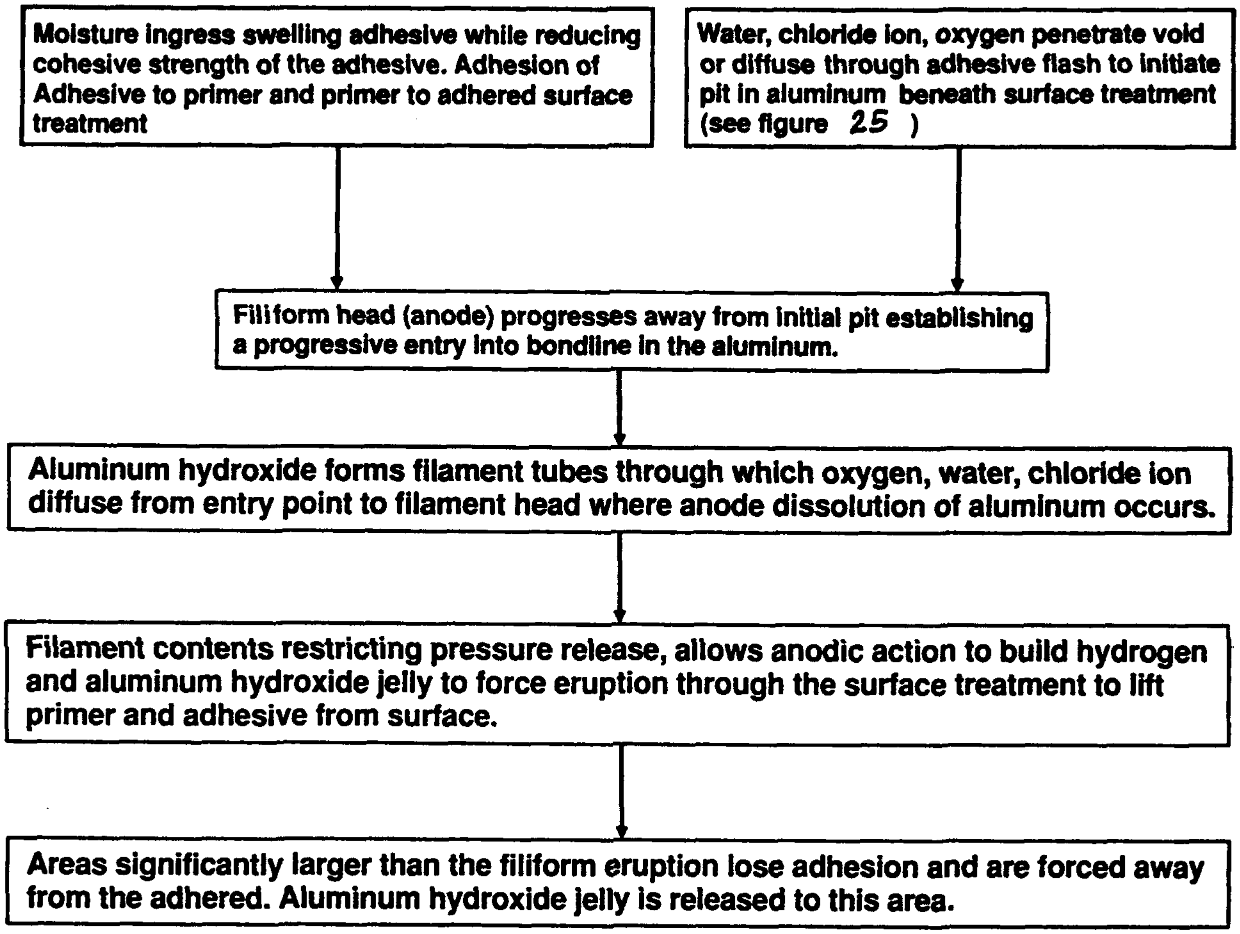


Figure 24: Crack Extension Specimens PAA/BR 127/FM 300M Showing Filiform Initiations after 10 years Exposure

Figure 25: Crack Extension Specimen Showing Filiform Initiation, Subanodize Progression, and Aluminum Hydroxide Eruption


Moisture ingress swelling adhesive while reducing cohesive strength of the adhesive. Adhesion of Adhesive to primer and primer to adhered surface treatment

Water, chloride ion, oxygen penetrate void or diffuse through adhesive flash to initiate pit in aluminum beneath surface treatment (see figure 25)

Filiform head (anode) progresses away from initial pit establishing a progressive entry into bondline in the aluminum.

Aluminum hydroxide forms filament tubes through which oxygen, water, chloride ion diffuse from entry point to filament head where anode dissolution of aluminum occurs.

Filament contents restricting pressure release, allows anodic action to build hydrogen and aluminum hydroxide jelly to force eruption through the surface treatment to lift primer and adhesive from surface.

Areas significantly larger than the filiform eruption lose adhesion and are forced away from the adhered. Aluminum hydroxide jelly is released to this area.

Figure 26: Filiform Progression into an Adhesive Bondline in 7075-T6 Aluminum Exposed to a Marine Atmosphere

Figure 27: Initiation of Filiform from an Untreated Drilled Hole in the PAA/BR 127/FM 300M

Figure 28: Aluminum Hydroxide Gel Eruption from Filiform Near the Adhesive Edge

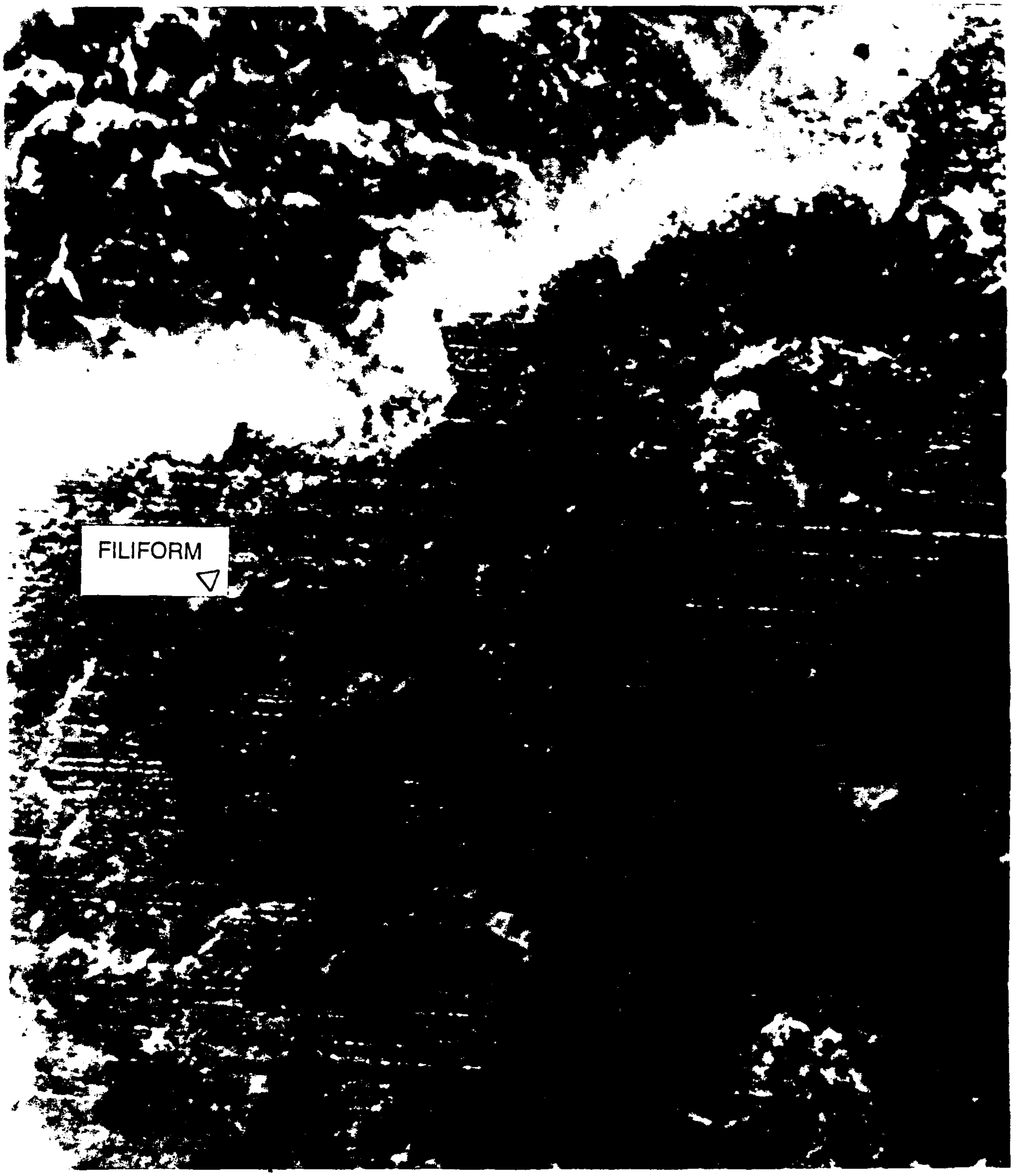


Figure 29: Filiform Progressing Towards Adhesive Edge

Figure 30: Filiform Progressing Under Adhesive Edge

Figure 31: Mature Corrosion Area of Aluminum Hydroxide Masking Prior Filiform Initiation

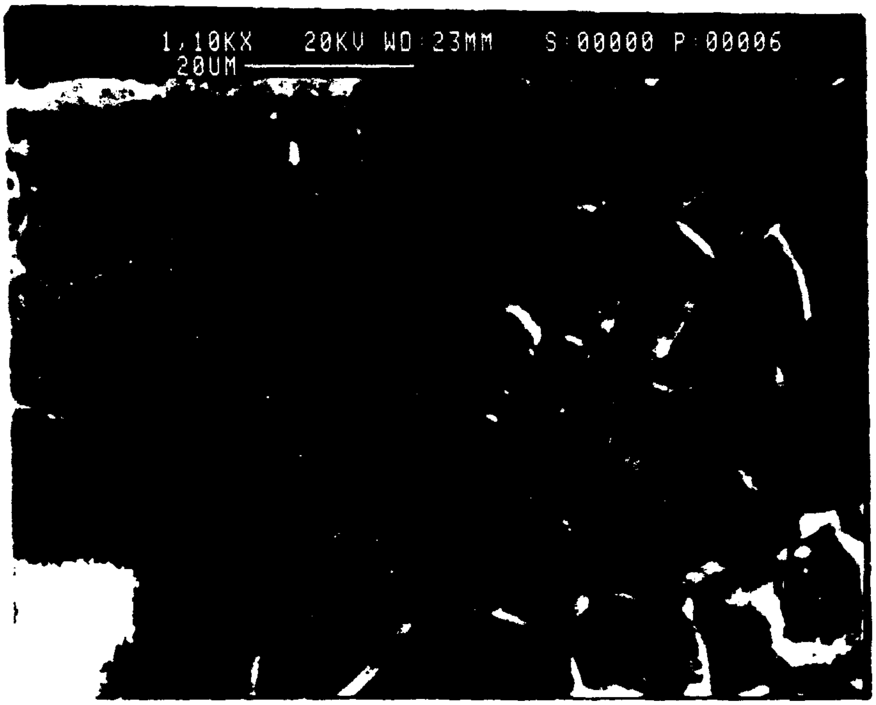


Figure 32: Filiform on OFPL Treated Crack Extension Specimen

Figure 33: Oxygen Depleted Zone in OFPL Specimen Adjacent to Filiform