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OPTIMIZATION OF PROCESSING VARIABLES WHICH AFFECT ADHESION OF ORGANIC COATINGS TO ANODIZED ALUMINUM ALLOYS

A. B. Featherston

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Prepared for:

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October 1975

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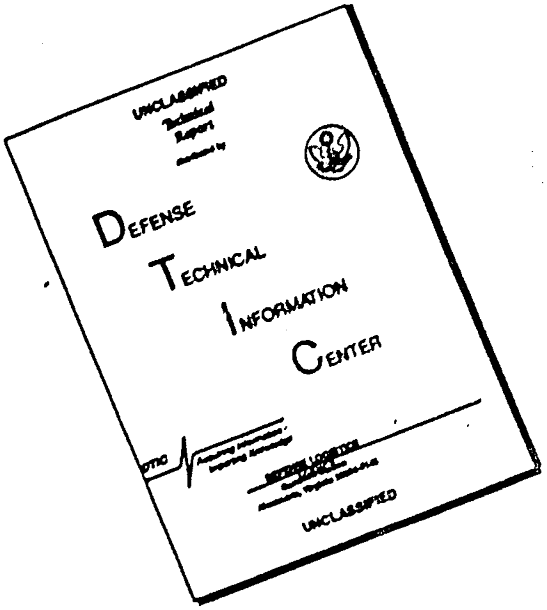

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OPTIMIZATION OF PROCESSING VARIABLES WHICH AFFECT ADHESION OF ORGANIC COATINGS TO ANODIZED ALUMINUM ALLOYS

FINAL REPORT

(16 October 1974 thru 15 October 1975)

October 1975

By

A. B. Featherston

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For

Material Acquisition Group
Engineering Division
MATERIALS AND PROCESSES BRANCH
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By

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LTV AEROSPACE CORPORATION
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This report describes the results obtained in a study program to improve adhesion between anodized aluminum and presently used organic coating systems. The blister test method was used which utilizes fluid pressure under the coating through a hole in the substrate to cause adhesive failure. Specimens were evaluated in both the "as prepared" condition and after being subjected to 30 day alternate salt water immersion conditioning. Several anodizing processes were compared for adhesion characteristics. Special

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VOUGHT SYSTEMS DIVISION

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FINAL REPORT

TECHNICAL REPORT

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ABSTRACT

This report describes the results obtained in a study program to improve adhesion between anodized aluminum and presently used organic coating systems. The blister test method was used which utilizes fluid pressure under the coating through a hole in the substrate to cause adhesive failure. Specimens were evaluated in both the "as prepared" condition and after being subjected to 30 day alternate salt water immersion conditioning. Several anodizing processes were compared for adhesion characteristics. Special emphasis was placed on determining the anodizing variables which affect adhesion and in the determination of optimum processing parameters for both chromic acid and sulfuric acid anodizing. These evaluations utilized 2024 and 7075 aluminum alloy which were anodized, contaminated and cleaned prior to coating with epoxy polyamide primer. All specimens were conditioned 30 days by alternate salt water immersion prior to evaluation. Additional tests were made on anodized surfaces using polyurethane finish and polyurethane elastomer on the primed surfaces. A phosphomolybdic acid spot test was evaluated for correlation with salt spray endurance evaluation.

FOREWORD

The program designed to study the effects various combinations of anodizing variables and coating application techniques on the adhesion of organic coatings was initiated in October 1974 under Naval Air Systems Command, Contract N00019-75-C-0087. The project has been administered by Mr. Tom Johnston who was later succeeded by Mr. David P. Hornick of the Engineering Division of the Materials Acquisition Group of Naval Air Systems Command. The object of the program was to study the effect of variations in the anodizing processes on aluminum alloys for optimization of adhesion of coatings to anodizing surfaces. The evaluations were to determine the adhesion surface energy by the "Blister Test Method" so that the optimum anodizing parameters could be established which would produce a reliable adhesion between the substrate and coating.

The program success has been dependent on the cooperative efforts of individuals from a number of areas. The cooperation and guidance from Mr. Tom Johnson and Mr. David P. Hornick has greatly assisted and stimulated the effort. Technical personnel within and outside of Vought Systems Division have been vital to the accomplishment of this program. The successful completion of this program required specimens to be anodized by other companies following their standard anodizing processes for surfaces to be painted. Acknowledgement must be given for the cooperation and assistance to those suppliers of the specimens; Mr. George Van Derventer and Mr. Ken Porter of Bell Helicopter Company, Mr. D. M. Rosema of Boeing Airplane Company, Mr. W. H. Hyter of Douglas Aircraft Company, M. J. Puma and P. F. Wisely of General Dynamics, Convair Aerospace Division, Mr. Fred Falcone and Mr. H. M. Olesky of KAMAN Aerospace Corporation, Mr. Bernie Bowen of Northrop Corporation, Aircraft Division and Mr. S. C. Shaw of Texas Instruments, Inc. Although the number at Vought Systems Division precludes individual recognition, their efforts both technical and manufacturing as well as those above are recognized and appreciated.

TABLE OF CONTENTS

TABLE OF CONTENTS

(Continued)

TABLE OF CONTENTS
(Continued)

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES

(Continued)

1.0 INTRODUCTION AND SUMMARY

This report describes a study and test program in which various combinations of anodizing variables and coating application techniques were evaluated for effect on adhesion characteristics. The "Blister Test Method" was utilized in the evaluation so that the adhesion surface energy density could be determined between the substrate and the coating. The method utilizes fluid pressure under the coating through a hole in the substrate to cause adhesive failure. The coating must be thick enough to prevent a cohesive failure and allow a blister to form around the built-in flaw in the test specimen.

The investigation was designed to further study methods of improvement and optimization of adhesion of organic coatings to anodized aluminum alloys. Unclad aluminum alloys 2024 and 7075 were selected since these are the most used in aircraft manufacture. Variations of chromic acid anodize on 2024 aluminum processing parameters were investigated for optimization of adhesion characteristics. Aluminum alloy 7075 was utilized to study the effect in variations of sulfuric acid anodize on the adhesions characteristics. The organic coating utilized for the investigation was Mil-P-23377 Epoxy Polyamide Primer.

Additional evaluation of the processes were made with the primer overcoated with Mil-C-81773 Polyurethane Coating and LTV-VSD 9-427 Polyurethane Elastomeric Coating.

An unsuccessful attempt was made to modify the test specimen so that coatings of normal thickness could be evaluated. Each method evaluated converted the adhesion failure away from the primer/anodize interface to another location. This changed the failure mode from a single blister to a double blister which was unacceptable. The previously successful overcoating of specimens was utilized in the program.

A comparison of adhesion characteristics of several anodizing processes was accomplished utilizing the Blister Test Method. The specimens were processed by several companies following their different procedures and types of anodizing and then coated and evaluated. It was found that although the "as prepared" specimen's adhesion values were quite different once the specimens had been conditioned by a 30 day alternate salt water immersion the adhesion values were almost equal.

In the anodizing studies processing variables were selected to determine the parameters which affect the adhesion characteristics of the anodized surface. Epoxy polyamide primer was utilized for all testing using no overcoating materials. A practical approach was used during the investigation by intentionally contaminating the anodized specimens and then cleaning prior to coating. Additionally specimens were conditioned for 30 days by an alternate salt water immersion treatment prior to evaluation for adhesion.

With the sulfuric acid anodize it was found that unless the anodizing solution strength, current density, or time of anodizing varied beyond the normal expected limits the adhesion values were not affected. Pre-cleaning prior to anodizing was found to affect the adhesion values but following normal pre-cleaning practices all adhesion values were satisfactory. Sealing was found to be the most critical parameter of the processing, more especially when the anodized surface was contaminated and then cleaned prior to coating. The method of sealing apparently affects the ability of the contaminated anodized surface to be cleaned. Cleaning methods which utilized steam cleaning yielded the better adhesion values but even this method failed to thoroughly clean specimens sealed in 5% sodium dichromate solution.

Chromic acid anodizing studies also found that sealing was the most critical parameter in the anodizing process. Deionized water sealing yielded much lower adhesion values than no seal or other sealing methods investigated. Cleaning of contaminated anodized surfaces was found to be less difficult than with sulfuric acid anodize but steam cleaning was the most successful. With the more cleanable anodize the seal methods were less critical on adhesion values but no seal and sealing with 100 ppm chromic acid solution were superior to 5% sodium dichromate solution sealing. The solution strength, current density and time were found to have little affect unless large deviations from normal anodizing values were made. Pre-cleaning variations evaluated prior to anodizing did not result in appreciable differences in adhesion values.

Coating of epoxy polyamide primer with polyurethane finish and polyurethane elastomeric coating was investigated on both sulfuric acid and chromic acid anodize. Aging of the primer prior to overcoating as well as effects of thinner addition to the overcoating materials were investigated. The effects of cleaning methods on contaminated surfaces were continued to assess the effect on the two coating systems. Specimens which had received primer coating 30 days prior to overcoating yielded lower adhesion values than identical specimens which were coated within one hour after priming. The thinner dilutions investigated did not show detrimental affects to the adhesion values. Cleaning methods results followed the same pattern which was found for the epoxy polyamide primer in that steam cleaning was found to be the superior cleaning method of those evaluated. Other cleaning methods yielded poor to unsatisfactory adhesion values.

Since adhesion is only one requirement that anodized surfaces must meet an investigation was made on a proposed new method that would evaluate corrosion resistance. The method was a phosphomolybdic acid spot test which could rapidly determine if the anodize would meet the salt spray endurance test. Results of the study were inconclusive but some correlation was obtained with the limited evaluations. The method shows merit and further investigations and test modifications could establish a successful method.

2.0 TEST PROCEDURES

2.1 ADHESION MEASUREMENTS BY BLISTER TEST METHOD

2.1.1 Introduction - The Blister Test Method application to coating adhesion which was developed on a previous program (1) was utilized to determine adhesion characteristics of organic coatings to anodized surfaces. This is a relatively simple test in which the adhesion is measured by applying fluid under pressure through a hole in the substrate under the coating. From the pressure required to lift the coating from the substrate and the blister-height the adhesion strength can be determined.

The Blister Test Method had been utilized to measure adhesive strengths of other materials. A similarity between certain problems of adhesion and fracture was discussed by Williams (2, 3). It was noted that in both cases, if one considers the elastic stress analysis in the neighborhood of a sharp crack (or slight region of non-adhesion), a singularity in stress is found to exist. In the case of a central finite length crack in an infinite sheet subjected to tension, the classic Griffith problem gives a local stress variation which is proportional to the inverse square root of the distance from the crack tip.

Since this (mathematical) infinite stress exists here for even the smallest loading, it appears that instantaneous fracture would occur and that stress analysis would not be useful for predicting a finite stress which the sheet could withstand before fracture. However, Griffith (4) developed an overall energy balance, which incorporated the integrable stress singularity, by equating the reduction in strain energy to the energy required to create new surfaces. The result was the prediction of a finite applied tensile stress, σ_{cr} needed to initiate fracture, namely:

$$\sigma_{cr} = \sqrt{\frac{2E \gamma_c}{\pi a}}$$

where E and γ_c are the Young's modulus and energy to create new fracture surface, respectively, and 2a is the finite length of the crack in the thin sheet. Thus, the use of the integrated energy balance circumvented the question of how infinite the stress need become before fracture. It also suggests the way in which other problems in stress analysis having stress singularities can be attacked in order to predict a finite stress at failure notwithstanding an infinite stress at the origin of the fracture initiation.

The character of elastic stress singularities to be expected for various geometric discontinuities was investigated by Williams and later applied to the specific situation of the interface between dissimilar media. In this case, too, when a crack existed along a line of demarcation of the two materials, the stress singularity was likewise singular and the similarity between cohesion and adhesive failure becomes clear. In the Griffith problem the finite length of the central crack 2a lies along the x axis, with the upper and lower half planes occupied by the same material; in the second case, the materials above and below the x axis are different.

The adhesive mechanics approach is straightforward and consists of two parts:

- Conduct the stress analysis for the bonded materials including a flaw at the interface.
- Express the incremental new surface energy (γ_a) as the crack extends.

Williams developed the treatment for the blister test, first proposed by Dannenberg (5) but without the fracture mechanic treatment, for determination of the strength of an adhesive (i.e. γ_a).

The samples are easily constructed. The pressure uniformly distributes itself in the flaw, reducing alignment problems. The tests can be conducted with apparatus generally available in research and testing laboratories. To determine the strength of an adhesive only the critical pressure for failure, the flaw size, the system geometry, and the material properties are required. For a circular plate of incompressible elastic material bonded to a rigid plate, with air injected through a hole in the rigid member into a circular unbonded area (see Figure 1) the following relationship was developed:

$$P_c = \left[\frac{32}{3\,(1-\gamma^2)}\left(\frac{h}{a}\right)^3\right]^{1/2}\sqrt{\frac{E\,\gamma_a}{a}} \qquad (1)$$

where P_c = pressure necessary to initiate adhesive fracture

E = Young's Modulus

h = Plate thickness (coating)

γ = Poisson's Ratio

a = Radius of unbond

γ_a = Adhesive surface energy density

H. B. Jones, and Williams (6) did additional work which showed that the equation could be written in terms of the center plate deflection as:

$$P_c W_0 = 2\,\gamma_a \text{ (plate)} \qquad (2)$$

where W_o = center plate deflection (see Figure 1) which is a convenient description for an experimental test since both the pressure necessary to initiate adhesive fracture and the center deflection at that pressure can be measured directly. The adhesion surface energy density is then calculable. For the same plane form, if the plate is thin and deflections are large, the mid-plane stretching or membrane stresses predominate and criticality can be defined (reference 7).

$$P_c W_o = 2.4 \gamma_a \quad \text{(membrane)} \tag{3}$$

$$\text{or} \quad P_c = 1.532 \left(\frac{h}{a^{(3/4)}} \right) \sqrt[4]{\frac{E \gamma a}{a}} \tag{4}$$

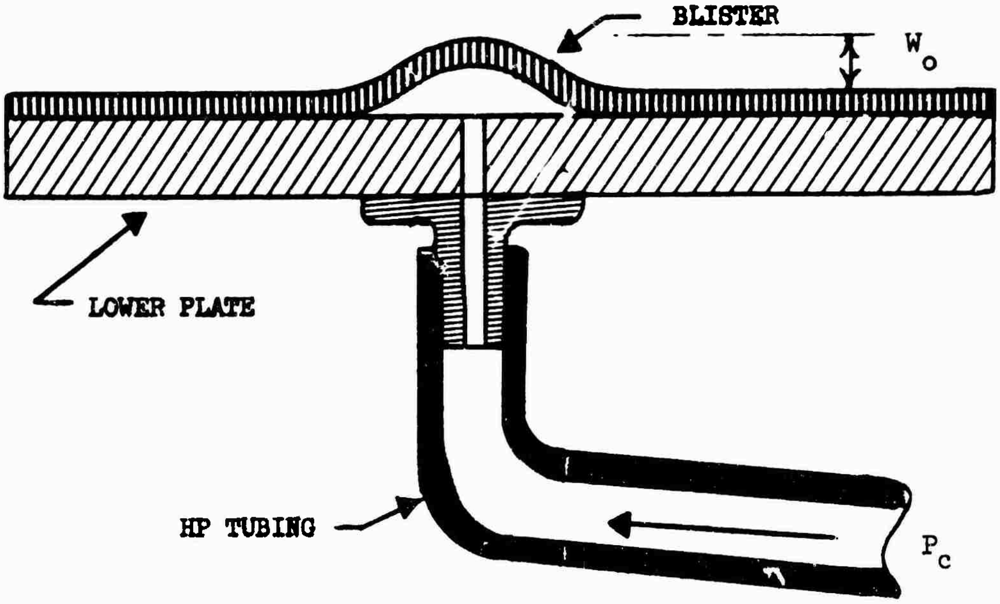


FIGURE 1 SCHEMATIC OF ADHESIVE TEST SPECIMEN

Tests using filled and unfilled elastomers indicate that the response of a specimen undergoes a rather smooth transition from plate to membrane behavior over a relatively narrow rangeof increasing deflections. This transition is indicated by the x's on Figure 2. This orderly transition in behavior, then, appears to present no insurmountable difficulties relative to the analysis of blister test data.

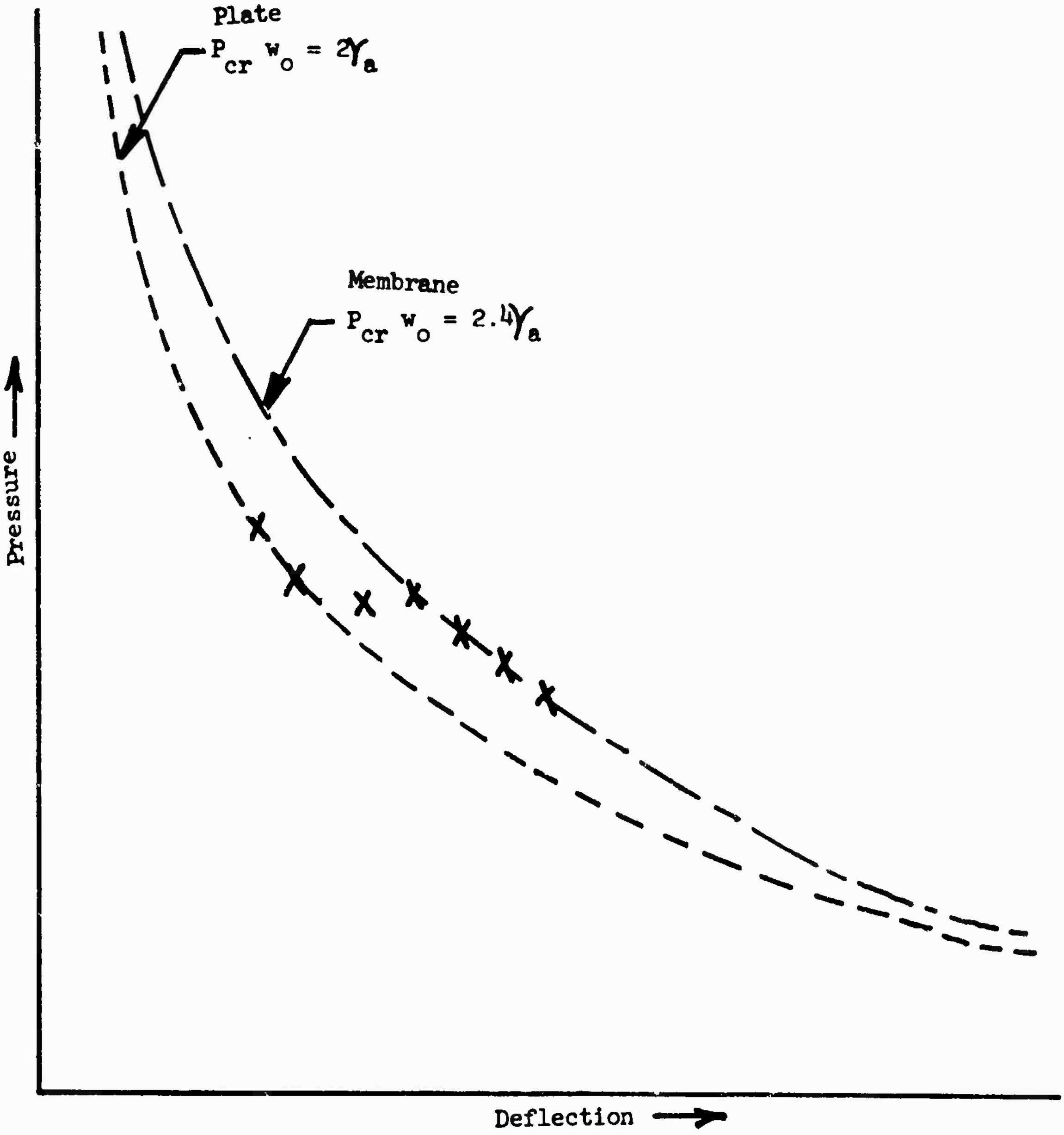


FIGURE 2 CHARACTERISTIC SPECIMEN PRESSURE-DEFLECTION AND FRACTURE BEHAVIOR

During repeated tests on a specimen, where deflections may range from small to large, there will, of course, be intermediate values for which neither the plate solution nor the membrane solution is valid.

The analyses have also been developed for other geometries such as a bond between two disks of different elastic properties (double blister), for two rigid plates bonded together by an adhesive and for multiple layers of elastic materials bonded to a rigid plate. All of these can be handled mathematically and according to Williams (8) since the value determined is γ_a and the relationship includes film thickness, it is not necessary that the test specimens have the same thickness as the practical coating.

Depending on the system to be studied the test apparatus may be as simple as that shown in a paper by Williams, et al (9), or a more sophisticated one such as that diagrammed in Figure 3. This was used at VSD in the previous study (1).

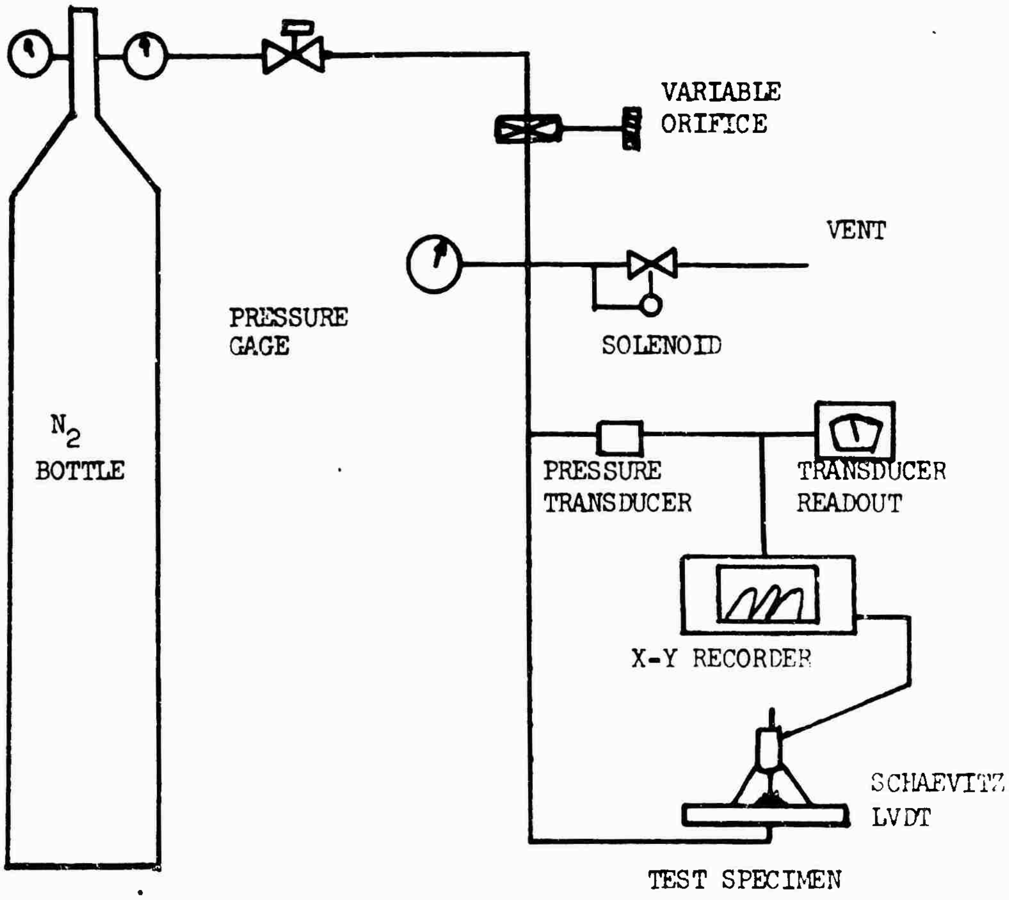


FIGURE 3 DIAGRAM OF APPARATUS FOR BLISTER TEST

2.1.2 Design and Assembly of Test Equipment - The "Blister Test" apparatus was assembled as diagrammed in Figure 3 using a Statham Instrument Inc. strain gauge, model UC3 in a body shell adapter, model U6P4-B in which selected diaphrams may be installed. A Statham Universal Readout, model SC1001 was attached to the pressure transducer and then relayed to a Hewlett Packard X-Y recorder, model 7004B. The system was pressurized with cylinder nitrogen through a cylinder pressure gauge/regulator, cutoff valve and a micrometering valve, model 1B22RS4. System pressure was also monitored, and calibrated with a Ashcroft 0-60 psig. test gauge which had previously been calibrated. A 110 volt solenoid operated pressure release valve and specimen holder, Figure 4 completed the pressurization side of the apparatus.

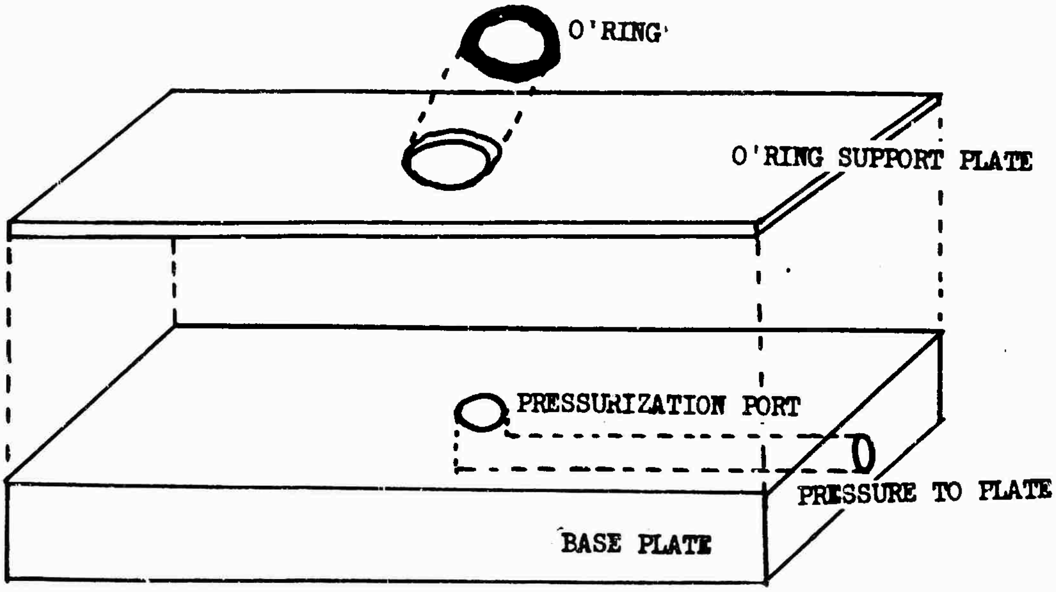


FIGURE 4

SCHEMATIC OF SPECIMEN HOLDER

The blister height measurement utilized a Schaevitz Liner Displacement Transducer (LVDT) which operated on 32 volts DC supplied by a Lambda Electronics Corporation regulated power supply, series LCS-4. The transducer which is mounted in a tripod holder to place on the specimen, was then connected to the X-Y recorder. The entire system was powered through a Freed 115 volt power regulator to minimize line voltage fluctuations.

2.1.3 Test Specimen Preparation - The test specimens were fabricated by shearing a 3 inch by 3 inch specimen from approximately 1/4 inch sheet stock. A 1/4 inch diameter hole was then punched in approximately the center. The simplified specimen design was made possible by using an "o-ring" and retainer plate with clamps to hole the specimen to the test assembly specimen holder to form a seal.

Prior to coating the specimens after all processing had been completed a 3/4 inch masking tape disk was placed over the pressurization port to serve as the initial flaw or blister.

2.1.4 Specimen Conditioning - Specimens were evaluated in both the "as prepared" condition as well as after being subjected to an alternate salt water immersion treatment. The "as prepared" specimens were held under laboratory storage conditions with no special humidity controls.

The conditioned specimens were placed in an alternate immersion apparatus (Figure 5) and subjected to an alternate immersion cycle of 10 minutes immersion in a 3.5% sodium chloride solution maintained between 6.6 pH and 6.8 pH. The immersion was followed by air drying for 50 minutes. The alternate immersion apparatus shown in the figure is completely covered which maintains the relative humidity at approximately 60% so that the drying time is extended.

After removal from alternate immersion the specimens were rinsed in deionized water, wiped off, and allowed to air dry for a minimum of 24 hours.

2.1.5 Specimen Evaluation - Before the specimens were subjected to Blister Test evaluation all specimens were placed in a 50% relative humidity cabinet for a minimum of 7 days. The specimens were then removed from the relative humidity cabinet and clamped into place on the Blister Test specimen holder. The Schaevitz LVDT tripod, previously calibrated, was placed on the specimen as shown in Figure 6. The displacement probe was located over the built in flaw made with the masking tape disk covering the pressurization port in the center of the specimen.

Previous to installing the specimen, the system was calibrated so that the X-Y recorder reads directly in psig and blister height in inches. The following general procedure was followed for specimen evaluation.

1. Install pressure transducer assembly with proper diaphram and calibrate.
2. Calibrate the X-Y recorder to plot signals from the pressure transducer and the Schaevitz LVDT.
3. Install specimen to be tested in specimen holder and locate the LVDT tripod assembly so that the displacement probe is over the pressurization port.
4. Regulate nitrogen bottle gauge pressure.
5. Set micrometer valve.
6. Turn on power to X-Y recorder.
7. Depress solenoid pressure release switch and open hand valve.
8. Release solenoid pressure release switch and allow pressure to increase in system until blister size starts to increase noted by change in slope of produced curve.
9. Depress solenoid pressure release switch to lower pressure below critical pressure.
10. Repeat steps 8 and 9 to obtain additional data.

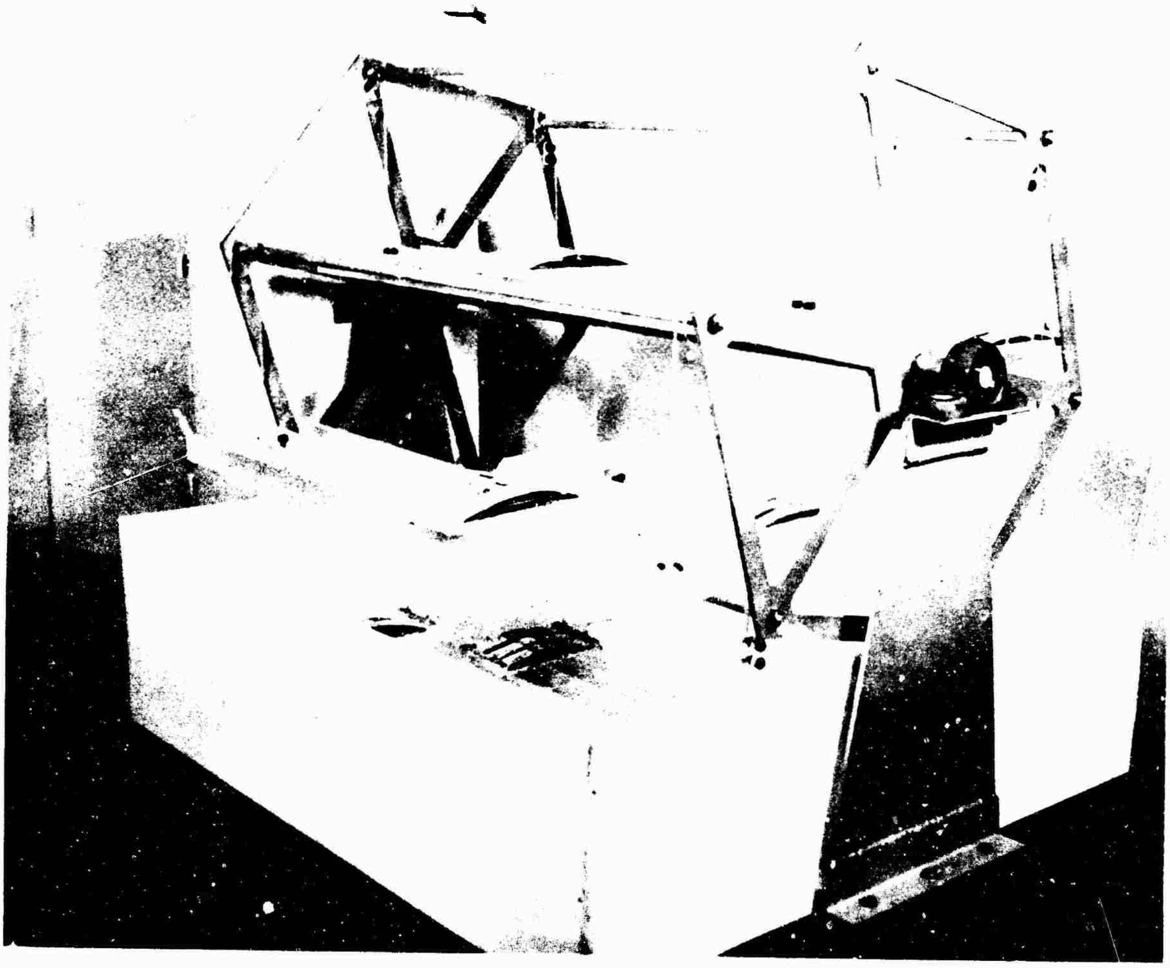


FIGURE 5 ALTERNATE IMMERSION APPARATUS

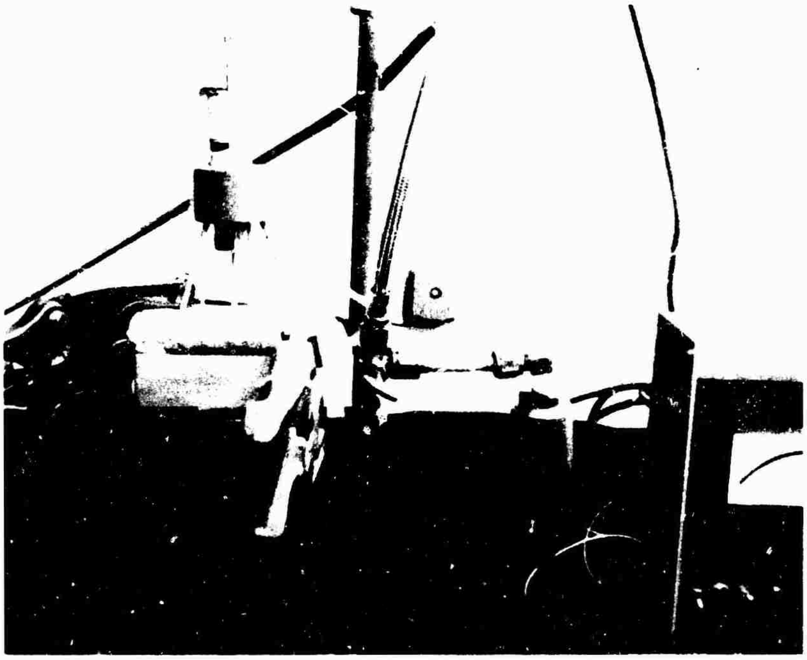


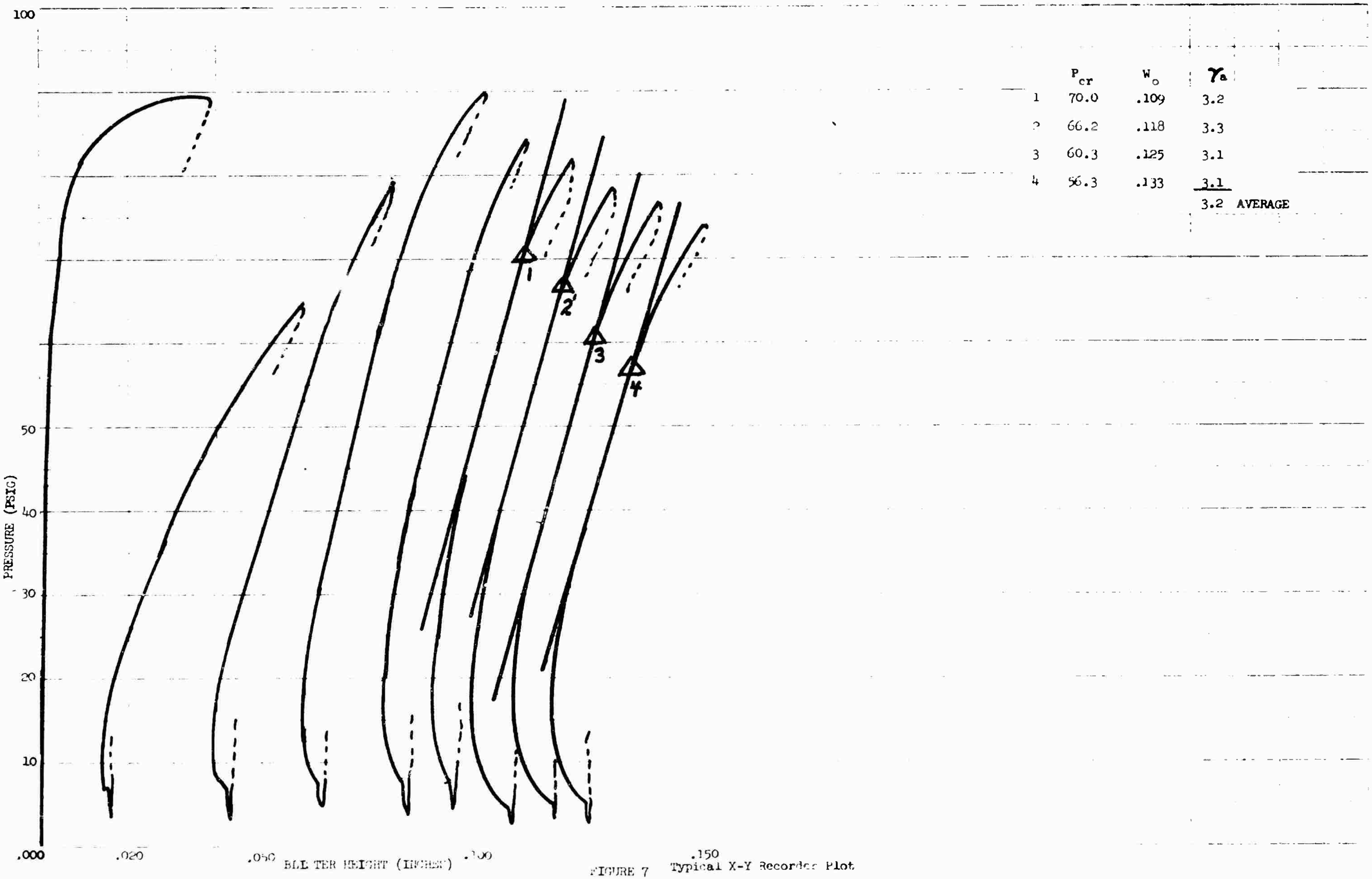
FIGURE 6 SCHAEVITZ LVDT ON SPECIMEN

Upon completion of the test a direct plot of critical pressure (P_c) versus blister height (W_o) has been recorded on the X-Y recorder. The adhesion surface energy γ_a may then be calculated from equation 3. Several plots were obtained from each specimen and results calculated as shown on a typical plot (Figure 7). The point where the slope changes, indicating adhesion failure, is located by drawing a line along the straight portion of the curve. The coordinates where the curve departs from the drawn line are determined and the adhesion value calculated. With this arrnagement several values are obtained for each specimens and results averaged. Data scatter between duplicate specimens using this method have been found to be ±0.3 in.lb/in2 on adhesion values between 2.0 and 3.0 in.lb/in^2.

2.2 MODIFICATION OF COATING SPECIMEN

2.2.1 Methods of Modification - Since it would be desirable to have the capability to evaluate specimens having normal coating thickness by the Blister Test Method an investigation to modify the coating technique was made. Some type of over coating materials was required which would prevent cohesive failure of the coating without affecting the adhesion surface energy density of the original coating. It was realized that the over-coating material would probably have a different modulus of elasticity which would render the results obtained "relative".

Materials investigated for over-coating the specimens were flexible potting materials such as polyurethane and silicones which could be applied by casting the necessary thickness. Sealant materials which might require injection into special molds to insure uniform coating thickness were also studied. Materials were evaluated



	P_{cr}	W_o	γ_a
1	70.0	.109	3.2
2	66.2	.118	3.3
3	60.3	.125	3.1
4	56.3	.133	3.1
			3.2 AVERAGE

FIGURE 7 Typical X-Y Recorder Plot

with and without reinforcement materials. The reinforcement materials investigated included cloths and films. Films were also investigated by bonding to the coated surface with different types of adhesives such as pressure sensitive. contact and time curing adhesives. Additional evaluations were made bonding fabric directly to the specimen.

2.2.2 Specimen Preparation - Eighty specimens were fabricated from aluminum alloy 7075-T6. All specimens were sheared to 3 inch by 3 inch from 1/4 inch sheet and a 1/4 inch hole was punched in the approximate center to serve as a pressurization port. The specimens were then anodized in the shop in accordance with LTV-CVA 9-14 "Process Specification, Anodic Treatment, Sulfuric Acid of Aluminum Alloys".

The specimens were placed on cardboard for spraying with double back tape in a random order. The pressurization ports were then covered with a 3/4 inch masking tape disk and coated with epoxy polyamide primer (Mil-P-23377). The coating was applied in a cross coat pattern to accumulate a thickness of approximately 3 mils. The specimens were then allowed to dry and cure.

2.2.3 Overcoating of Specimens - A total of 18 modification methods were selected for evaluation and specimen were prepared in triplicate. These modifications were as follows:

epoxy polyamide primer reinforced with glass cloth
epoxy polyamide primer reinforced with nylon cloth
epoxy polyamide primer reinforced with cotton cloth
spray epoxy adhesive reinforced with glass cloth
spray epoxy adhesive reinforced with nylon cloth
spray epoxy adhesive reinforced with cotton cloth
polyurethane finish reinforced with glass cloth
polyurethane finish reinforced with nylon cloth
polyurethane finish reinforced with nylon cloth
polyurethane finish reinforced with cotton cloth
silicone potting compound
silicone potting compound reinforced with nylon cloth
vinyl pressure sensitive tape
aluminum foil pressure sensitive tape
tedlar pressure sensitive tape
vinyl film adhesive bonded with spray epoxy
cotton cloth adhesive bonded with spray epoxy
polyurethane elastomer reinforced with nylon cloth

Some of the above applications were modified slightly by applying a fresh coat of epoxy polyamide primer prior to coating with polyurethane elastomer and polyurethane finish.

2.2.4 Specimen Conditioning - All specimens were allowed to cure a minimum of 10 days prior to placement in a 50% relative humidity for a minimum of 7 days prior to evaluation by the Blister Test method.

2.3 COMPARISON OF ALUMINUM ANODIZING PROCESSES

2.3.1 Introduction - To compare the anodizing processes, several companies were contacted and requested to participate in the study. Each was requested to anodize 18 specimens supplied to them following their current process and return the specimens for coating and comparative evaluation of adhesion by the Blister Test Method. At the time of contact each was informed that their specimens would be coated and evaluated at LTV-VSD along with samples supplied by other companies as well as VSD. They were also told that there would be no designation of what company supplied the specimens but that the data obtained would be made available to them. Seven companies were contacted and each agreed to participate in the study.

Since the production specifications varied as to the type of anodize being applied two aluminum alloys were selected for use in the evaluation, 2024 and 7075. To minimize variations in the coating systems, sufficient quantities of the coatings were obtained for the program to eliminate lot variances. Coatings used in the evaluation were:

epoxy-polyamide primer (Mil-P-23377)
epoxy-polyamide primer (Mil-P-23377) overcoated with polyurethane coating (Mil-C-81773)
epoxy-polyamide primer (Mil-P-23377) overcoated with polyurethane elastomer (LTV-VSD 207-9-427)

Two of the participating companies specifications required that the primer be applied within a specific time limit after anodizing. Each was supplied with sufficient primer from the lot of material obtained for the evaluation and paint masking disks to prime coat their specimens.

2.3.2 Specimen Fabrication - Specimens were fabricated from both 2024 and 7075 aluminum alloys. All specimens of the same alloy were sheared from the same sheet of approximately 1/4 inch sheet stock to a size of 3 inches by 3 inches. A 1/4 inch hole was punched in the center to serve as a pressurization port during Blister Test evaluation. The edges of the specimens were then sanded smooth and specimens, in sets of 18, were marked for identification. After vapor degreasing in 1, 1, 1 trichloroethane the specimens were shipped to the participating companies.

2.3.3 Anodizing Processing - Each participant was requested to anodize the specimens and return the specimens along with processing data for coating and evaluation. A set of each alloy was processed at LTV-VSD for inclusion in the program.

2.3.4 Coating of Specimens - Processed specimens were held in their original packaging until all had been received. The specimens were then placed on cardboard with double back tape so that 6 specimens from each source would be coated in random placement at the same time. The three groups of specimens thus divided were coated to obtain a minimum coating thickness of .030 inches by repeated spraying utilizing a cross coat pattern. One group of 54 specimens were coated with epoxy polyamide primer until adequate coating thickness was obtained for Blister Test evaluation. Another group of 54 specimens were coated with epoxy polyamide primer, including those that had been previously primed at the participating companies plant. The specimens were then overcoated repeatedly with white polyurethane finish to obtain desired thickness. The third group was primed in the same manner and overcoated with black polyurethane elastomer until an adequate coating for Blister Test evaluation was obtained.

All specimens were allowed to cure for 10 days after application of the final coating.

2.3.5 Conditioning of Specimens for Evaluation - Three specimens from each participant for each coating system were selected for 30 day alternate salt water immersion. These 81 specimens were placed in the alternate immersion apparatus containing 3.5% salt water maintained at a pH from 6.6 to 6.8. The system cycled so that each specimen was submerged for 10 minutes then exposed to air for 50 minutes. After the salt water conditioning the specimens were rinsed with distilled water, wiped dry and allowed to air dry for 48 hours.

The specimens were then placed in a 50 ± 5% relative humidity cabinet for seven days prior to evaluation by the Blister Test Method. The remaining 3 specimens representing each coating system, which had been held under laboratory conditions were also placed in the humidity cabinet at the same time. All specimens were evaluated using the Blister Test Method and the adhesion surface energy density calculated from the results.

2.4 SULFURIC ACID AND CHROMIC ACID ANODIZE STUDIES

2.4.1 Introduction - Greatly improved corrosion resistance is obtained when anodize can be used as the interface surface treatment on aluminum. The study examined the various parameters of the anodizing process and cleaning of the surface prior to coating.

The processing variables were selected to determine the parameters which affect adhesion. It was felt that the optimum adhesion with adequate corrosion protection would be obtained with an anodize coating which is thick enough for corrosion protection, yet is thin enough to prevent failure in the anodize. The anodize must also be porous enough or have the topography for good adhesion.

It has been found that many factors affect the chemical and physical make-up of an anodized surface. The precleaning procedures prior to anodizing have been found to affect the anodize bath in uniformity and in physical appearance (10). The current density and solution strength both affect the porosity and abrasion resistance of the anodize with much work having been done by the Aluminum Company of America (11). Sealing of the anodize surfaces affects both the porosity and the corrosion resistance of the anodize surface. Many investigations have attacked this problem but some controversy still exists (12) although many facts have been firmly established.

In addition to the above parameters most aircraft parts that are anodized see much handling and additional work prior to the painting operation. During this time span many materials can contaminate the surface so that adequate cleaning procedures are essential to obtaining good adhesion. Studies have been made of solvent cleaning of contaminated surfaces which indicate that this too is a complex problem (13). Other cleaning methods have also been investigated, but for practical purposes many must be eliminated when working with a completed aircraft.

2.4.2 Sulfuric Acid Anodizing Parameters - The processing parameters selected for evaluation included pre-cleaning, anodizing solution concentration, current density, anodizing time and sealing methods. This approach was to investigate the adhesion characteristics of the more porous and the more dense anodized surfaces of varying thickness and the effects of sealing these coatings.

Since most anodized parts become contaminted during subsequent operations in building aircraft, all specimens, except controls, were contaminated with Mil-H-5606, "Hydraulic Fluid, Petroleum Base, Aircraft, Missiles and Ordnance," prior to cleaning for painting. This allowed a more realistic evaluation as well as gave a basis for the evaluation of cleaning methods prior to paint applications.

The study outlined in Table I was accomplished in three parts which required 174 specimens. The specimens were fabricated from 7075-T6 bare aluminum alloy and marked for identification.

Part A - This part of the study was to compare precleaning effects as well as sealing methods on the adhesion characteristics of the anodize. In addition prepainting cleaning methods of contaminated surfaces were evaluated.

Two deoxidizer solutions were utilized following vapor degreasing and alkaline cleaning in accordance with LTV-CVA 9-14, "Sulfuric Acid Anodic Treatments of Aluminum and Aluminum Alloys." A 22% sulfuric acid solution containing 2% sodium dichromate was compared to a 7% nitric acid solution containing a proprietary product, for desmut deoxidizing at a concentration of 0.05 gallons per gallon. Both solutions were used at room temperature with time in the solution based on visual inspection of the processed specimen.

The anodizing was in accordance with the Specification LTV-CVA 9-14 with variations in the sealing process. Elimination of the sealing process was compared to two sealing processes presently in use which yield satisfactory results for paint adhesion. One method sealed the anodize for 8 minutes at 180°F in a 100 ppm solution of chromic acid maintained at approximately pH 3.0. The other method sealed the anodize for 5 minutes in boiling 5% potassium dichromate solution maintained at approximately pH 6 with chromic acid.

The specimens, except for 12 controls, were contaminated with hydraulic fluid and allowed to stay in the wetted condition for 48 hours, minimum. Three cleaning and processing variations were evaluated to determine effectiveness in removing contamination as measured by the adhesion characteristics. The first variation was a simple wipe with solvent, 1, 1, 1 trichloroethane which should show minimum effectiveness, especially on unsealed surfaces. The hydraulic fluid should not be completely removed which would yield low adhesion results. Another variation followed procedures which would be expected to remove contaminants. This included a solvent wipe with 1, 1, 1 trichloroethane followed by scrubbing using a nylon pad and mild detergent, repeating until after thoroughly flushing, the surface supports an unbroken water film.

The third method utilized the current practice at VSD which includes solvent wipe with 1, 1, 1 trichloroethane to remove excessive contamination followed by steam cleaning until the cleaned and flushed surface supports an unbroken water film. The cleaned surfaces were brush treated with a chemical conversion coating, prior to coating.

TABLE I

SULFURIC ACID ANODIZE OF 7075 ALUMINUM ALLOY*

PART	Pre-Cleaning	Solution Concentration	Current Density	Anodize Time	Sealing	Cleaning Befor Coating	Coating Material	Number of Specimens
A	2 variations	Specification	Spec.	Spec.	3 variations	Uncontaminated +3 variations	Epoxy Polyamide Primer	48
B	Specification	3 variations	Spec.	3 variations	3 variations	Specification+	Epoxy Polyamide Primer	54
C	Specification	Specification	4 variations	3 variations	3 variations	Specification+	Epoxy Polyamide Primer	72

* LTV Specification CVA 9-14, Sulfuric Acid Anodic Treatment of Aluminum and Aluminum Alloys.

\+ LTV Specification 208-9-222, Finishing Exterior of A-7A, B, E and TA-7C Aircraft.

Part B - This task compared the porosity variations caused by the concentration of sulfuric acid anodize and thickness variations caused by processing time in the solutions on adhesion. The three anodizing solutions were 25%, 15%, and 7% sulfuric acid with anodizing times of 5, 10, and 15 minutes following current density in accordance with LTV-CVA 9-14.

The three sealing variations on these specimens were the same as in Part A.. All specimens were contaminated with hydraulic fluid and allowed to stand 48 hours minimum, prior to cleaning. Cleaning followed normal procedures at VSD which include solvent wipe, steam cleaning and prepaint treatment with a chemical conversion coating.

Part C - This task varied the current density which affects the porosity and abrasive resistance of the anodized product. The processing time was also varied to obtain different coating thicknesses. The anodizing solution was 10% sulfuric acid operated at room temperature with current densities of 9, 12, 15, and 18 amperes per square foot. Time of anodizing was varied to include 5, 10, and 15 minutes for each current density variation.

The three sealing variations on these specimens were the same as in Part A and contamination and cleaning procedures prior to painting as in Part B.

2.4.3 Chromic Acid Anodizing Parameters - The processing parameters selected for evaluation included precleaning, anodize solution concentration, current density, anodizing time and sealing methods. This approach was to investigate the adhesion characteristics of the more porous and the more dense anodized surfaces of varying thickness and the effects of sealing of these coatings.

Since most anodized parts become contaminated during subsequent operations in building aircraft, all specimens, except controls, were contaminated with Mil-H-5606 hydraulic fluid prior to cleaning for painting. This allowed for a more realistic evaluation as well as giving a basis for the evaluation of cleaning methods prior to paint application.

The study outlined in Table II was accomplished in three parts which required 174 specimens. The specimens were fabricated from 2024-T3 bare aluminum alloy and marked for identification.

Part A - This study was to compare precleaning effects as well as sealing methods on the adhesion characteristics of the anodize. In addition, cleaning methods for contaminated surfaces were investigated.

Two cleaning procedures were utilized following vapor degreasing of the specimens. Both methods utilize proprietary compounds and are detailed in LTV-CVA 9-4, "Process Specification, Chromic Acid Anodic Treatment of Aluminum and Aluminum Alloys." "Type A" is normally used for general corrosion and "Type B" as an alternate method for adhesive bonding when specified.

The anodizing was in accordance with LTV-CVA 9-4, Type B, which utilizes 5.0 to 5.1 oz chromic acid per gallon at 95°F ± 3 at 22 ± 2 volts for 25 minutes after reaching operating voltage. Elimination of the sealing process was compared to two sealing processes presently in use which yield satisfactory results for paint adhesion. One method sealed the anodize for 15 minutes at 195°F in a 5 percent solution of sodium dichromate maintained at a pH 5 with chromic acid. The other method sealed the anodize for 15 minutes in deionized water.

TABLE II

CHROMIC ACID ANODIZE OF 2024 ALUMINUM ALLOY *

PART	Pre-Cleaning	Solution Concentration	Current Density	Anodize Time	Sealing	Cleaning Be-for Coating	Coating Material	No. of Specimens
A	2 Variations	Specification	Spec.	Spec	3 Variations	Uncontaminated + 3 Variations	Epoxy-Poly-amide	48
B	Specification	3 Variations	Spec.	3 Vari-ations	3 Variations	Specification +	Epoxy Poly-amide	54
C	Specification	Specification	4 Vari-ations	4 Vari-ations	3 Variations	Specification +	Epoxy Poly-amide	72

* Specification CVA 9-4, Chromic Acid Anodic Treatment of Aluminum and Aluminum Alloys.

\+ LTV Specification 208-9-222, Finishing Exterior of A-7A, B, E and TA-7C Aircraft.

The specimens, except for 12 controls, were contaminated with hydraulic fluid and allowed to stay in the wetted condition for 48 hours, minimum. Three cleaning and processing variations were evaluated to determine effectiveness in removing contamination as measured by adhesion characteristics. The first variation was a simple wipe with solvent, 1, 1, 1 trichloroethane, which was expected to show minimum effectiveness, especially on unsealed surfaces. This cleaning method should not remove hydraulic fluid which had soaked into the anodize and thus yield low adhesion results.

Another variation followed procedures which would be expected to remove contaminants. This method included a solvent wipe, 1, 1, 1 trichloroethane followed by scrubbing using an abrasive nylon pad and mild detergent, repeating washing procedure until after thoroughly flushing, the surface supports an unbroken water film.

The third method utilized current practice at VSD which includes solvent wipe with 1, 1, 1 trichloroethane to remove excessive contamination followed by steam cleaning until cleaned surface supports an unbroken water film. The cleaned surfaces were brush treated with chemical conversion coating material prior to coating.

Part B - This task compared the porosity variations caused by the concentration of chromic acid anodize solution and thickness variations caused by processing time in the solution on adhesion. The three anodizing solutions were 2 oz/gal, 8 oz/gal, and 14 oz/gal with anodizing times of 10, 30, and 60 minutes following current density in accordance with LTV-CVA 9-4.

The three sealing variations on these specimens were the same as in Part A, except the distilled water seal was replaced by 100 ppm chromic acid solution at 180°F for 10 minutes. All specimens were contaminated with hydraulic fluid and allowed to stand 48 hours, minimum, prior to cleaning. Cleaning followed normal procedures at VSD which include solvent wipe, steam cleaning and pre-paint treatment with a chemical conversion coating material, the third method in Part A.

Part C - This task varied the current density which affects the porosity and abrasive resistance of the anodized product. The processing time was also varied to obtain different coating thicknesses. The anodizing solution was 5 oz/gal chromic acid with voltages of 6, 10, 30, 40. Time of anodizing was varied to include 10, 30 and 60 minutes for each voltage variation.

The three sealing variations on these specimens was the same as in Part B and contamination and cleaning procedures prior to painting as in Part B.

2.4.4 Specimen Preparation and Coating - The specimens which had previously been fabricated and marked for identification were anodized using a model SD 760 Selectrodizer manufactured by Selectrons Ltd., New York, New York. Each variation was processed in duplicate and held so that all sulfuric acid anodized specimens were coated at the same time and all chromic acid anodized specimens were coated together.

Twelve specimens of each anodize were held in a clean "as anodized" condition to serve as controls. The remaining specimens were contaminated by dipping into the hydraulic fluid then laying flat, surface to be coated up, on gause pads. This approach was found to keep the surface wet with the hydraulic fluid. After 48 hours the excess fluid was wiped from the specimen and cleaned in accordance with the plan.

All specimens were then mounted on cardboard panels in a random order for coating. The pressurization ports were covered with paint masking disks (3/4 inch diameter) and epoxy polyamide primer (Mil-P-23377) applied by spraying in a cross coat pattern. Repeated coats were applied until a minimum of .030 inch film was obtained. The specimens were then removed from the panels and allowed to cure.

2.4.5 Specimen Conditioning - After curing for 10 days the specimens were placed in the alternate salt water immersion apparatus for 30 days. The parts were immersed in a 3.5% salt water solution maintained at pH from 6.6 to 6.8 for 10 minutes. The specimen were then allowed to dry for 50 minutes enclosed in the apparatus in a relative humidity of about 60 percent.

The specimens were then removed, rinsed with distilled water, the excess wiped off and allowed to dry for 48 hours. At this time the specimens were placed in a 50 ± 5% relative humidity cabinet for a minimum of 7 days prior to evaluation by the Blister Test method.

2.5 COATING OF EPOXY POLYAMIDE PRIMED SURFACES

2.5.1 Introduction - The time and method of application of the top coatings over primed surfaces has been a problem for many years. In production many items are primed after fabrication or subassembly and do not receive the top coat until much later. The lack of bond between the top coat and primer has, at times caused pealing of the top coat.

Many approaches have been used to overcome this problem some as simple as a solvent wipe to make the primer "tacky". Others apply a fresh coat of primer or use other adhesion improvement approaches. The type of coating of course plays an important role in the adhesion characteristic. The problem for this study was limited to the presently used primer and two presently used top coating materials.

2.5.2 Polyurethane Finish Coating Parameters - The processing parameters selected for evaluation included the effect of cleaning on the primer adhesion, primer cure time and thinner concentration of the enamel. In addition these parameters were evaluated on both chromic acid and sulfuric acid anodized surfaces.

The study outlined in Tasks A and B of Table III required 120 specimens of 2024 aluminum alloy. The specimens were anodized following LTV-CVA specification 9-14, sulfuric acid anodize.

Twelve specimens of each anodize were held in the as anodized condition and the remaining 48 were contaminated with Mil-H-5606, "Hydraulic Fluid, Petroleum Base, Aircraft Missiles and Ordnance," and let stand 48 hours.

Before applying the epoxy polyamide primer the 48 specimens representing each anodize were divided into four sets for cleaning. One set was solvent wiped with 1, 1, 1 trichloroethane after excess fluid had been wiped from the surface. Another set was cleaned by solvent wipe with 1, 1, 1 trichloroethane, detergent washed scrubbing with a nylon pad and rinsed with distilled water. The other two methods consisted of solvent wipe with 1, 1, 1 trichloroethane, steam clean and rinsed with distilled water. One of the sets was then chemical conversion coated by the brush method.

TABLE III

COATINGS ON EPOXY POLYAMIDE PRIMED ANODIZED ALUMINUM SURFACES

Task	Anodize Type *	Coating	Time Between Primer Application & Coating	Thinner (Type & Percentage)	Cleaning Prior to Coating	Number of Specimens
A	Sulfuric Acid Anodized 7075 Aluminum	Polyurethane Coating (Mil-C-81773)	2 variations	3 variations	None	12
			2 variations	3 variations	4 variations	48
B	Chromic Acid Anodized 2024 Aluminum	Polyurethane Coating Mil-C-81773	2 variations	3 variations	None	12
			2 variations	3 variations	4 variations	48
C	Sulfuric Acid Anodized 7075 Aluminum	Polyurethane Elastomer LTV-VSD-207-9-427	2 variations	3 variations	None	12
			2 variations	3 variations	4 variations	48
D	Chromic Acid Anodized 2024 Aluminum	Polyurethane Elastomer LTV-VSD 207-9-427	2 variations	3 variations	None	12
			2 variations	3 variations	4 variations	48

* Anodize processed in accordance with LTV specifications CVA 9-14 and 9-4.

The specimens were then mounted on cardboard with double back tape so that each board contained duplicate specimens representing each cleaning process or controls. The pressurization port was then covered with a masking tape disk and epoxy polyamide primer applied by spraying using the cross stroke pattern to obtain a coating of about .001 inches.

Half of the specimens were then painted with a top coat of polyurethane finish within one hour of the primer coating. The remaining specimens were held 30 days and then coated.

The three thinner concentration used on the primed specimens were as mixed, as mixed plus 10% Mil-T-81772 thinner and as mixed plus 20% Mil-T-81772 thinner. Additional coats were applied until a total coating thickness in excess of .030 inches was obtained.

2.5.3 Polyurethane Elastomer Coating Parameters - The processing parameters selected for evaluation were the same as in 2.5.2 and outlined under Tasks C and D in Table III.

All specimens were processed at the same time in a like manner with the thinner dilution being the only difference.

The polyurethane elastomer was applied in the as mixed conditioned, diluted with 5% methylisobutyl ketone and diluted with 5% cyclohexanone.

2.5.4 Specimen Conditioning - All specimens were conditioned for 20 days in the alternate salt water immersion apparatus after curing. The specimens were then rinsed in distilled water allowed to air dry and placed in a 50% relative humidity cabinet for 7 days minimum.

2.5.5 Evaluation of Specimens - The specimens were evaluated by the Blister Test Method as soon as possible after the 7 days at 50% ± 5% relative humidity. This held the time from applying top coating to evaluation relatively the same to prevent any deviations caused by time elapsed difference.

The method of evaluation of the elastomeric coated specimens was modified slightly in an attempt to obtain more realistic values for the elastomeric coatings. It had been found in previous work on the program that the elastomer stretched which caused an increased adhesion surface energy density when calculated. The value increased as the blister size increased.

To overcome some of this stretching effect care was taken to lift the paint masking disk to form the built in flaw then increasing the diameter of the blister beyond 3/4 inches. The Blister Test measurement was then made on elastomer with a minimum blister size. This allowed the paint masking disk to serve as reinforcement and minimize stretching.

2.6 PHOSPHOMOLYBDIC ACID SPOT TEST

2.6.1 Introduction - Corrosion resistance of an anodized surface is of prime interest along with the adhesion characteristics. The present method is time consuming as the method requires many days in a salt spray endurance test to determine a satisfactory coating. A more rapid method would be desirable and Boeing Vertol Company (14) had developed a quick test which showed merit. The test is a basic spot test for copper as detailed by F. Fiegel (15) which produces a "molybdeum blue" when the phosphomolybdates are reduced by the copper ion. The amount of copper present determines the deepness of the blue color. The work had been done on 2024 aluminum alloy which contains from 3.8% to 4.9% copper so the measurement of copper on the surface of the anodize surface was felt to be indicative of the effectiveness of the anodize coating.

Boeings evaluations indicated that a positive reaction; i.e., the development of a blue color, occurred on all specimens of chromic acid anodized 2024 aluminum alloy whose salt spray endurance was less than 12 days. No reaction occurred on specimens which lasted 14 days or longer in the salt spray. Specimens in the 12-14 day endurance range were marginal and could either fail or pass the spot test.

The test method consisted of dipping an anodized specimen into a 10% solution of phosphomolybdic acid containing a small amount of wetting agent. The specimen was then placed on a paper towel and allowed to stand for 15 minutes. The specimens were then examined for evidence of a blue color which would indicate failure. Any edge effect was disregarded.

2.6.2 Spot Test Evaluation - An evaluation of the spot test method was made on anodized specimens furnished by Boeing, specimens of Boeing furnished material anodized at LTV-VSD and LTV material processed in house.

A total of 8 anodized specimens were received from Boeing representing specimens which had been evaluated by phosphomolybdic acid and salt spray endurance in their laboratory and the results which they obtained. These specimens were each sheared into 3 pieces for evaluation. One specimen for evaluation with the phosphomolybdic acid spot test, one for salt spray evaluation in VSD Quality Control Laboratory and one for evaluation in VSD Engineering Materials Laboratory.

The Boeing unanodized material received consisted of 6 box-skins of 2024-T81 aluminum alloy measuring 12" by 12". These were sheared into 4 specimens 3" by 12" for anodizing. Two sets of four specimens were anodized per LTV-CVA 9-4, Type B "Chromic Acid Anodic Treatment". The remaining two sets were anodized per LTV-CVA 9-4, Type A, which is equivalent to Boeing Vertol Chromic Acid Anodizing Process per D8-0097 except for the seal solution. These specimens were sealed in 100 ppm chromic acid solution as called for in D8-0097 in the VSD Engineering Materials Laboratory.

One specimen from each of the 6 sets was evaluated by the phosphomolybdic acid spot test, one by salt spray in the Quality Laboratory, one by salt spray in the Engineering Materials Laboratory and the remaining specimen was utilized for determination of anodic coating weight.

From LTV-VSD material 6 sets of 2024 aluminum alloy specimens were prepared for processing and evaluation along with the box skin material. Preparation, anodizing, sealing and evaluation was the same as for the Boeing supplied material.

In addition 4 sets of 4 specimens each were prepared from 7075 and 6061 aluminum alloys for sulfuric acid anodize evaluation. All specimens were processed per LTV-CVA 9-14 "Anodic Treatment, Sulfuric Acid", except that two sets of each alloy were sealed in 100 ppm chromic acid solution. The evaluation of the specimens followed the plan outlined for the box skin specimens.

3.0 RESULTS

3.1 RESULTS OF MODIFICATION OF SPECIMEN COATING TECHNIQUE

The investigation to select a method of overcoating specimens so that coatings of normal thickness could be evaluated was completed without producing a satisfactory method. A much greater understanding of multilayer coatings resulted from the study which substantiated the continued use of the specimen coating technique previously developed.

All specimens overcoated with unreinforced potting materials ruptured through the base coat of epoxy polyamide primer. The failure then travelled along the interface of the coating and the overcoating material. No adhesion values were obtained from these specimens.

All specimens overcoated with reinforcing fabrics ruptured through the epoxy polyamide primer and overcoating material to a new failure mode between the overcoating material and the reinforcing material. This failure mode was also found when additional epoxy polyamide primer was utilized to contain the reinforcing material. No adhesion values were obtained from any of the reinforced top coat modifications.

Modification using films did not yield any adhesion measurements as the primer coating was ruptured. In these modifications some films pulled loose from the primer as the primer ruptured and the failure mode travelled to the primer adhesive interface. In others the film itself would rupture. No adhesion values were obtained from any of the film modifications.

Work on the modification investigation was terminated as time scheduled for the task had expired and none of the methods had yielded any positive results.

3.2 RESULTS OF ALUMINUM ANODIZING PROCESSES COMPARISON

3.2.1 Comparisons of Processes - Table IV shows the results obtained from the Blister Test evaluation. Each set of specimens reported was anodized by a different process but were coated in a like manner at the same time with the same coating material. The only coating variation was found in Sets 3 and 4 which were primer coated shortly after anodizing at the participating company's facility. Primer from the same can was sent along with the specimens so that the material was the same. These specimens were then overcoated along with the other specimens after a time lapse in excess of 30 days.

The aluminum alloy from which the specimen was prepared and the processing details are also listed in Table IV. All the processes are anodic type treatments except for set number 4.

3.2.2 Epoxy Polyamide Primer - The results are shown for each specimen both the "as prepared" as well as the alternate salt water immersion condition. Each value listed is an average of three or more Blister Test evaluations made on the same specimen.

TABLE IV, ADHESION CHARACTERISTICS OF SOME ANODIZING PROCESSES

COATING	SPECIMEN CONDITION	SET NO. 1 CHROMIC ACID ANODIZE ON 7075-T6 γ_a	SET NO. 2 CHROMIC ACID ANODIZE ON 7075-T6 γ_a	SET NO. 3 PHOSPHORIC ACID ANODIZE ON 7075-T6 γ_a	SET NO. 4 WELDBOND ON 7075-T6 γ_a	SET NO. 5 SULFURIC ACID ANODIZE ON 7075-T6 γ_a	SET NO. 6 SULFURIC ACID ANODIZE ON 7075-T6 γ_a	SET NO. 7 CHROMIC ACID ANODIZE ON 2024-T3 γ_a	SET NO. 8 CHROMIC ACID ANODIZE ON 2024-T3 γ_a	SET NO. 9 CHROMIC ACID ANODIZE ON 2024-T3 γ_a
Epoxy-Polyamide Primer	As Prepared	2.0 2.0 2.6	2.3 2.0 2.7	3.5 3.8 3.5	3.4 2.8 3.5	3.4 3.6 3.0	2.6 2.6 2.2	3.0 3.1 2.2	1.1 1.4 1.8	3.4 2.9 3.4
	After 30 Day Alternate Salt Water Immersion	2.2 2.5 1.9	2.0 3.7 2.8	2.0 1.9 2.5	2.0 2.4 1.7	1.8 2.2 2.3	2.2 1.6 2.6	1.8 1.8 2.5	1.8 2.0 2.4	2.2 1.8 2.4
Polyurethane Finish Over Epoxy-Polyamide Primer	As Prepared	2.4 2.5 2.1	1.6 1.8 1.9	2.4 2.3 2.7	1.2 2.1 1.5	1.9 2.3 2.3	1.8 2.3 1.8	1.8 1.8 2.0	1.4 2.2 1.9	2.6 2.9 2.5
	After 30 Day Alternate Salt Water Immersion	2.4 2.2 2.0	2.0 1.9 1.7	2.0 1.9 2.5	2.0 2.0 2.0	1.7 2.0 1.7	2.1 2.3 2.1	2.1 2.1 2.3	2.2 1.7 2.0	2.5 2.3 2.4
Polyurethane Elastomer Over Epoxy-Polyamide Primer	As Prepared	7.3 7.1 6.7	4.5 6.4 6.0	4.8 4.4 6.5	3.8 4.2 4.1	7.4 7.3 7.7	7.0 7.3 7.7	6.1 7.1 7.3	7.4 7.0 7.4	4.1 7.4 6.3
	After 30 Day Alternate Salt Water Immersion	6.8 7.1 7.4	6.3 6.5 6.7	7.0 5.7 6.6	7.5 7.4 7.5	6.8 Lost + 7.6	7.3 7.2 7.4	6.8 6.9 6.9	7.2 7.4 7.1	6.3 6.8 6.6
Alkaline Cleaning		Alkaline Clean 10-15 min at 145°-155°F	Alkaline Clean 10-15 min at 160-180°F	Alkaline Clean 10 min at 140°F	Alkaline Clean 10-15 min at 155°F	Alkaline Clean 5 Min - Alkaline Etch - 2 min.	Alkaline Clean 5 min at 150°F	Alkaline Clean 5-10 min at 160°F	Alkaline Clean 8-12 min at 130°F	Alkaline Clean 5 min at 165°F
Deoxidizer (Desmut)		10% chromic acid 5% nitric acid 1% hydrofloric 10-15 min RT	Deoxidizer 3-5 min at 145±10°F	Deoxidizer 15 minutes Room Temp	FPL Etch sulfuric/ sodium dichromate	50% nitric acid 3 min Deoxidizer 4 min.	5% Deoxidizer 10% nitric acid 1-20 min.	25% sulfuric 2-3% sodium dichromate 10 min at 150°F	50% nitric acid trace hydrofluoric 1-5 min RT'	19% Deoxidizer 8% nitric acid 1-5 min Room Temp
Anodize		5% chromic acid 22 volt dc 35-40 min at 95°F	Chromic acid 40 volts 45 min 90-95°F	11-16oz/gal phosphoric 10 volts, 22 min at 66°F	Not an anodize process	9.5% sulfuric acid 12 amps - 30 min. at 70°F	10% sulfuric acid 16 amps 20 min at 70°F	6-10% chromic acid - 40 volts 30 min at 95°F	6.6-1.3g/gal chromic acid 40 volt-40 min at 90-95°F	4 oz/gal chromic acid 40volt-40 min at 90-96°F
Sealing		Deionized Water pH5-7 15 min. at 160-190°F	5% sodium dichromate pH5, 15 min at 190-200°F	Water, 150 ppm max 15 min Room Temp	5-6.5% Na dichromate 90 min at 210°F	5.2% sodium dichromate 15 min at 208°F	5-6% potassium dichromate 20-30 min at 200°F	100 ppm chromic acid - 7-9 min at 180°F	Demineralized Water 4-6 min	Refined Water pH-6 with chromic acid min at 165°F
Special Precoating Requirements		May be oven dried, 225°F maximum	Oven dry at 150°F Max 212°F	Oven Dry 140°F	None	Chemical Drier Solution	May oven dry 210°F maximum	Dry without rinse, 160°F maximum	Not Prepaint Treatment	May oven dry 210°F max.
Primer Primer Coating		Prime within 4 hours or solvent wipe	Primed within 2 Hrs.	Primed in 3 Hrs - Max 16 Hrs	Coat within 48 Hrs	None	As soon as practical	None, clean if contaminated	Not Specified	As soon as practical

* Results Relative Due to Being An Elastic Material γ_a = Adhesion Surface Energy Density (in-lb/in^2) + Specimen Lost in Anodizing Bath

It will be noted that although some variation exists between specimens most of the results are in agreement. Only one set (Number 8) in the "as prepared" specimens show excessive spread. After conditioning for 30 days by alternate salt water immersion three sets exhibit excessive spread, sets numbers 2, 5, and 7.

The effect of alternate salt water immersion can also be noted in some of the sets as the adhesion value changes in excess of the data scatter expected.

Polyurethane Finish over Epoxy Polyamide Primer - The results are shown for each specimen both in the "as prepared" as well as the alternate salt water immersion condition. Each value listed is an average of three or more Blister Test evaluations made on the same specimen. The results presented shows very little data scatter between specimens of the same set except for one specimen in sets 4 and 8 in the "as prepared" condition.

3.2.4 Polyurethane Elastomer - The results are shown for each specimen both in the "as prepared" as well as the salt water alternate immersion condition. Each value listed is an average of three or more Blister Test evaluations made on the same specimen. The values obtained are only relative since the material is elastomeric. This allows the membrane in the blister to stretch thus increasing the blister height to yield higher values for the adhesion surface energy density. The results obtained are a little more erratic, especially in the as prepared condition. Here again the adhesion values between sets are very slight although the surface treatments vary considerably.

3.3 RESULTS OF SULFURIC ACID ANODIZE STUDIES

3.3.1 Part A - Table V presents the results obtained when the effects of pre-cleaning and sealing methods on adhesion characteristics were evaluated. In addition variation of cleaning methods on these contaminated surfaces were evaluated for affects on adhesion.

All specimens were processed in a like manner except as noted in the table. The aluminum alloy was 7075-T6 and specimens were coated with epoxy polyamide primer at the same time. Evaluation of the specimens were made after 30 day alternate salt water immersion treatment and 7 days conditioning at 50 ± 5% relative humidity. The tests were accomplished using the Blister Test method in as short a time period as possible to minimize aging differences. All data shown are the average of three or more evaluations on the same specimen.

The two pre-cleaning methods did not result in appreciable difference in the adhesion characteristics of the anodized surface and epoxy polyamide primer. The desmut method of LTV-CVA 9-14 yielded slightly higher values, discounting specimen 7A10, on the non-contaminated control specimens.

Sealing of uncontaminated specimens failed to show a significant difference in adhesion values with all results being equal within data scatter range. The sealing effects become more apparent when the contaminated specimens which received the best cleaning method were taken into consideration with no seal being superior to the sealed surfaces.

A review of the results of cleaning methods clearly indicates that the solvent wipe followed by steam cleaning and chemical conversion method is superior

TABLE V

STUDY OF EFFECTS OF PRECLEANING, SEALING AND PRECOATING CLEANING OF SULFURIC ACID ANODIZE ON ADHESION TASK A BLISTER TEST RESULTS

SPECIMEN NUMBER	PRECLEAN	ANODIZE	SEALING SOLUTION	CONTAMINATION	PRE COATING CLEANING	γ_a*
7A1	Process Specification LTV-CVA 9-14	Process Specification LTV-CVA 9-14	No Seal	None	None	3.1
7A2						2.9
7A3				Mil-H-5606 Hydraulic Fluid	Solvent Wipe +	1.3
7A4						0.5
7A5				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean Chemical Conversion Coating	3.4
7A6						3.2
7A7				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.1
7A8						1.8
7A9			100 ppm chromic acid 8 Minutes at 180°F	None	None	3.0
7A10						1.4
7A11				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	0.9
7A12						0.6
7A13				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean Chemical Conversion Coating	3.1
7A14						2.0
7A15				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.1
7A16						2.7
7A17			5% potassium dichromate 5 minutes at 212°F	None	None	2.6
7A18						3.4
7A19				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	1.9
7A20						1.1
7A21				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean Chemical Conversion Coating	3.3
7A22						2.9
7A23				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.3
7A24						2.8
7A25	Process Specification LTV-CVA 9-14 Except Sulfuric Acid/ Sodium Dichromate Desmut		No Seal	None	None	3.0
7A26						2.5
7A27				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	0.6
7A28						0.8
7A29				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean Chemical Conversion Coating	3.7
7A30						2.8
7A31				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.9
7A32						1.1
7A33			100 ppm chromic acid 8 minutes at 180°F	None	None	2.4
7A34						2.7
7A35				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	0.9
7A36						0.6
7A37				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean Chemical Conversion Coating	2.6
7A38						1.9
7A39				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.3
7A40						2.9
7A41			5% potassium dichromate 5 minutes at 2[illegible]°F	None	None	2.7
7A42						2.6
7A43				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	0.6
7A44						0.5
7A45				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean Chemical Conversion Coating	2.1
7A46						2.9
7A47				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	2.1
7A48						2.5

* Adhesion surface energy density (in-lb/in^2)

\+ MIL-T-81533, 1,1,1 Trichloroethane used for solvent wipe.

to the other two methods. The adhesion values obtained using a solvent wipe method were very low in all instances showing very little difference which could be related to the seal.

3.3.2 Part B - Table VI presents the results obtained which evaluated the effects of porosity variations caused by anodizing solution strength and thickness variations caused by anodizing time on the adhesion characteristics.

All specimens were processed in a like manner except as noted in the table. Specimens were contaminated and cleaned by solvent wipe with 1,1,1, trichloroethane and steam cleaning followed by chemical conversion coating after anodizing just prior to coating. The aluminum alloy was 7075-T6 and the specimens were coated with epoxy polyamide primer at the same time.

The evaluations with the Blister Test Apparatus were conducted to prevent age differences after being subjected to hostile environment and conditioned as in Part A. The effect of sulfuric acid concentration failed to produce a very significant difference in the adhesion characteristics when all processing times and sealing methods are considered. The 7% concentration of acid gave slightly higher values but within the data scatter range.

Sealing methods, upon over all averaging, did not yield significant differences in adhesion characteristics.

The differences found in this part of the investigation failed to produce significant differences in adhesion values which could be correlated to the parameters.

3.3.3 Part C - Table VII presents the results obtained when the effect of current density and anodizing time on the adhesion characteristics were evaluated.

All specimens were processed in a like manner except as noted in the table. After anodizing all specimens were contaminated and then cleaned by solvent wipe and steam cleaning. Prior to coating, specimens received a chemical conversion coating treatment. The aluminum alloy was 7075-T6 and the specimens were coated with epoxy polyamide primer at the same time.

Evaluation of the specimens with the Blister Test Apparatus were conducted to minimize aging effects. All specimens were subjected to 30 day alternate salt water immersion treatment and 7 day 50% ±5% relative humidity conditioning prior to testing

The effect of current density was be noted mainly in the 15 minute anodizing time range. Here the 12, 15 and 18 amp current density yield higher adhesion values with both the no seal and the 100 ppm chromic acid seal. When the results obtained at 10 minutes are reviewed 15 and 18 amp current density yielded the higher adhesion values. At 5 minutes anodizing time the results were scattered but the 18 amp current appears to be best based on all three seal methods. From this data 15 to 18 amp current density appeared to yield the best adhesion characteristics.

Time of anodizing which controls the anodize thickness for each current density showed significant differences in adhesion values. The 18 amp current density appeared with the limited testing to peak out at 10 minutes. The 12 and 15 amp current density specimens yielded higher adhesion values when anodizing time was 15 minutes. The 9 amp current density failed to reach the high level of adhesion values obtained with the other current density variations.

TABLE VI

STUFY OF EFFECT OF ANODIZE SOLUTION CONCENTRATION, TIME AND SEALING OF SULFURIC ACID ANODIZE ON ADHESION TASK B BLISTER TEST RESULTS

SPECIMEN NUMBER	PRECLEAN	ANODIZE	ANODIZING TIME	SEALING CONDITION	γ_a*
7B1	Process Specification LTV-CVA 9-14	25% v sulfuric acid 16 volts dc at 70°F	5 Minutes	No Seal	2.3
7B2					3.2
7B3				15 minutes at 195°F 5% sodium dichromate	1.8
7B4					2.7
7B5				10 minutes at 180°F 100 ppm chromic acid	1.9
7B6					2.0
7B7			10 Minutes	No Seal	2.7
7B8					1.8
7B9				15 minutes at 195°F 5% sodium dichromate	1.7
7B10					2.7
7B11				10 minutes at 180°F 100 ppm chromic acid	2.6
7B12					2.5
7B13			15 Minutes	No Seal	3.1
7B14					3.4
7B15				15 minutes at 195°F 5% sodium dichromate	2.5
7B16					3.1
7B17				10 minutes at 180°F 100 ppm chromic acid	1.4
7B18					1.6
7B19		15% v sulfuric acid 16 volts dc at 70°F	5 Minutes	No Seal	2.3
7B20					1.7
7B21				15 minutes at 195°F 5% sodium dichromate	3.1
7B22					2.6
7B23				10 minutes at 180°F 100 ppm chromic acid	1.9
7B24					1.6
7B25			10 Minutes	No Seal	2.1
7B26					2.9
7B27				15 minutes at 195°F 5% sodium dichromate	3.0
7B28					2.4
7B29				10 minutes at 180°F 100 ppm chromic acid	2.2
7B30					3.1
7B31			15 minutes	No Seal	2.8
7B32					2.9
7B33				15 minutes at 195°F 5% sodium dichromate	2.7
7B34					2.8
7B35				10 minutes at 180°F 100 ppm chromic acid	2.8
7B36					2.8
7B37		7% v sulfuric acid 16 volts dc at 70°F	5 Minutes	No Seal	2.3
7B38					1.7
7B39				15 minutes at 195°F 5% sodium dichromate	2.8
7B40					2.4
7B41				10 minutes at 180°F 100 ppm chromic acid	2.4
7B42					2.5
7B43			10 minutes	No Seal	3.1
7B44					3.2
7B45				15 minutes at 195°F 5% sodium dichromate	2.8
7B46					2.9
7B47				10 minutes at 180°F 100 ppm chromic acid	2.8
7B48					Void
7B49			15 Minutes	No Seal	3.5
7B50					1.7
7B51				15 minutes at 195°F 5% sodium dichromate	2.8
7B52					2.2
7B53				10 minutes at 180°F 100 ppm chromic acid	3.4
7B54					3.1

* Adhesion surface energy density (in-lbs/in^2)

TABLE VII
STUDY OF EFFECT OF CURRENT DENSITY, TIME AND SEALING OF SULFURIC ACID ANODIZE ON ADHESION
TASK C BLISTER TEST RESULTS

SPECIMEN NUMBER	PRECLEAN	ANODIZE	ANODIZING TIME	SEALING CONDITION	γ_a^*
7C1	Process Specification LTV-CVA 9-14	Process Specification LTV-CVA 9-14 Except 9 volts DC	5 Minutes	No Seal	2.0
7C2					3.4
7C3				100 ppm chromic acid 10 minutes at 180°F	1.6
7C4					2.0
7C5				5% sodium dichromate 15 minutes at 195°F	1.5
7C6					2.3
7C7			10 Minutes	No Seal	2.3
7C8					[illegible]
7C9				100 ppm chromic acid 10 minutes at 180°F	[illegible]
7C10					2.4
7C11				5% sodium dichromate 15 minutes at 195°F	2.5
7C12					1.9
7C13			15 minutes	No Seal	2.6
7C14					2.3
7C15				100 ppm chromic acid 10 minutes at 180°F	3.6
7C16					2.8
7C17				5% sodium dichromate 15 minutes at 195°F	2.4
7C18					2.1
7C19		Process Specification LTV-CVA 9-14 Except 12 Volts DC	5 minutes	No Seal	1.5
7C20					2.7
7C21				100 ppm chromic acid 10 minutes at 180°F	2.4
7C22					2.6
7C23				5% sodium dichromate 15 minutes at 195°F	1.8
7C24					.9
7C25			10 minutes	No Seal	1.8
7C26					2.4
7C27				100 ppm chromic acid 10 minutes at 180°F	2.9
7C28					2.4
7C29				5% sodium dichromate 15 minutes at 195°F	2.1
7C30					2.6
7C31			15 minutes	No Seal	2.9
7C32					3.5
7C33				100 ppm chromic acid 10 minutes at 180°F	2.9
7C34					3.3
7C35				5% sodium dichromate 15 minutest at 195°F	2.4
7C36					1.8
7C37		Process Specification LTV-CVA 9-14 Except 15 Volts DC	5 minutes	No Seal	2.5
7C38					1.4
7C39				100 ppm chromic acid	3.0
7C40					1.7
7C41				5% sodium dichromate 15 minutes at 195°F	2.2
7C42					2.5
7C43			10 minutes	No Seal	3.1
7C44					2.2
7C45				100 ppm chromic acid 10 minutes at 180°F	3.2
7C46					[illegible]
7C47				5% sodium dichromate 15 minutes at 195°F	1.7
7C48					1.9
7C49			15 minutes	No Seal	3.1
7C50					3.0
7C51				100 ppm chromic acid 10 minutes at 180°F	[illegible]
7C52					3.3
7C53				5% sodium dichromate 15 minutes at 195°F	[illegible]
7C54					2.7
7C55		Process Specification LTV-CVA 9-14 Except 18 Volts DC	5 minutes	No Seal	1.8
7C56					2.5
7C57				100 ppm chromic acid 10 minutes at 180°F	3.3
7C58					2.7
7C59				5% sodium dichromate 15 minutes at 195°F	2.4
7C60					[illegible]
7C61			10 minutes	No Seal	3.4
7C62					3.0
7C63				100 ppm chromic acid 10 minutes at 180°F	[illegible]
7C64					[illegible]
7C65				5% sodium dichromate 15 minutes at 195°F	1.7
7C66					2.3
7C67			15 minutes	No Seal	3.2
7C68					[illegible]
7C69				100 ppm chromic acid 10 minutes at 180°F	3.0
7C70					3.2
7C71				5% sodium dichromate 15 minutes at 195°F	2.4
7C72					2.3

* Adhesion surface energy density (in-lbs/in^2)

Examination of sealing variation of the data revealed that the adhesion values obtained with no seal and with 100 ppm chromic acid solution were higher than obtained with 5% sodium dichromate solution.

3.4 RESULTS OF CHROMIC ACID ANODIZING STUDIES

3.4.1 Part A - Table VIII presents the results obtained when the effects of pre-cleaning and sealing methods on adhesion characteristics were evaluated. In addition, variations of cleaning methods on these contaminated surfaces were evaluated for effects on adhesion.

All specimens were processed in a like manner except as noted in the table. The aluminum alloy was 2024-T3 and specimens were coated with epoxy polyamide primer at the same time. Evaluation of the specimens were made after 30 day alternate salt water immersion treatment and 7 days conditioning at 50 ± 5% relative humidity. The tests were accomplished using the Blister Test method in as short a time period as possible to minimize aging differences. All data shown are the average of three or more evaluations on the same specimen.

The two pre-cleaning methods investigated did not result in appreciable difference in the adhesion characteristics of the anodized surface and epoxy polyamide primer.

Sealing of uncontaminated specimens studies found that adhesion values obtained using deionized water as the sealing solution were lower than sealing with 5% sodium dichromate solution or no seal. The same trend of lower adhesion values for specimen receiving the deionized water seal was found on specimens which were contaminated and then cleaned. Very little difference was found between the 5% sodium dichromate seal and no seal.

A review of the results of cleaning methods clearly indicates the solvent wipe with 1,1,1, trichloroethane followed by steam cleaning and chemical conversion coating treatment was the superior method. The adhesion results obtained were equivalent to the results obtained on specimens which were not contaminated. The values obtained with only a solvent wipe gave low adhesion values in most of the evaluations. The solvent wipe and detergent scrub method yielded slightly higher values but did a poor job on the specimens which were anodized for the longer time.

3.4.2 Part B - Table IX presents the results obtained when the effects of porosity variations caused by anodizing solution strength and thickness variations caused by anodizing time on the adhesion characteristics were evaluated.

All specimens were processed in a like manner except as noted in the table. Specimens were contaminated and cleaned by solvent wipe with 1,1,1 trichloroethane and steam cleaning followed by chemical conversion coating treatment. The specimens were cleaned just prior to coating with all specimens being coated at the same time. The aluminum alloy was 2024 T3 and the coating was epoxy polyamide primer.

TABLE VIII
STUDY OF EFFECT OF PRECLEANING, SEALING AND PRECOATING CLEANING OF CHROMIC ACID ANODIZE ON ADHESION
TASK A BLISTER TEST RESULTS

SPEC. NO.	PRECLEAN	ANODIZE	SEALING SOLUTION	CONTAMINATION	PRE COATING CLEANING	γ_a^*
2A1	Process Specification LTV-CVA 9-4 Type A	Process Specification LTV-CVA 9-4 Type B	No Seal	None	None	2.3
2A2						2.3
2A3				Mil-H-5606 Hydraulic Fluid	Solvent Wipe +	1.9
2A4						1.2
2A5				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean Chemical Conversion Coating	1.8
2A6						2.2
2A7				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.4
2A8						1.5
2A9			5% sodium dichromate 15 minutes at 175°F	None	None	2.1
2A10						1.9
2A11				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	2.0
2A12						1.5
2A13				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean, Chem. Conversion	2.0
2A14						2.1
2A15				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.7
2A16						1.6
2A17			Deionized Water 15 minutes at 175°F	None	None	1.0
2A18						1.8
2A19				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	1.3
2A20						1.2
2A21				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean, Chem. Conversion	0.9
2A22						1.1
2A23				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	0.7
2A24						0.9
2A25	Process Specification LTV-CVA 9-4 Type B		No Seal	None	None	2.2
2A26						2.2
2A27				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	1.7
2A28						2.1
2A29				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean, Chem. Conversion	1.8
2A30						2.2
2A31				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.9
2A32						1.7
2A33			5% sodium dichromate 15 minutes at 175°F	None	None	2.4
2A34						2.0
2A35				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	1.7
2A36						1.6
2A37				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean, Chem. Conversion	1.9
2A38						2.3
2A39				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.6
2A40						1.9
2A41			Deionized Water 15 minutes at 175°F	None	None	1.5
2A42						1.3
2A43				Mil-H-5606 Hydraulic Fluid	Solvent Wipe	0.8
2A44						1.2
2A45				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Steam Clean, Chem. Converstion	1.4
2A46						1.1
2A47				Mil-H-5606 Hydraulic Fluid	Solvent Wipe, Detergent Scrub with Nylon Pad	1.1
2A48						0.8

* Adhesion Surface Energy Density (in-lb/in^2)

\+ MIL-T-81533 1,1,1 Trichloroethane used for solvent wipe

TABLE IX
STUDY OF EFFECT OF ANODIZE SOLUTION CONCENTRATION, TIME AND SEALING OF CHROMIC ACID ANODIZE ON ADHESION
TASK B BLISTER TEST RESULTS

SPECIMEN NUMBER	PRECLEAN	ANODIZE	ANODIZING TIME	SEALING SOLUTION	γ_a*
2B1	Process Specification LTV-CVA 9-4 Type A	2 oz. chromic acid/gal. 22 volts dc, 93°F	10 Minutes	No Seal	1.9
2B2					2.4
2B3				5% sodium dichromate 15 minutes at 195°F	1.2
2B4					1.6
2B5				100ppm chromic acid 10 minutes at 180°F	2.0
2B6					1.9
2B7			30 Minutes	No Seal	2.3
2B8					2.0
2B9				5% sodium dichromate 15 minutes at 195°F	1.4
2B10					1.9
2B11				100ppm chromic acid 10 minutes at 180°F	2.0
2B12					2.0
2B13			60 Minutes	No Seal	1.8
2B14					2.1
2B15				5% sodium dichromate 15 minutes at 195°F	2.0
2B16					2.5
2B17				100ppm chromic acid 10 minutes at 180°F	2.3
2B18					2.5
2B19		8 oz. chromic acid per gallon 22 volts dc, 93°F	10 Minutes	No Seal	2.3
2B20					2.3
2B21				5% sodium dichromate 15 minutes at 195°F	1.6
2B22					1.4
2B23				100ppm chromic acid 10 minutes at 180°F	2.9
2B24					2.1
2B25			30 Minutes	No Seal	2.7
2B26					2.2
2B27				5% sodium dichromate 15 minutes at 195°F	2.4
2B28					2.0
2B29				100ppm chromic acid 10 minutes at 180°F	2.1
2B30					2.3
2B31			60 Minutes	No Seal	2.2
2B32					2.2
2B33				5% sodium dichromate 15 minutes at 195°F	1.7
2B34					2.1
2B35				100ppm chromic acid 10 minutes at 180°F	2.3
2B36					2.2
2B37		14 oz. chromic acid per gallon	10 Minutes	No Seal	1.3
2B38					1.2
2B39				5% sodium dichromate 15 minutes at 195°F	2.0
2B40					2.2
2B41				100ppm chromic acid 10 minutes at 180°F	2.0
2B42					2.0
2B43			30 Minutes	No Seal	2.4
2B44					1.8
2B45				5% sodium dichromate 15 minutes at 195°F	1.8
2B46					2.3
2B47				100ppm chromic acid 10 minutes at 180°F	2.4
2B48					2.1
2B49			60 Minutes	No Seal	2.1
2B50					2.6
2B51				5% sodium dichromate 15 minutes at 195°F	2.1
2B52					2.7
2B53				100ppm chromic acid 10 minutes at 180°F	2.4
2B54					2.6

* Adhesion surface energy density (in-lbs/in^2).

Evaluations with the Blister Test Apparatus were conducted to minimize aging differences after the specimens had been subjected to 30 day alternate salt water immersion treatment. Specimens were conditioned for 7 days at 50% relative humidity prior to testing.

The effect of chromic acid concentration in the anodizing solution failed to produce a significant variation in the adhesion values. It was noted that at 14 oz/gal. chromic acid concentration the 10 minute anodizing time yielded low values on the no seal variation. This trait was not exhibited in the sealed specimens nor in no seal specimens anodized for longer times.

Evaluation of sealing methods found that the adhesion values of the 100 ppm chromic acid seal were equivalent to the no-seal and better than the 5% sodium dichromate seal in both the 2 oz and 8 oz chromic acid/gallon. In the 14 oz chromic acid anodizing solution all appeared equivalent except for the 10 minute no seal previously noted.

Anodize time indicating anodizing thickness failed to produce significant differences in adhesion values within the limits evaluated.

3.4.3 Part C - Table X presents the results obtained which evaluated the effect of current density and anodizing time on the adhesion characteristics.

All specimens were processed in a like manner except as noted in the table. Specimens were contaminated and cleaned by solvent wipe with 1,1,1 trichloroethane and steam cleaning followed by chemical conversion coating treatment. The specimens were cleaned just prior to coating with all specimens being coated at the same time. The aluminum alloy was 2024 T3 and the coating was epoxy polyamide primer.

Evaluations with the Blister Test Apparatus were conducted to minimize aging difference after the specimens had been subjected to 30 day alternate salt water immersion treatment. Specimens were conditioned for 7 days at 50% ±5% relative humidity prior to testing.

The effect of current density on the adhesion characteristics showed very little difference in adhesion values except when using 40 volts DC. The lower values were obtained on all three anodizing times and all three sealing methods.

Time of anodizing which controls the anodize thickness for each current density showed slight increases from the 10 minute anodize to the 60 minute anodize time except for 40 volts DC. Data scatter and the small differences in the adhesion values failed to show time of anodize as a significant variable within the limits evaluated.

Sealing variation examination of the data found only small differences in adhesion values over all in the three seal methods evaluated. All appeared equally as good with 6 volt DC and 10 volts DC anodizing. At 30 volt DC anodizing the 5% sodium dichromate seal produced slightly higher adhesion values. At 40 volt DC anodizing all adhesion values were lower but almost equal.

TABLE X
STUDY OF EFFECT OF CURRENT DENSITY, TIME AND SEALING OF CHROMIC ACID ANODIZE ON ADHESION
TASK C BLISTER TEST RESULTS

SPECIMEN NUMBER	PRECLEAN	ANODIZE	ANODIZING TIME	SEALING SOLUTION	γ_a*
2C1	Process Specification LTV-CVA 9-4 Type A	Process Specification LTV-CVA 9-4 Type B Except 10 volts DC	10 Minutes	No Seal	2.5
2C2					1.5
2C3				5% sodium dichromate 10 minutes at 195°F	1.8
2C4					1.8
2C5				100ppm chromic acid 10 minutes at 180°F	2.1
2C6					1.9
2C7			30 Minutes	No Seal	2.6
2C8					2.0
2C9				5% sodium dichromate 10 minutes at 195°F	2.0
2C10					2.2
2C11				100ppm chromic acid 10 minutes at 180°F	2.0
2C12					1.8
2C13			60 Minutes	No Seal	1.9
2C14					2.0
2C15				5% sodium dichromate 10 minutes at 195°F	2.3
2C16					2.5
2C17				100ppm chromic acid 10 minutes at 180°F	2.5
2C18					2.1
2C19		Process Specification LTV-CVA 9-4 Type B Except 30 volts DC	10 Minutes	No Seal	1.8
2C20					2.0
2C21				5% sodium dichromate 10 minutes at 195°F	2.1
2C22					1.8
2C23				100ppm chromic acid 10 minutes at 180°F	1.6
2C24					2.0
2C25			30 Minutes	No Seal	2.2
2C26					1.7
2C27				5% sodium dichromate 10 minutes at 195°F	2.3
2C28					2.8
2C29				100ppm chromic acid 10 minutes at 180°F	2.9
2C30					1.9
2C31			60 Minutes	No Seal	2.8
2C32					1.8
2C33				5% sodium dichromate 10 minutes at 195°F	2.7
2C34					2.6
2C35				100ppm chromic acid 10 minutes at 180°F	2.0
2C36					1.0
2C37		Process Specification LTV-CVA 9-4 Type B Except 40 volts DC	10 Minutes	No Seal	2.0
2C38					1.9
2C39				5% sodium dichromate 10 minutes at 195°F	2.2
2C40					1.6
2C41				100ppm chromic acid 10 minutes at 180°F	1.1
2C42					1.9
2C43			30 Minutes	No Seal	1.5
2C44					1.7
2C45				5% sodium dichromate 10 minutes at 195°F	1.7
2C46					1.3
2C47				100ppm chromic acid 10 minutes at 180°F	1.6
2C48					1.5
2C49			60 Minutes	No Seal	1.5
2C50					1.6
2C51				5% sodium dichromate 10 minutes at 195°F	1.6
2C52					1.5
2C53				100ppm chromic acid 10 minutes at 180°F	2.0
2C54					1.1
2C55		Process Specification LTV-CVA 9-4 Type B Except 6 volts DC	10 Minutes	No Seal	2.0
2C56					1.7
2C57				5% sodium dichromate 10 minutes at 195°F	1.9
2C58					1.9
2C59				100ppm chromic acid 10 minutes at 180°F	2.0
2C60					1.7
2C61			30 Minutes	No Seal	2.1
2C62					1.8
2C63				5% sodium dichromate 10 minutes at 195°F	1.8
2C64					1.6
2C65				100ppm chromic acid 10 minutes at 180°F	2.2
2C66					2.0
2C67			60 Minutes	No Seal	2.4
2C68					2.4
2C69				5% sodium dichromate 10 minutes at 195°F	2.1
2C70					1.7
2C71				100ppm chromic acid 10 minutes at 180°F	1.8
2C72					2.2

* Adhesion surface energy density (in-lbs/in^2)

3.5 RESULTS OF COATING OF PRIMED SURFACES

3.5.1 Polyurethane Finish on Primed Sulfuric Acid Anodize - Table XI presents the results obtained which evaluated the effects of primer age prior to coating and thinner concentration on the adhesion characteristics. In addition, the effect of methods of cleaning of contaminated surfaces on the adhesion of the coating system was evaluated.

The specimens were fabricated from 7075-T6 aluminum alloy and sulfuric acid anodized in accordance with LTV-CVA 9-14. All specimens were processed together in accordance with the variations shown in Table XI. The uncontaminated specimens were held in the clean condition until the remainder of the specimens had been contaminated and cleaned. All of the specimens were primer coated with epoxy polyamide primer at the same time. One half of the specimens were immediately overcoated with the polyurethane finish thinner concentration variation specified. The remaining primer coated specimens were held under clean condition for 30 days and then the polyurethane finish thinner concentration variations were applied.

Specimens, upon curing, were placed in the alternate salt water immersion apparatus for twenty days followed by 7 days conditioning at 50% ±5% relative humidity. The specimens in each set were evaluated within as short a time as possible to minimize aging effects. The time from application of polyurethane finish to evaluation by the Blister Test Method was the same for each of the two sets as close as practical.

It was found that the adhesion values obtained on specimens that had been held in the primed condition for 30 days yielded lower adhesion values. Looking at the values obtained for the uncontaminated specimens, the ones coated within 1 hour were much higher in all cases. The values obtained with solvent wipe or detergent scrub cleaning methods were erratic and did not confirm these results.

The addition of thinner to the mixed polyurethane finish did not show a significant difference in either the 1 hour or 30 day elapsed time specimens. This held true throughout the various cleaning methods.

A review of the results obtained by the cleaning method variation showed that the solvent wipe with 1, 1, 1 trichloroethane followed by steam cleaning did the best job. The adhesion values were higher for both the 1 hour and 30 day lapsed time specimens. The use of the chemical conversion coating prior to painting yielded slightly higher adhesion values.

3.5.2 Polyurethane Finish on Primed Chromic Acid Anodize - Table XII presents the results obtained when the effects of primer age prior to coating and thinner concentration on the adhesion characteristics were evaluated. In addition the effect of methods of cleaning of contaminated surfaces on the adhesion of the coating system was evaluated.

The specimens were fabricated from 2024-T3 aluminum alloy and chromic acid anodized in accordance with LTV-CVA 9-4. All specimens were processed together in accordance with the variations shown in Table XII. The uncontaminated specimens were held in the cleaned condition until the remainder of the specimens had been contaminated and cleaned. All specimens were primer coated with epoxy polyamide

TABLE XI

COATINGS ON EPOXY POLYAMIDE PRIMED ANODIZED ALUMINUM SURFACES
TASK A POLYURETHANE FINISH ON SULFURIC ACID ANODIZE

SPECIMEN NUMBER	CLEANING PRIOR TO PRIMING	ELAPSED TIME BETWEEN PRIMING AND COATING	MIL-T-81772 THINNER ADDED	γ_a*
4A1	Uncontaminated No Cleaning Required	1 Hour	None	2.7
4A2				2.9
4A3			10%	2.9
4A4				2.9
4A5			20%	2.6
4A6				1.7
4A7		30 Days	None	1.3
4A8				1.3
4A9			10%	1.3
4A10				1.2
4A11			20%	1.3
4A12				1.2
4A13	Solvent Wipe 1, 1, 1 Trichloroethane	1 Hour	None	1.4
4A14				1.6
4A15			10%	---
4A16				1.4
4A17			20%	1.5
4A18				1.5
4A19		30 Days	None	1.1
4A20				0.7
4A21			10%	1.1
4A22				0.8
4A23			20%	0.8
4A24				0.5
4A25	Solvent Wipe Detergent Scrub with Nylon Pad	1 Hour	None	Blew
4A26				2.4
4A27			10%	1.7
4A28				2.0
4A29			20%	1.9
4A30				2.1
4A31		30 Days	None	1.3
4A32				1.2
4A33			10%	0.7
4A34				0.7
4A35			20%	0.9
4A36				0.8
4A37	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry	1 Hour	None	2.1
4A38				1.7
4A39			10%	1.8
4A40				2.5
4A41			20%	2.3
4A42				2.1
4A43		30 Days	None	1.1
4A44				1.1
4A45			10%	1.2
4A46				1.2
4A47			20%	1.1
4A48				1.1
4A49	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry Chemical Conversion Coating	1 Hour	None	2.4
4A50				1.8
4A51			10%	2.4
4A52				3.1
4A53			20%	3.0
4A54				2.5
4A55		30 Days	None	0.8
4A56				1.3
4A57			10%	1.2
4A58				1.4
4A59			20%	1.3
4A60				1.4

* Adhesion Surface Energy Density (in-lb/in^2)

TABLE XII

COATINGS ON EPOXY POLYAMIDE PRIMED ANODIZED ALUMINUM SURFACES
TASK B POLYURETHANE FINISH ON CHROMIC ACID ANODIZE

SPECIMEN NUMBER	CLEANING PRIOR TO PRIMING	ELAPSED TIME BETWEEN PRIMING AND COATING	MIL-T-81772 THINNER ADDED	γ_a*
4B1	Uncontaminated No Cleaning Required	1 Hour	None	2.5
4B2				2.6
4B3			10%	2.3
4B4				2.4
4B5			20%	2.4
4B6				2.4
4B7		30 Days	None	1.2
4B8				1.3
4B9			10%	1.1
4B10				1.1
4B11			20%	0.7
4B12				1.0
4B13	Solvent Wipe 1, 1, 1 Trichloroethane	1 Hour	None	1.8
4B14				2.2
4B15			10%	2.6
4B16				2.2
4B17			20%	1.5
4B18				1.3
4B19		30 Days	None	1.5
4B20				1.3
4B21			10%	1.2
4B22				1.4
4B23			20%	1.1
4B24				1.2
4B25	Solvent Wipe Detergent Scrub with Nylon Pad	1 Hour	None	2.8
4B26				2.9
4B27			10%	3.0
4B28				2.7
4B29			20%	[illegible]
4B30				[illegible]
4B31		30 Days	None	1.4
4B32				1.3
4B33			10%	1.3
4B34				1.4
4B35			20%	1.4
4B36				1.4
4B37	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry	1 Hour	None	[illegible]
4B38				2.5
4B39			10%	2.7
4B40				[illegible]
4B41			20%	2.4
4B42				2.3
4B43		30 Days	None	1.2
4B44				1.0
4B45			10%	1.2
4B46				1.1
4B47			20%	1.3
4B48				1.3
4B49	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry Chemical Conversion Coating	1 Hour	None	[illegible]
4B50				[illegible]
4B51			10%	[illegible]
4B52				2.4
4B53			20%	[illegible]
4B54				[illegible]
4B55		30 Days	None	1.3
4B56				1.3
4B57			10%	1.3
4B58				1.4
4B59			20%	1.3
4B60				1.2

* Adhesion Surface Energy Density (in-lb/in^2)

primer at the same time. One half of the specimens were immediately overcoated with the polyurethane finish thinner variation specified. The remaining primer coated specimens were held under clean conditions for 30 days and then the polyurethane finish thinner variations were applied.

Specimens, upon curing, were placed in the alternate salt water immersion apparatus for 20 days followed by 7 days conditioning at 50% ±5% relative humidity. The specimens in each set were evaluated within as short a time as possible to minimize aging effects. The time from application of polyurethane finish to evaluation by the Blister Test Method was approximately the same for each of the two sets.

The effect of primer age on the adhesion values was very pronounced reviewing the uncontaminated specimens. Values are much lower for the 30 day aged specimens than the values obtained when the polyurethane finish was applied within one hour after the specimens were primed. The same effect was found with the adhesion values obtained on all the cleaning variation specimens as well. Even the data scatter caused by the less effective cleaning methods fail to eliminate the pattern.

The effect of solvent addition failed to make much difference in uncontaminated specimens which were overcoated in 1 hour. With the specimens receiving the less effective cleaning method the addition thinner yielded higher adhesion values as was noted in the solvent wipe cleaning variation.

On the 30 day aged primer specimens the additional thinner may have lowered the adhesion values slightly. The data scatter was such that no real trend could be found.

Cleaning variations of contaminated anodize prior to primer coating showed that all of the cleaning methods produced surfaces equal in adhesion values to the uncontaminated results. The adhesion values obtained for both the 1 hour and the 30 day primer age variation showed these results. The solvent wipe method was the only method of the 4 variations which did not obtain adhesion values equivalent to the one hour uncontaminated specimens containing no additional thinner in the polyurethane finish. The remainder of the specimens were equivalent within the data scatter.

3.5.3 Polyurethane Elastomer on Primed Sulfuric Acid Anodize - Table XIII presents the results obtained when the effects of primer age prior to coating and the type of thinner on the adhesion characteristics were evaluated. In addition the effects of methods of cleaning of contaminated surfaces on the adhesion of the coating system was evaluated.

The specimens were fabricated from 7075-T6 aluminum alloy and sulfuric acid anodized in accordance with LTV-CVA 9-14. All specimens were processed together in accordance with the variations shown in Table XIII. The uncontaminated specimens were held in the clean condition until the remainder of the specimens had been contaminated and cleaned. All of the specimens were primer coated with epoxy polyamide primer at the same time. One half of the specimens were immediately overcoated with the polyurethane elastomer variation specified in the table. The remaining primer coated specimens were held under clean conditions for 30 days and then the polyurethane elastomer variation was applied.

TABLE XIII
COATINGS ON EPOXY POLYAMIDE PRIMED ANODIZED ALUMINUM ALLOYS
TASK C POLYURETHANE ELASTOMER ON SULFURIC ACID ANODIZE

SPECIMEN NUMBER	CLEANING PRIOR TO PRIMING	ELAPSED TIME BETWEEN PRIMING AND COATING	THINNER ADDED TYPE AND PERCENT	γ_a*
4C1	Uncontaminate: No Cleaning Required	1 Hour	None	1.5
4C2				1.9
4C3			Methyl Isobutyl Ketone 5%	0.3
4C4				2.1
4C5			Cyclohexanone 5%	1.6
4C6				2.3
4C7		30 Days	None	1.8
4C8				1.7
4C9			Methyl Isobuytl Ketone 5%	1.6
4C10				1.5
4C11			Cyclohexanone 5%	1.2
4C12				1.1
4C13	Solvent Wipe 1, 1, 1 trichloroethane	1 Hour	None	0.9
4C14				0.9
4C15			Methyl Isobutyl Ketone 5%	0.7
4C16				0.9
4C17			Cyclohexanone 5%	[illegible]
4C18				1.1
4C19		30 Days	None	0.5
4C20				0.2
4C21			Methyl Isobutyl Ketone 5%	0.2
4C22				0.4
4C23			Cyclohexanone 5%	0.3
4C24				0.3
4C25	Solvent Wipe Detergent Scrub with Nylon Pad	1 Hour	None	0.8
4C26				---
4C27			Methyl Isobutyl Ketone 5%	0.8
4C28				0.8
4C29			Cyclohexanone 5%	0.9
4C30				1.0
4C31			None	0.6
4C32				0.4
4C33			Methyl Isobutyl Ketone 5%	0.5
4C34				0.5
4C35			Cyclohexanone 5%	0.6
4C36				0.5
4C37	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry	1 Hour	None	1.6
4C38				1.5
4C39			Methyl Isobutyl Ketone 5%	1.4
4C40				---
4C41			Cyclohexanone 5%	[illegible]
4C42				1.2
4C43		30 Days	None	1.5
4C44				1.5
4C45			Methyl Isobutyl Ketone 5%	1.2
4C46				---
4C47			Cyclohexanone 5%	1.5
4C48				0.?
4C49	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry Chemical Conversion Coating	1 Hour	None	2.0
4C50				2.1
4C51			Methyl Isobutyl Ketone 5%	2.2
4C52				1.6
4C53			Cyclohexanone 5%	2.1
4C54				2.0
4C55		30 Days	None	1.5
4C56				---
4C57			Methyl Isobutyl Ketone 5%	1.1
4C58				1.2
4C59			Cyclohexanone 5%	1.8
4C60				1.6

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* Adhesion Surface Energy Density (in-lb/in^2)

Specimens, upon curing, were placed in the alternate salt water immersion apparatus for twenty days followed by seven days conditioning at 50% ±5% relative humidity. The specimens in each set were evaluated in as short a time as possible to minimize aging effects. The time from application of polyurethane elastomer to evaluation by the Blister Test Method was approximately the same for each of the two sets.

Special attention was given to the specimens during evaluation since the coating was an elastomer. Data was developed as soon as possible after the blister diameter had exceeded the 3/4 inch built-in flaw caused by the paint masking disk so that excessive stretching would be minimized. Data was reduced in the normal manner disregarding the elastomeric properties of the specimens.

The results obtained with the polyurethane elastomer on sulfuric acid anodized surfaces showed considerable data scatter. The aged primer effect was found not to be significant although some variations did yield lower adhesion values with the 30 day aged primer.

The thinner variations failed to affect the adhesion values obtained on either the one hour or the 30 day primer age variation to a significant degree.

The cleaning method variation results were found to vary greatly. Only two of the cleaning variations yielded results equivalent to the uncontaminated adhesion values. These were the more stringent methods involving steam cleaning.

3.5.4 Polyurethane Elastomer on Primed Chromic Acid Anodize - Table XIV presents the results obtained when the effects of primer age prior to coating and the type of thinner on the adhesion characteristics were evaluated. In addition the effects of method of cleaning of contaminated surfaces on the adhesion of the coating system was evaluated.

The specimens were fabricated from 2024 T3 aluminum alloy and chromic acid anodized in accordance with LTV-CVA 9-4. All specimens were processed together in accordance with the variations shown in the table. The uncontaminated specimens were held in the clean condition until the remainder of the specimens had been contaminated and cleaned. All of the specimens were primer coated with epoxy polyamide primer at the same time. One half of the specimens were immediately overcoated with the polyurethane elastomer thinner variation. The remaining primer coated specimens were held under clean conditions for 30 days and then the polyurethane elastomer thinner variation was applied.

Specimens, upon curing, were placed in the alternate salt water immersion apparatus for twenty days followed by seven days conditioning at 50% relative humidity. The specimens in each set were evaluated in as short a time as possible to minimize aging effects. The time from application of polyurethane elastomer to evaluation by the Blister Test method was approximately the same for each of the two sets.

Special attention was given to the specimens during evaluation since the coating was an elastomer. Data was developed as soon as possible after the blister diameter had exceeded the 3/4 inch built-in flaw caused by the paint masking disk so that excessive stretching would be minimized. Data was reduced as if the coating were not an elastomer.

TABLE XIV
COATINGS ON EPOXY POLYAMIDE PRIMED ANODIZED ALUMINUM ALLOYS
TASK D, POLYURETHANE ELASTOMER ON CHROMIC ACID ANODIZE

SPECIMEN NUMBER	CLEANING PRIOR TO PRIMING	ELAPSED TIME BETWEEN PRIMING AND COATING	THINNER ADDED TYPE AND PERCENT	γ_a*
4D1	Uncontaminated No Cleaning Required	1 Hour	None	3.0
4D2				1.6
4D3			Methyl Isobutyl Ketone 5%	1.9
4D4				1.9
4D5			Cyclohexanone 5%	2.0
4D6				1.8
4D7		30 Days	None	1.6
4D8				1.9
4D9			Methyl Isobutyl Ketone 5%	1.6
4D10				1.5
4D11			Cyclohexanone 5%	1.5
4D12				1.7
4D13	Solvent Wipe 1, 1, 1 trichloroethane	1 Hour	None	1.7
4D14				2.1
4D15			Methyl Isobutyl Ketone 5%	3.3
4D16				1.8
4D17			Cyclohexanone 5%	1.7
4D18				1.8
4D19		30 Days	None	1.3
4D20				1.4
4D21			Methyl Isobutyl Ketone 5%	1.6
4D22				1.5
4D23			Cyclohexanone 5%	1.7
4D24				1.6
4D25	Solvent Wipe Detergent Scrub with Nylon Pad	1 Hour	None	2.5
4D26				1.9
4D27			Methyl Isobutyl Ketone 5%	1.6
4D28				1.6
4D29			Cyclohexanone 5%	1.8
4D30				1.7
4D31		30 Days	None	[illegible]
[illegible]				[illegible]
4D33			Methyl Isobutyl Ketone 5%	1.6
4D34				1.7
4D35			Cyclohexanone 5%	1.7
4D36				1.7
4D37	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry	1 Hour	None	2.0
4D38				2.0
4D39			Methyl Isobutyl Ketone 5%	1.9
4D40				1.7
4D41			Cyclohexanone 5%	2.1
4D42				1.6
4D43		30 Days	None	1.8
4D44				1.4
4D45			Methyl Isobutyl Ketone 5%	1.5
4D46				1.5
4D47			Cyclohexanone 5%	1.3
4D48				1.5
4D49	Solvent Wipe Steam Clean Distilled Water Rinse Air Dry Chemical Conversion Coating	1 Hour	None	1.7
4D50				1.7
4D51			Methyl Isobutyl Ketone 5%	1.8
4D52				2.3
4D53			Cyclohexanone 5%	1.9
4D54				2.0
4D55		30 Days	None	1.6
4D56				1.3
4D57			Methyl Isobutyl Ketone 5%	1.8
4D58				1.6
4D59			Cyclohexanone 5%	1.9
4D60				1.3

* Adhesion Surface Energy Density (in/lb/in^2)

The data scatter although not excessive somewhat precludes an overall major trend in the adhesion results obtained. In general the adhesion values obtained on the 30 day aged primer were slightly lower than the values obtained on the 1 hour specimens. The difference is not large but except for one exception (4D2), all 1 hour specimens yielded higher values than the equivalent 30 day specimen using as mixed polyurethane elastomer.

The solvent additions to the as mixed polyurethane elastomer yielded slightly lower values with the uncontaminated specimens but within the data scatter range after 30 day aging of the primer coat. The 1 hour variation failed to yield a trend as did the cleaning variations. The values obtained for the thinner dilutions yielded approximately the same adhesion values as the as mixed polyurethane elastomer.

The variation in cleaning methods failed to show significant variation in the adhesion values obtained, however the general trend was lower values with most specimens receiving the less stringent cleaning method variation.

3.6 RESULTS OF PHOSPHOMOLYBDIC ACID SPOT TEST

3.6.1 Boeing Vertol Supplied Anodize Specimens - Table XV presents the results obtained on specimens anodized and evaluated at Boeing and supplied to LTV-VSD for additional evaluation. The specimen number indicates the number of days to failure in Boeing salt spray evaluation.

The evaluations, as noted in the table, were made on under size specimens. It was also reported that the specimens had been processed for some time. The specimen size, age of anodize and previous handling prior to evaluation may have effected the results.

The data does not appear to be in agreement for all specimens but in some instances, specimens number 14, 15 and 17 the agreement is good.

3.6.2 Boeing Supplied Box Skin Material. - Table XVI presents the results obtained on LTV-VSD chromic acid anodized 2024-T81 aluminum alloy box skin material supplied by Boeing. The material was received in six sheets about 12" by 12" and the specimens were fabricated by shearing prior to anodizing. LTV-CVA 9-4 specification was followed during anodizing except as noted in the table. The two sets in each variation were processed together and then the specimens were distributed to the laboratories for independent evaluation.

The data appears to be in agreement except for specimen set number 6 which failed the phosphomolybdic acid spot test and passed both salt spray endurance tests.

3.6.3 LTV-VSD Aluminum Alloys - Table XVII presents the results obtained on three aluminum alloys, 2024, 6061 and 7075, which were sheared and anodized in duplicate sets. Both sulfuric acid and chromic acid anodized specimens were evaluated as detailed in the table. Three different seal methods were utilized with the chromic acid anodized aluminum alloy after all specimens had been anodized together.

TABLE XV

BOEING VERTOL SUPPLIED ANODIZED SPECIMENS

SPECIMEN[1] NUMBER[2]	PHOSPHOMOLYBDIC ACID SPOT TEST	QUALITY CONTROL SALT SPRAY	ENGINEERING LAB SALT SPRAY	REMARKS
7	Passed	14* Days to Failure	Passed 21 Days	3" X 3.5" Specimens
9	Passed	14* Days to Failure	Passed 21 Days	3" X 3.5" Specimens
10	Passed	14* Days to Failure	6* Days to Failure	2.3" X 6" Specimens
11	Failed (Slight Blue)	10 Days to Failure	6* Days to Failure	2.3" X 6" Specimens
12	Passed	10 Days to Failure	6* Days to Failure	2.3" X 6" Specimens
14	Passed	14* Days to Failure	13* Days to Failure	2.3" X 6" Specimens
15	Passed	17 Days to Failure	13* Days to Failure	3" X 6" Specimens
17	Passed	18 Days to Failure	Passed 21 Days	2.5" X 6" Specimens

1. Specimens were sheared into 3 pieces for evaluation at LTV-VSD.
2. Specimen number indicates number of days passed salt spray test at Boeing Vertol.

* MONDAY EXAMINATION

TABLE XVI

BOEING VERTOL 2024-T81 BOX SKINS ANODIZED AT LTV-VSD

SPECIMEN SET	ANODIZED PER SPECIFICATION	SEALED	PHOSPHOMOLYBDIC ACID SPOT	QUALITY CONTROL SALT SPRAY	ENGR LAB SALT SPRAY	ANODIC COATING WT Mg/Sq Ft
1	CVA 9-4 Type A	10-15 min, 150-160°F pH 3.5 to 6.0 with chromic acid	Passed	Passed 21 Days	Passed 21 Days	720
2	CVA 9-4 Type A		Passed	Passed 21 Days	Passed 21 Days	480
3	CVA 9-4 Type B	150-160°F, distilled water to 15% hydration	Failed (Blue)	3 Days to Failure	6* Days to Failure	60
4	CVA 9-4 Type B		Failed (Blue)	3 Days to Failure	6* Dayr to Failure	60
5	CVA 9-4 Type A except seal	7-9 min, 185°F 100 ppm chromic acid solution	Passed	17 Days to Failure	Passed 21 Days	300
6	CVA 9-4 Type A except seal		Failed (Slight Blue)	17 Days to Failure	21 Days to Failure	360

1. Skin material sheared into 3" X 12" specimens at VSD prior to anodizing

* MONDAY EXAMINATION

TABLE XVII

LTV ALUMINUM ALLOYS ANODIZED AT LTV-VSD

SPECIMEN SET	ANODIZED PER SPECIFICATION	SEALED	PHOSPHOMOLYBDIC ACID SPOT	QUALITY CONTROL SALT SPRAY	ENGR LAB SALT SPRAY	ANODIC COATING Mg/Sq Ft
7	2024, CVA 9-4 Type A	10-15, 150-160°F Distilled water pH 3.5-6.0 with chromic acid	Failed (Slt Blue)	17 Days to Failure	21 Days to Failure	840
8	2024, CVA 9-4 Type A		Passed	Passed 21 Days	Passed 21 Days	960
9	2024, CVA 9-4 Type B	Distilled water 150-160°F to 15% Hydration	Failed (Blue)	3 Days to Failure	6* Days to Failure	120
10	2024, CVA 9-4 Type B		Failed (Blue)	3 Days to Failure	6* Days to Failure	180
11	2024, CVA 9-4 Type A	7-9 min, 185°F 100 ppm chromic acid	Passed	Passed 21 Days	Passed 21 Days	1020
12	2024, CVA 9-4 Type A		Passed	Passed 21 Days	Passed 21 Days	980
13	7075, CVA 9-14	5% potassium dichromate 200°F 20-30 min	Passed	Passed 21 Days	Passed 21 Days	1860
14	7075, CVA 9-14		Passed	Passed 21 Days	Passed 21 Days	1920
15	7075, CVA 9-14	7-9 min, 185°F 100 ppm chromic acid	Passed	Passed 21 Days	Passed 21 Days	1500
16	7075, CVA 9-14		Passed	Passed 21 Days	Passed 21 Days	1500

1. Specimens were sheared into 3" X 12" prior to anodizing at VSD

* MONDAY EXAMINATION

TABLE XVII

(Continued)

SPECIMEN SET	ANODIZED PER SPECIFICATION	SEALED	PHOSPHOMOLYBDIC ACID SPOT	QUALITY CONTROL SALT SPRAY	ENGR LAB SALT SPRAY	ANODIC COATING Mg/Sq Ft
17	6061, CVA 9-14	5% potassium dichromate 200°F 20-30 min	Passed	Passed 21 Days	Passed 21 Days	1680
18	6061, CVA 9-14		Passed	Passed 21 Days	Passed 21 Days	1800
19	6061, CVA 9-14	7-9 min, 185°F 100 ppm chromic acid	Passed	Passed 21 Days	16 Days to Failure	1500
20	6061, CVA 9-14		Passed	Passed 21 Days	20* Days to Failure	1440

1. Specimens were sheared into 3" X 12" prior to anodizing at VSD

* MONDAY EXAMINATION

The only failures obtained were with specimen sets numbers 9 and 10 which were sealed in distilled water. The failures occurred with the phosphomolybdic acid spot tests as well as both salt spray endurance tests. It was also noted that the anodic coating weight was lower on these two sets of specimens than on specimen sets 7, 8, 11 and 12, even though the specimens were anodized together.

4.0 DISCUSSION OF RESULTS

4.1 BLISTER TEST METHOD

The blister test method as utilized in this program is a good method to obtain data which may be utilized to compare variations in adhesion characteristics. The method requires some skill but is a rather simple method to determine the bond strength between the adherend and the substrate.

Correlation with the standard wet tape test and the blister test values was investigated without success. The blister test values are real numbers while the tape tests are go-no go. An estimate of the bonding strength of several specimens which had been blister tested was made by pulling the 0.030 inch coating of epoxy polyamide primer which was lifted from the surface. It was found that when the adhesion surface energy density (γ_a) was approximately 1.0 in lb/in^2 or below the film would peal from the surface. When the adhesion strength was approximately 1.3 in lb/in or higher the film would break. From this limited data, a value of 1.0 in lb/in^2 was selected as the point below which the adhesion is unsatisfactory.

A review of the data was made in an attempt to establish an accuracy value for the analysis. It was found that in the range of 2.0 to 3.0 most of the duplicate specimens agreed within ±.3. This value although not as accurately established by a specific evaluation with a large number of specimens could be used as a rule of thumb. Some duplicate specimens vary considerably more and the differences could be the result of several factors. If the built in flaw doesn't develop in a circular mode the results obtained will be low or high depending on the location of the LVDT. Cracking or flaws in the coating material will affect the blister height and the calculated results.

Stretching of the film in the blister was found to be the most critical problem in obtaining accurate results. This fact was realized from previous work so adhesion values on the elastomeric coating specimens were made when the blister heights were almost the same. This allowed stretching of the film and yielded very high results. It was felt that even though the numbers obtained were valid. This would mean that a comparison of numbers would gain valuable information even if the values were relative.

Further along in the study program, a method was developed which was felt would yield more valid numbers for the elastomeric type coatings. This method was utilized and described in paragraph 2.5.3 and results reported in paragraph 3.5.2 and 3.5.4. The method simply developed the data as soon as possible after the built in flaw had produced a blister in the coating. This yielded a circular blister with the paint masking disk serving as reinforcement and prevented excess stretching of the elastomeric membrane. Results are believed to be much more accurate than those obtained by the previous technique.

The blister test apparatus as described in the procedures was utilized through the entire program with no problems. It was found that the calibrations held well and allowed fairly rapid evaluation of the specimens with satisfactory duplication of results.

4.2 MODIFICATION OF SPECIMEN COATING TECHNIQUE

The investigation to modify the method of coating specimens for blister test evaluation failed to produce a satisfactory method which would allow specimens of normal thickness to be tested. Two requirements must be met if a method is to be found to accomplish testing of coatings of normal thickness. One, the material must adhere to the surface equally as well as the original coating is adhering to the surface. Two, the modulus of elasticity of the material must approximate the modulus of the original coating. Each method of modification failed to meet one or both of these requirements.

A review of the literature found that any reinforcement in the system would change the mode of failure from a simple single blister mode to a double blister mode (Ref. 8). This results in a cohesive-adhesive fracture with the impregnated cloth serving as the more flexible substrate.

4.3 COMPARISON OF ALUMINUM ANODIZING PROCESSES

The comparison of aluminum anodizing processes yielded some results which would suggest that evaluation of "as prepared" specimens fail to produce meaningful results and only conditioned specimens should be evaluated. In these tests adhesion values on the many anodized methods yielded almost equal results of a 30 day alternate salt water immersion treatment. Equivalent specimens when tested in the "as prepared" condition yielded quite different values indicating much higher adhesion values and in one case lower values. Some data scatter occurred but the general trend is present in both the epoxy polyamide primer specimens and in the polyurethane finish specimens to a lesser degree.

The polyurethane elastomer results were more erratic in the "as prepared" condition although all still fell in a fairly narrow range after the 30 day alternate salt water immersion treatment.

4.4 SULFURIC ACID ANODIZE STUDIES

The variations in the sulfuric acid anodize studies were selected to establish which specification parameters affected the adhesion properties of the coating. All testing utilized epoxy polyamide primer as the coating material and specimens were subjected to 30 days alternate salt water immersion treatment prior to evaluation by the Blister Test method.

The results obtained found no real differences in adhesion values within a reasonable variation in the pre-cleaning or anodizing process. Time of anodizing was found to yield erratic results using very short anodizing times but adhesion was satisfactory within normal time periods.

Sealing was shown to affect adhesion. This effect is much more evident on specimens which were contaminated and then cleaned than on specimens which were tested in the uncontaminated condition.

The cleaning method used to clean contaminated specimens showed this to be a very critical step in the coating processing. Improper or inadequate cleaning failed to produce adequate adhesion. The type of sealing and its ability to be cleaned can easily be identified in the data. When good adhesion values had been obtained with the 5% sodium dichromate seal, poor or unsatisfactory adhesion values were obtained after contamination. This was true with all cleaning methods evaluated even though the same methods were able to clean up both unsealed and 100 ppm chromic acid sealed specimens.

4.5 CHROMIC ACID ANODIZE STUDIES

The variations in chromic acid anodize studies were selected to establish which specification parameters affected the adhesion properties of the coating. All testing utilized epoxy polyamide primer as the coating material and specimens were subjected to 30 days alternate salt water immersion treatment prior to evaluation by the blister test method.

The results obtained found no real differences in adhesion values within a reasonable variation in the pre-cleaning or anodizing process. Time of anodizing was found to yield erratic results using very short anodizing times but adhesion was satisfactory within normal time periods.

Sealing was shown to be an area which affects adhesion. This effect was very impressive using a distilled water seal. Unsatisfactory adhesion values were obtained with every sample sealed with deionized water. It was also found that on contaminated and cleaned specimens the no seal and 100 ppm chromic acid seal were better in adhesion then 5% sodium dichromate seal. This was probably due to the inability to clean the 5% sodium dichromate sealed specimens by the methods evaluated.

The cleaning method appears to be the most critical step in applying a coating system if the anodize has been contaminated. Of the methods evaluated the most effective was to solvent wipe with 1, 1, 1 trichloroethane and steam cleaning followed by a chemical conversion coating treatment immediately prior to painting. The less severe methods of cleaning failed to obtain satisfactory adhesion values.

4.6 RESULTS OF COATING ON PRIMED SURFACES

4.6.1 Polyurethane Finish on Primed Sulfuric Acid Anodize - The variations were selected to determine the effect on adhesion values caused by the age of the primer coating. Thinner concentrations of the polyurethane finish and pre-cleaning variations of the contaminated anodized surface were included in the investigation.

The fully cured and aged primer did not produce as good an adhesion value as when the primer is applied and the top coat is applied within 1 hour. The exact time limit was not established as to the optimum time to apply the polyurethane finish over the primer as only the two points were established. It would appear from this data that the top coat should be applied before a full cure takes place in the primer coat. The limited number of specimens examined showed separation between the anodize and the primer.

Cleaning of the contaminated sulfuric acid anodized surfaces appeared to be very critical in obtaining adequate adhesion. As was found previously the anodize surfaces seem to retain the contamination within the pores unless the cleaning procedure is very stringent. Steam cleaning appears to be the only satisfactory method of those evaluated to obtain good adhesion.

4.6.2 Polyurethane Finish on Primed Chromic Acid Anodize - The variations selected were the same as for the sulfuric acid anodize. The results obtained were about the same as for as primer aging lowering the adhesion value of the coating system. The main difference with the chromic acid anodize surface was that the cleaning methods were more effective on the chromic acid anodize. This could be caused by the much thinner coating which retains less contamination and allows easier clean up. The additional thinner in the polyurethane finish yielded higher results than the as mixed, probably due to the additional dilution of the lesser amount of contamination present.

The steam cleaning methods still appeared to be the best and safest way to obtain satisfactory adhesion values on anodized surfaces which have been contaminated.

The use of the chemical conversion coating did not yield any additional increase in the adhesion values. This result was expected since the anodized specimens had not been mechanically damaged as surfaces would probably be in production.

4.6.3 Polyurethane Elastomer on Primed Sulfuric Acid Anodize - The aging effect of the primer coating did not yield as significant a variation in adhesion values as was found with the polyurethane finish. Different solvents in the "as mixed" polyurethane elastomer and the thinner addition may have affected in the cured primer so that better adhesion was obtained. The actual adhesion values were not compared on a numerical basis with the polyurethane finish due to the differences in the elasticity of coating materials.

The sulfuric acid anodize again failed to clean up satisfactorily except when steam cleaning was utilized. The coating system lifted at the anodize/primer interface on all of the specimens examined.

Both thinners used appeared satisfactory as neither affected the adhesion values within the data scatter limits.

4.6.4 Polyurethane Elastomer on Primed Chromic Acid Anodize - The same parameters were investigated as with the sulfuric acid anodize. Although the data scatter affected the analysis of the results, better adhesion was obtained on freshly primed surfaces than on the aged primed surface.

The chromic acid anodize cleaned up much more satisfactorily after contamination than did the sulfuric acid anodize which may be due to the thinner coating. The steam cleaning methods still yielded the most reliable results.

Both thinners utilized in the evaluation yielded satisfactory results indicating that their use would be acceptable for use with the polyurethane elastomer.

4.7 PHOSPHOMOLYBDIC ACID SPOT TEST

The correlation between the phosphomolybdic acid spot test and the salt spray endurance test was rather variable on the specimens submitted which had been previously anodized. Some very good correlation was obtained on specimens anodized at LTV-VSD but results were not in total agreement. The evaluation was very limited with insufficient data to reject or accept the test method as valid.

The data accumulated from the specimens received in the anodized condition should be reviewed with allowance for non-representative specimens. Visual examination showed marred surfaces from mishandling which could have effected the results. Also, since the specimens were very small some discrepancies could have been in the coating which would not be included in the small specimen.

The phosphomolybdic acid spot test shows merit in that when inadequate protection is afforded by the anodic treatment the specimen will show the blue color which indicates that it will fail in salt spray test. The precise cut off point was not determined in these tests nor was the effect of the phosphomolybdic acid effect on the anodize determined. This would be essential if parts were screened instead of test specimens.

5.0 CONCLUSIONS

- The method of coating the blister test specimens utilized previously was found to be the most atisfactory. Other methods investigated caused changes in the failure mode.

- Normal deviations in precleaning, anodizing solution strength, current density and time of anodizing by the sulfuric acid anodize process do not affect the adhesion characteristics of the surface.

- The method of sealing sulfuric acid anodized surface was found to affect the adhesion characteristics. The results were more significant when the anodize has been contaminated and then cleaned. The anodized specimens sealed in 5% sodium dichromate solution and then contaminated and cleaned yielded unsatisfactory adhesion values.

- Cleaning of contaminated sulfuric acid anodize proved to be an extremely difficult problem, more especially with some types of sealing methods. A cleaning process employing steam cleaning was found to be the most successful but unsatisfactory on specimens sealed with 5% sodium dichromate solution.

- Normal deviations in precleaning, anodizing solution strength, current density and time of anodizing by the chromic acid anodize process do not affect the adhesion characteristics of the surface.

- The method of sealing of chromic acid anodize was found to affect the adhesion characteristics. The results found that a distilled water seal was unsatisfactory. On contaminated specimens it was found that no seal or 100 ppm chromic acid solution seals produced better adhesion values.

- Cleaning of contaminated chromic acid anodize surface was easier to achieve than the sulfuric acid anodize surface. Steam cleaning produced the higher adhesion values for both anodize methods.

- Coating of both epoxy polyamide primed surfaces of chromic acid and sulfuric acid anodized produced higher adhesion values when coated within one hour of priming. Specimens held 30 days after primer application yielded much lower adhesion values.

- The primed anodized surfaces did not yield as much difference between the 1 hour and 30 day aging effect with the polyurethane elastomer as found with the polyurethane finish. The specimen coated within one hour yielded slightly better adhesion results.

- The use of steam cleaning to remove contamination found with the epoxy polyamide primer was confirmed to be the superior cleaning method. Both the epoxy polyamide primer/polyurethane finish and the epoxy polyamide/polyurethane elastomer coating systems yielded better adhesion values on contaminated specimens cleaned by steam cleaning.

- The phosphomolybdic acid spot test to determine corrosion resistance comparable to the salt spray endurance test shows merit. Additional work and possible test method modifications will be required prior to acceptance of this much more rapid method as substitute for salt spray endurance testing.

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