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DEVELOPMENT OF IMPROVED ELECTRODEPOSITED
CORROSION INHIBITING PRIMERS

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JUNE 1979

Final Report

April 1978 — March 1979

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This technical report has been reviewed and is approved for publication.


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Two electroprimers, SA-6411 and SA-6412, have been developed which meet the goals of the program. They cure at 220F in 30 minutes and provide tensile shear strengths above 8000 psi at -65F with minimal data scatter and 100% cohesive failure in both T-Peel and notched tensile shear strength tests at -65F. These electroprimers perform excellently as adhesive bonding primers with FM-73 adhesive on 7075-T6 aluminum substrates. They are compatible with normal aircraft corrosion inhibiting primers, paint primers, and paints. The electroprimer coating baths are stable. Primer film thickness is uniform and reproducible to about 0.01 mil. The electropriming process is a significant cost savings over current spray priming procedures. It is a water-based system containing very little solvent and is therefore ecologically desirable. The electropriming system is unique in that it is a self-limiting electroplating process that easily coats, to a uniform thickness, all areas of parts including those that are difficult to coat by other conventional priming methods.

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FOREWORD

The work described in this report was performed under Contract No. F33615-78-C-5050. This contract, "Improved Electrodeposited Corrosion Inhibited Primers," was initiated and administered by the Composite and Fibrous Materials Branch, Non-metallic Materials Division, Air Force Materials Laboratory, with Mr. T. J. Aponyi as project monitor.

The work described in this report was conducted jointly by Northrop Corporation, Aircraft Group, and The Sherwin-Williams Company with Mr. S. L. Diener directing all activities at Northrop Corporation and Dr. S. J. Mels directing all activities at The Sherwin-Williams Company. The assistance of Messrs. G. G. Richards, T. P. Rummel, and G. H. Bischoff is gratefully acknowledged.

This report covers work conducted from April 1978 through March 1979.

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SUMMARY

This report covers the work accomplished from April 1978 through March 1979.

During the past seven years, Northrop, under independent research funds, has been actively investigating the electropiming of aluminum substrates. A feasibility study confirmed compatibility of electropimers with current state-of-the art epoxy film adhesives. The Air Force Materials Laboratory, under Contract F33615-76-C-5301⁽¹⁾ then sponsored the development of a universal corrosion inhibiting electropimer, i. e., one that will serve as a preparation for adhesive bonding and as corrosion protection for aluminum alloy parts. This contract effort evolved a modified epoxy electropimer curing at 325F which provided high adhesive bonding strengths except that the -65F bonding strengths were somewhat lower than desired. Therefore, the current program was established to develop a 250F curing corrosion resistant electropimer with enhanced -65F adhesive bonding properties.

This program was divided into five phases:

- | | |
|---------|--|
| Phase 1 | Develop 250F Cure Electropimer |
| Phase 2 | Develop -65F Adhesive Bond Properties |
| Phase 3 | Assess Primer Performance |
| Phase 4 | Assess Cost/Uniformity/Reproducibility |
| Phase 5 | Assess Ecological Effects |

All phases have been successfully completed. Accomplishments on each phase are summarized below and are presented in detail in Section II or the Appendix E of this report.

PHASE 1 — DEVELOP 250F CURE ELECTROPRIMER

The modified epoxy electropimer, C-5301, developed under AFML Contract F33615-76-C-5301 is the baseline in this development effort. Four crosslinkers⁽²⁾

⁽¹⁾ Exploratory Development of Corrosion Inhibiting Primers, Northrop Corporation, Technical Report No. AFML-TR-77-71, May 1977.

⁽²⁾ See Appendix A — Definition of Terms.

were formulated, produced, and compounded into eleven electropriming formulations, all curing below 300F. The effects of the coalescing solvent ⁽¹⁾ on the temperature at which the electroprimer cures were established, and an acceptable coalescing solvent was developed that permitted completion of the development of the 250F curing system.

The SA-6300 formulation utilizes the new coalescing solvent and is compounded with the fourth crosslinker ⁽¹⁾ formulated for this contract effort. The SA-6300 formulation which cures at 275F, yields an average tensile shear strength at -65F of 9150 psi with total cohesive failure (within the FM-73 adhesive), and total cohesive failures at -65F and ambient temperature in T-Peel tests.

This formulation provided the basis for formulations SA-6410, SA-6411, SA-6412 and SA-6413 which were compounded as potential 250F curing electroprimers to meet the contract goals. All four of these formulations cure at 220F in 30 minutes based on MEK rub test ⁽²⁾ and wedge crack extension tests. These four formulations were evaluated for tank and cure stability at four, six and eight week time periods in a stability test cell. Formulations SA-6411, SA-6412 and SA-6413 were determined to have acceptable stability. The SA-6410 stability was evaluated as marginal after a four-week time period.

All four of these formulations meet the contract objectives. Since some tank stability problems did arise with the SA-6410 formulation, it was eliminated from the final candidate selection group. SA-6413 shows somewhat lower -65F tensile shear strength than SA-6411 and SA-6412 and, therefore, final selection was between these two formulations. SA-6412 gave slightly higher -65F T-Peel strength and was selected as the best formulation to complete the contract effort. SA-6411 was retained in the program as the alternate electroprimer for Phase 3 evaluations.

PHASE 2 - DEVELOP -65F BONDING PROPERTIES

Eight formulations were developed to improve the -65F adhesive bond properties. Tensile tests at -65F were performed on all formulations as an evaluation of -65F adhesive bond properties.

⁽¹⁾See Appendix A - Definition of Terms

⁽²⁾See Appendix C for Test Description.

Further screening tests were performed on the four best electroprimer formulations SA-6410, SA-6411, SA-6412 and SA-6413 developed in Phase I. All four formulations produce average -65F tensile shear strengths over 8175 psi with FM-73 adhesive with total cohesive failure (within the FM-73 adhesive). The -65F and ambient temperature average T-peel strengths for all four candidates were 8.4-9.6 pounds per inch and 14-18 pounds per inch, respectively, with 7075-T6 bare aluminum alloy substrate. These values compare well with the BR-127 control primer values of 14.4 inch pounds at ambient temperature and 7.0 inch pounds at -65F. Wedge crack extension on specimens electroprimed with formulations SA-6410, SA-6411, SA-6412, and SA-6413 exposed to 120F, 95% R. H. for 30 days showed no significant growth after the initial 24-hour exposure.

PHASE 3 — ASSESS PRIMER PERFORMANCE

The two electroprimers selected for final evaluation, SA-6411 and SA-6412, were evaluated to assess paint system compatibility and adhesive bond characteristics. After formulation modifications were complete, the laboratory identifications were changed to the final formulation designation of AF-C-5050-11 and AF-C-5050-12, respectively.

In the paint system compatibility assessment, all specimens were 10-volt phosphoric acid anodized and the two electroprimers were compared to MIL-P-23377 primer. Specimens were prepared with and without MIL-C-83286 top coat. Testing included flexibility per FTMS 141 Method 6222, Salt Spray per FTMS 141 Method 6061 (1000 hours exposure to 5% salt fog at 95F) and Humidity Exposure (1000 hours exposure to 95-100% relative humidity at 140F). The performance of the electroprimed specimens was equal to the MIL-P-23377 primed specimens in the compatibility tests.

In the adhesive bonding assessment, the two electroprimers were compared to the BR-127 primer using FM-73 adhesive. All specimens were 10 volt phosphoric acid anodized. The assessment tests included (1) tensile shear testing as fabricated and after 1000 hours exposure to 5% salt spray at 95F at test temperatures of -65F, ambient, and 180F; (2) metal to metal T-peel testing per MMM-A-132, "As Fabricated", at -65F, ambient, and 180F; (3) stress durability testing per MIL-A-83377, measuring ambient temperature strength retention after 1000 hours exposure at 140F, 95-100% relative humidity loaded to 40% of ambient temperature ultimate lap shear tensile strength. The performance of the electroprimed specimens was equal to or better than that of the BR-127 primed specimens.

PHASE 4 — ASSESS COST/UNIFORMITY/REPRODUCIBILITY

Cost Assessment

An engineering assessment of the electroprime process accomplished by Northrop determined the feasibility and cost effectiveness of installing an automated electroprime line for corrosion protection of detail aluminum parts. The engineering assessment recommended the procurement and installation of an electropriming facility with a projected savings of 2 million dollars based on a seven-year amortization period with a 2.2-year payback.

The comparative costs of hand sprayed primers versus the automated electroprime application of the developed contract primer show a potential annual savings of \$425,000. An investment of approximately \$800,000 would be required to implement a completely automated cathodic electropriming facility.

Uniformity and Reproducibility Assessment

The comparative evaluation of the uniformity and reproducibility of the contract developed electroprimer versus the hand-sprayed BR-127 adhesive primer show the contract electroprimer is far superior in these respects. The study shows the electroprimer film to be reproducible, uniform, and independent of operator technique. Electroprimer films applied to 0.00015 inch in thickness were reproducible within 0.00001 inch and uniform to within ± 0.00005 inch.

PHASE 5 — ASSESS ECOLOGICAL EFFECTS

Ecological impact of this water base electropriming process is negligible. Over 98 percent of the material is utilized (deposited film on parts). Overspray is eliminated, contrasted to a normal 50+ percent loss by hand spray methods. The deposited electroprimer film contains approximately 2 percent solvent to be released during film cure, compared to 50 percent of the sprayed primer which is lost during cure of the film. Further, the water based electroprimer contains no chromates which might present a material manufacturing problem or a users disposal problem. Electroprime eliminates the need for spray application of organic materials.

SECTION I

INTRODUCTION

For the past several years, adhesive bonding technology development in the aerospace industry has been given a strong impetus by the desire to expand the application of adhesive bonding to encompass primary aircraft structures. Supporting research effort required to achieve this goal includes the development and study of surface preparations, characterization of bonding substrates, development of corrosion inhibiting adhesive bonding primers and the development of moisture resistant adhesives.

The current state of the art in preparing aluminum alloy substrates for adhesive bonding is to chemically produce a stable Boehmite oxide on the aluminum surface, followed by oven drying and hand-spray application of an adhesive primer. This process is subject to several limitations: (1) the Boehmite oxide is subject to change during the time between oven drying and primer application, (2) the oxide surface is subject to contamination between oven drying and primer application, (3) the hand-sprayed application of the adhesive primers is limited in its ability to provide films that are uniform and reproducible in film thickness, to uniformly disperse corrosion inhibiting agents and to coat blind areas, and (4) the current state-of-the-art spray method for primers is costly.

Solutions to these limitations were developed on the Air Force contract, "Exploratory Development of Corrosion Inhibiting Primers,"⁽¹⁾ performed by Northrop. This program developed a cathodically deposited modified epoxy electroprimer, C-5301, suitable for application by cost effective, automated methods.

The electropriming process incorporates the application of the primer as part of the surface treatment and eliminates intermediate oven drying and reduces transport currently required between the surface preparation and primer application steps. Consequently, the prepared Boehmite oxide surface is not subject to change or contamination prior to priming. The electropriming process provides a uniform, reproducible film, independent of operator technique or material stratification. The electropriming process

⁽¹⁾Exploratory Development of Corrosion Inhibiting Primers, Northrop Corporation Technical Report No. AFML-TR-77-71, May 1977.

is cost effective, since it is readily adaptable to automated processing methods and eliminates overspray and solvent losses.

The C-5301 electroprimer developed under the referenced Air Force contract provided corrosion-resistant, reproducible thin films which were uniform in thickness and composition over all areas of a given part, from part to part and in "blind" areas. Adhesive bond strength levels were generally high, 5300 psi at R. T. ; however, the -65F strengths were somewhat lower than desired, 5000 psi with wide data scatter, compared to the control primer values of 8000 psi. Also, the electroprimer required a cure at 325 to 345F, a temperature range that may cause some deterioration of aluminum alloy properties. An improved corrosion-inhibiting electrodeposited primer was desired to correct these deficiencies.

The overall objective of this program was to develop improved electrodeposited corrosion inhibiting primers for adhesive bonding of aluminum alloys which would provide corrosion protection for aluminum alloys when used alone, and would be compatible with standard paint primers and topcoats. The primers should be: (1) easy to process, (2) uniform in coverage, (3) reproducible, and (4) adaptable to complex structural shapes and automated processing.

To meet the objectives of the program, the work effort was divided into five phases as outlined below:

PHASE 1 — DEVELOP 250F CURE ELECTROPRIMER

- A. Formulate and Compound Candidate Crosslinkers
- B. Screen Formulated Crosslinkers
- C. Determine Optimum Crosslinker Concentration Level
- D. Define Optimum Cure Schedule
- E. Evaluate Selected Electroprimers.

PHASE 2 — DEVELOP -65F ADHESIVE BOND PROPERTIES

- A. Establish Effect of Inert Filler on Bond Properties
- B. Select Best Flexibilizer Formulation.

PHASE 3 — ASSESS PRIMER PERFORMANCE

- A. Assess Paint System Compatibility
- B. Assess Adhesive Bonding Characteristics

PHASE 4 — ASSESS COST, UNIFORMITY AND REPRODUCIBILITY

PHASE 5 — ASSESS ECOLOGICAL EFFECTS

The overall approach to meeting the program objectives was as follows:

Development of the electropriming resin formulations was accomplished by The Sherwin-Williams Company. Materials and process evaluation and definition of the electroprime adhesive bond properties was accomplished by Northrop Corporation.

The approach to lowering the cure temperature of the modified epoxy resin system was through the crosslinking chemistry of the base resin and the crosslinking agent. Selective building and mating of the monomer resin and crosslinker* functionality provided a 75F lowering in cure temperature of the modified epoxy electroprimer developed under the initial Air Force contract development program ⁽¹⁾. This approach was continued to provide the 250F curing electroprimer system.

The development of a modified epoxy electroprimer with enhanced low-temperature adhesive bonding properties was accomplished by establishing an optimum level of inert filler, and by incorporating a flexibilizer into the primer formulation.

Upon completion of the development of the 250F curing electroprimer with improved -65F adhesive bonding properties, a bonding and paint system compatibility performance assessment of the developed electroprimer was made.

General assessments of cost, uniformity, reproducibility and ecological impact completed the program requirements.

*See Appendix A, Definition of Terms

SECTION II

TECHNICAL DISCUSSION

BACKGROUND

The electrodeposition of organic materials is accomplished by solubilizing a resin system and electrically depositing the resin from a water solution onto a conductive substrate. The cathodic film deposition mechanism is illustrated in Appendix B. Since the organic resin is nonconductive, the deposition is forced onto conductive areas of the "work-piece" until the entire surface has been insulated. The thickness of the deposited film is regulated by the applied potential. The SA-6411 and SA-6412 primers developed under this contract deposit a 0.2-mil film at 30 volts. The film deposition time is approximately 30 seconds. The following features of the electropriming process make it uniquely attractive for applying corrosion-inhibiting primers.

- 1) Oxide change, contamination and damage on the prepared metal substrate are eliminated by including the priming process as an extension of the pretreatment process.
- 2) Total surface coverage with primer including recesses and "blind" areas.
- 3) Uniform primer film thickness independent of operator technique.
- 4) Cost effective, since the process is readily automated and material losses are greatly reduced.
- 5) Ecologically effective by coating from a water-base system.

PHASE 1 — DEVELOP 250F CURE ELECTROPRIMER

Summary

The Air Force Contract F33615-76-C-5301, "Exploratory Development of Corrosion Inhibiting Primers," performed at Northrop resulted in a cathodically applied modified epoxy electroprimer. This electroprimer, C-5301, develops full cure at 325F in 60 minutes or at 345F in 30 minutes. Current state-of-the-art modified epoxy electroprimers cure in the 400 to 500F range, which is primarily established by the crosslinking components in the electropriming formulation. A study of the crosslinking chemistry by The Sherwin-Williams Company evolved a crosslinking monomer

class which permitted lower cure temperatures for the modified epoxy electroprimer. Starting with a 400F curing system, the cure temperature was incrementally lowered to the 325F for the C-5301 electroprimer and, subsequently, to 220F under the current contract.

The objective of Phase 1 of the test program was successfully met. Our goal to develop a 250F curing modified epoxy electroprimer was met and surpassed with the development of a 220F curing electroprimer. To achieve this goal, eleven electroprimers have been developed and evaluated. These are given in Table 1. Based on the evaluation of the electrodeposited film cure, formulation bath stability, cure stability, and low temperature mechanical properties, formulations SA-6411 and SA-6412 were selected as the best overall electroprime formulations to complete the contract effort. Details of the development work leading to the development of the SA-6410 — SA-6413 formulations are given in Appendix E.

Results and Discussion

The goals in Phase 1 were to formulate a modified epoxy electroprimer that would (1) cure in 30 minutes at 250F, and (2) have acceptable bath stability. These two goals are somewhat contradictory. To achieve a lower temperature cure, a more reactive curing system is required, and the more reactive the curing system the less the bath stability. Acceptable bath stability is defined as the ability of the electroprime solution to produce identical cured films over a minimum one year time period with a total bath solids turn-over rate of two per year. Bath stability has three aspects to it. Over the life of the bath, first, the electroprimer must not coagulate or polymerize into large particles that will precipitate out of suspension or plate out as a rough surface; second, the electroprime material must plate out at the same voltage/time conditions yielding the same film thickness and other film characteristics; and third, the cure of the deposited electroprimer film must be constant, and the cured films must provide the identical performance properties as the film deposited from a new solution.

The main ingredients of an electroprimer formulation are the base resin and the crosslinker.* These two components are rendered water soluble with a solubilizing agent and combined in a water solution. Therefore, the electroprime formulation is essentially a one-part resin system containing all the functional chemical groups required to cure. The formulation must be balanced so that cure will take place at about

*See Appendix A — Definition of Terms

TABLE 1. FORMULATIONS OF CANDIDATE ELECTROPRIMER RESINS

Formulation Sequence	Formulation Identification	Base Resin ⁽²⁾	Crosslinker	Pigment	Coalescing Solvent
Reference	C-5301	Modified Epoxy	Cr X ⁽¹⁾	(3)	Co A ⁽⁴⁾
1	SA-5641 ⁽⁷⁾	Modified Epoxy	Cr A ⁽¹⁾	None	Co A
2A	SA-6029 ⁽⁸⁾	Modified Epoxy	Cr B ⁽¹⁾	None	Co B ⁽⁵⁾
2B	SA-6029M ⁽⁹⁾	Modified Epoxy	Cr B	None	Co A + Co B
3	SA-6082 ⁽¹⁰⁾	Modified Epoxy	Cr C ⁽¹⁾	None	Co B
4A	SA-6106 ⁽¹⁰⁾	Modified Epoxy	Cr C	None	Co C ⁽⁶⁾
4B	SA-6106M ⁽¹¹⁾	Modified Epoxy	Cr C	None	Co C
5	SA-6166 ⁽¹²⁾	Modified Epoxy	Cr B Mod.	None	Co C
6	SA-6167 ⁽¹³⁾	Modified Epoxy	Cr A Mod.	None	Co C
7	SA-6300 ⁽¹⁴⁾	Modified Epoxy	Cr D ⁽¹⁾	None	Co C
8	SA-6410 ⁽¹⁵⁾	Modified Epoxy	Cr B Mod	TiO ₂ & Clay	Co C
9	SA-6411 ⁽¹⁶⁾	Modified Epoxy	Cr D	TiO ₂ & Clay	Co C
10	SA-6412 ⁽¹⁷⁾	Modified Epoxy	Cr B Mod + Cr D	None	Co C
11	SA-6413 ⁽¹⁸⁾	Modified Epoxy	Cr B Mod + Cr D	TiO ₂ & Clay	Co C

NOTES:

- (1) Sherwin-Williams experimental crosslinker.
- (2) All formulations are made with the C-5301 modified epoxy resin.
- (3) NALZIN SC-1, SiO₂/TiO₂/SC-1, Product of National Lead Company.
- (4) Co A = "Isophorone" Coalescing Solvent (3,5,5-trimethyl-2-cyclohexen-1-one).
- (5) Co B = "Butylate" Coalescing Solvent (n-butyl acetate).
- (6) Co C = "Cellate" Coalescing Solvent (Cellusolve Acetate).
- (7) SA-5641 is the first modification of the C-5301 electroprimer and utilizes a new crosslinker which lowered the cure temperature from 325F/60 minutes to 290F/30 minutes.
- (8) SA-6029 is the first experimental formulation with crosslinker B and coalescing solvent B.
- (9) SA-6029M is SA-6029 with coalescing solvent, Co A, added.
- (10) SA-6082 and SA-6106 are similar to C-5301 but have different resin/crosslinker ratios and different coalescing solvents.
- (11) SA-6106M contains an elastomer which aids in film coalescence.
- (12) SA-6166 is similar to SA-6029 except the crosslinker B has a built-in flexibilizer, and the coalescing solvent Cellusolve Acetate is used.
- (13) SA-6167 is similar to SA-5461 except the crosslinker has been modified and contains an elastomer which also aids in film coalescence.
- (14) SA-6300 is the first experimental formulation utilizing crosslinker Cr D.
- (15) SA-6410 is the SA-6166 with sufficient inert filler ingredient (TiO₂ and clay) to reduce the cured primer film gloss.
- (16) SA-6411 is SA-6300 with sufficient inert filler to define any effect of the inert filler on adhesive bonding properties.
- (17) SA-6412 is the base resin system of SA-6166 and SA-6300 with a blend of the SA-6166 and SA-6300 crosslinkers.
- (18) SA-6413 is the SA-6412 system with sufficient inert filler to maintain low gloss in the cured electroprimer film.

250F but polymerization or crosslinking will not take place to any appreciable extent in the electropimer plating bath. The Sherwin-Williams Co. performed this formulation phase of the program.

In this formulation development phase, the C-5301 base resin system, which was developed in previous contract work,⁽¹⁾ was combined with especially formulated crosslinkers to achieve the 250F cure capability and bath life stability. Inert fillers were added to modify the cured electropimer film characteristics, i.e., reduce gloss, and improve adhesion to epoxy adhesives. Coalescing solvents are incorporated which cause the plated electropimer particles to form a continuous film. The electropimer is a colloidal-like suspension of fine particles containing all the cured electropimer film ingredients and the coalescing solvent. In addition, the electropimer formulation must contain a solubilizing agent which will cause the electropimer material to disperse in water. Since the electropimer system selected for application to aluminum in this contract was to be cathodically deposited, the part to be coated was to be the cathode (-) in the electrical plating system, the formulation had to produce positively charged particles in the dispersed condition. Normally, acid or anhydride crosslinking agents give the resin particles a negative (-) charge and it will plate out at the anode (+); amine type crosslinking agents give the resin particle a positive (+) charge and it will plate out at the cathode (-). Since the requirement for the contract was a cathodic electropimer, only amine type agents were investigated.

In addition to the development and selection of the acceptable crosslinking system, another factor which may inhibit the cure reaction and influence bath stability is the coalescing solvent. The coalescing solvent is required to provide film flow continuity during electrical deposition of the resin-crosslinker system. The coalescing solvent also has the effect of keeping the resin and crosslinker separated and slowing down or inhibiting their chemical reactivity. The electropimer systems developed in this contract have six to twelve months bath life at room temperature. As a point of reference, normal epoxy adhesives and composite prepregs have three to six months shelf life at 0F.

All electropime formulations made for this phase of the program were made from the same base modified epoxy resin system, the C-5301 system. Four crosslinkers, Cr A, Cr B, Cr C, and Cr D were investigated and modifications of Cr B and Cr C were also used. In two formulations, SA-6412 and SA-6413, a mixture of crosslinkers Cr B Mod and Cr D was used. Three formulations were prepared using inert

filler, TiO_2 and clay. Three different coalescing solvents and a mixture of two of these were investigated. Eleven candidate formulations were prepared and tested. These are described in Table E-1. All formulations were evaluated for deposited film cure by the Meseran Test (see Appendix C) at The Sherwin-Williams Company and by the MEK Rub Test both at Northrop Corporation and The Sherwin-Williams Company. Results of these tests are given in Table E-2.

Bath life stability tests were run on the more promising formulations both at Northrop Corporation and at The Sherwin-Williams Company, and are presented in Table 2.

Data and details of the experimental work leading up to the development of the 220F curing SA-6410 — SA-6413 series are given in Appendix E.

PHASE 2 - DEVELOP -65F ADHESIVE BOND PROPERTIES

Summary

The objective of Phase 2 of the contract was successfully completed. The development and evaluation of electropimers SA-6410, SA-6411, SA-6412, and SA-6413 provided modified epoxy electropimers with improved -65F adhesive bond properties and ability to cure in 30 minutes at 220F.

Eight formulations were developed to improve the -65F bond properties. Tensile tests at -65F were performed on all formulations as an evaluation of -65F adhesive bond properties. Further screening tests were performed on the four best electropimer formulations, SA-6410, SA-6411, SA-6412, and SA-6413 developed in Phase 1. All four formulations produced average -65F tensile shear strengths over 8175 psi with FM-73 adhesive with total cohesive failure (within the FM-73 adhesive). The -65F and ambient temperature average T-peel strengths for all four candidates were 8.4-9.6 pounds per inch and 14-18 pounds per inch respectively with 7075-T6 bare aluminum alloy substrate. These values compare well with the BR-127 control primer values of 14.4 pounds per inch ambient temperature and 7.0 pounds per inch at -65F. Wedge crack extension on specimens electropimered with formulations SA-6410, SA-6411, SA-6412, and SA-6413 exposed to 120F, 95% R. H. for 90 days showed no significant growth after the initial 24-hour exposure.

**TABLE 2. BATH LIFE STABILITY TEST RESULTS*
OF CANDIDATE ELECTROPRIME FORMULATIONS**

Electroprimer Formulation	Tank Stability**	Application Stability†	Cure Stability††	Comments
SA-5641	Pass	Pass	Pass	Cures 40F above contract goal
SA-6029	Pass	Pass	Pass	Requires frequent addition of coalescing solvent
SA-6029M	Fail	Fail	Fail	Contains coalescing solvent blend
SA-6082	Fail	Fail	Pass	Requires frequent addition of coalescing solvent
SA-6106	Pass	Pass	Pass	Cures 40F above contract goal
SA-6106M	Pass	Pass	Pass	Requires 80 volt application potential
SA-6166	Pass	Pass	Pass	Excellent stability
SA-6167	Fail	Fail	Pass	Failed after 6 weeks
SA-6300	Pass	Pass	Pass	Excellent stability
SA-6410	See Comments	Pass	Pass	Passes at Sherwin-Williams Marginal at Northrop after 8 weeks
SA-6411	Pass	Pass	Pass	Excellent stability
SA-6412	Pass	Pass	Pass	Excellent stability
SA-6413	Pass	Pass	Pass	Excellent stability

*Bath life stability is determined weekly up to 8 weeks in a bath stability test cell.

**Acceptable Tank Stability: After 8 weeks in the test cell, the formulation must be completely redispersable to a homogeneous water solution after a 24-hour settling time (agitation off).

† Acceptable Application Stability: After 8 weeks in the test cell, the formulation must deposit the same film thickness with the same film appearance at the same application time and voltage as is deposited by a new freshly prepared solution.

††Acceptable Cure Stability: After 8 weeks in the stability cell, the deposited film must cure at the same time and temperature producing the same physical and mechanical characteristics as the film deposited from a new freshly prepared solution (cure is verified by MEK rub test).

Results and Discussion

The development work in this phase of the program began with an investigation of the C-5301 electroprimer. This electroprimer demonstrated inadequate -65F adhesive bond properties. This deficiency was postulated to be a result of either (1) a weakness in the anodic oxide film on the surface resulting from the cathodic deposition of the electroprimer, or (2) brittleness of the electroprimer attributable in part to the inert filler in the formulation.

To determine whether or not the cathodic deposition process was affecting the anodic oxide film, Scanning Electron Microscope (SEM) analyses on electroprimed specimens were made with plating potentials of 10 to 40 volts. These showed no change in the surface preparation anodic oxide thickness or character.

To reduce the brittleness of the cured electroprimer film, the inert filler was taken out of the C-5301 electroprimer. This became formulation SA-6029 which was then prepared and tested. At -65F, specimens with this primer and FM-73 adhesive gave tensile shear strengths about 2000 psi higher than the parent C-5301 electroprimer. In addition, the failure modes were about 50% cohesive (a 25% increase over C-5301). Wedge crack extension tests on specimens prepared with the SA-6029 electroprimer and FM-73 adhesive showed a peculiar type of slow continuing growth with time. A thorough SEM analysis was made of both the failed -65F tensile shear specimens and the failed wedge test specimens. The analysis revealed failure was in the primer and was due to high boiling coalescing solvent trapped in the primer. Two formulations, SA-6166 and SA-6167 were prepared replacing the high boiling coalescing solvent in SA-6029 with a lower boiling coalescing solvent, cellusolve acetate. Tensile shear test results at -65F using these electroprimers were excellent; shear strengths were about 8000 psi with very little data scatter, and the mode of failure in these specimens increased to about 75% cohesive (within the FM-73 adhesive).

Cocuring the FM-73 adhesive on top of the "B-staged" (200F/30 minutes) electroprimer, was tried as a method to improve the bond between the electroprimers and the FM-73 adhesive. Failures in -65F tensile shear specimens prepared by this cocuring technique were about 95% cohesive.

Test data indicated that the SA-6166 and SA-6167 formulations could be cured at temperatures less than 250F. In an attempt to maintain the low 250F cure temperature and improve the bond between the electroprimer film and the FM-73 adhesive, a formulation, SA-6300 was developed using a new crosslinker, Cr D. The cure required for this formulation was 275F, 25F above the contract goal, but the -65F tensile

shear specimens showed strengths higher than the BR-127 baseline primer and 100% cohesive failure. These last three formulations, SA-6166, SA-6167, and SA-6300, lead to the development of the final series of electroprimers, the SA-6410 — SA-6413 series.

Other areas of investigation to improve the electroprime formulation performance included:

- 1) Cocure tests on the SA-6300 (with the FM-73 adhesive) as a means of reducing the cure temperature were successful.
- 2) The BR-127 primer was evaluated in wedge crack extension tests "as is" and with the chromate corrosion inhibiting fillers removed. No difference in properties was observed.
- 3) A flexibilizer, PCP-0300, was added to formulation SA-6166 in an attempt to improve the -65F adhesive bond tensile strength, but no difference in performance could be ascertained.

Complete data on these developments are contained in Appendix E. The following discussion pertains only to the development work performed in the final selection of the Phase 3 electroprimers, SA-6411 and SA-6412.

1. Development of Phase 3 Electroprimers

Northrop's original work projection was to select the best electroprimer to meet the contract goals after evaluation of the SA-6300 electroprimer. However, Northrop was not totally satisfied with the SA-6300 or the other candidates produced up to this point in the contract although performance of some of the candidates did meet the program objectives. The SA-6300 formulation provided the best overall bonding performance but did not meet the contract cure objective of 30 minutes at 250F maximum (based on MEK rub tests). Two other candidate electroprimers, the SA-6166 and SA-6167 formulations, provided cure response within the contract goals; however, SA-6167 showed some sign of tank instability and SA-6166 intermittently yielded partial adhesive failures, between primer and adhesive, which was attributed to the high gloss of the SA-6166 electroprimer. The compositions of SA-6300, SA-6166 and SA-6167 are shown in Table 1 details and other data are given in Appendix E.

The optimum electroprimer should cure completely below 250F in 30 minutes, show no tank or cure instability, and provide totally cohesive failures (with the

adhesive) in mechanical test specimens. Therefore, four additional electroprime formulations that would have a high probability of meeting the program objectives were developed. These four formulations are defined as follows:

- SA-6410 - This is the SA-6166 formulation with sufficient inert filler ingredient (TiO_2 and clay) to reduce the cured primer film gloss.
- SA-6411 - This is SA-6300 with an inert filler level high enough to define any effect on adhesive bonding properties by the inert constituent.
- SA-6412 - This is the base resin system of SA-6166 and SA-6300 with a blend of the SA-6166 and SA-6300 crosslinkers. This system is projected to cure below 250F and provide an adhesive bonding strength compromise of the SA-6166 and SA-6300 electroprimers. It has no inert filler.
- SA-6413 - This the SA-6412 system with sufficient inert filler to maintain low gloss in the cured electroprimer film. (High gloss was considered a possible contribution to partial adhesive failures in some mechanical test specimens)

Three of these formulations are based on SA-6300 and one is modified SA-6166 formulation.

The four candidates were reduced to plating consistency with water in one-gallon stability test evaluation cells. MEK rub test cure evaluation panels, 3 in. x 6 in. x 0.032 in., of 7075-T6 aluminum alloy were 10-volt phosphoric acid anodized and electroprimed with each of the four electroprimers. One electroprimed panel for each candidate formulation was cured at 220F for 30 minutes. All four candidate formulations passed a 200 MEK rub cycle test showing complete cure had been accomplished at 220F in 30 minutes. Since there was no sign of discoloring or loss of gloss in the electroprimer film in 200 rub cycles, the tests were discontinued at that point.

The SA-6410 to SA-6413 series are direct derivatives of the SA-6166 and SA-6300 which cure at 235F and 275F in 30 minutes, respectively. The original cure projection of the SA-6410 to SA-6413 series was 245F; the MEK rub test indicated that all four electroprimers cure at 220F, 25F below the projected 245F cure temperature. It is

unknown at this time why the SA-6410 to SA-6413 series cures below the parent formulations. However, a duplicate MEK rub test cure evaluation was also performed independently in the Sherwin-Williams Research Laboratory and the result also indicated full cure at 220F in 30 minutes.

The four electroprime formulations, SA-6410 to SA-6413, were exposed for eight weeks in the stability test cells. Formulations SA-6411, SA-6412 and SA-6413 showed no signs of settling or coagulation and were readily redispersed after a 24-hour settling period with the tank circulation turned off. The SA-6410 formulation, after four weeks in the Northrop tank, showed signs of coagulation (separation) of the resin/water system. This separation of SA-6410 was not noted in the Sherwin-Williams stability tank. This difference is attributed to the higher circulation rate in the Northrop tanks produced by the different type of circulation pumps.

After four weeks exposure and again after eight weeks exposure time in the stability tank cells, the cure stability was evaluated on formulations SA-6411, SA-6412, and SA-6413. Test panels were electroprimed with each formulation and cured at 220F for 30 minutes. All three formulations passed a 200 MEK rub test indicating satisfactory cure stability after four weeks and after eight weeks exposure to the stability test cells.

2. Selection of Phase 3 Electroprimers

The basic adhesive bonding screening test assessment of SA-6410, SA-6411, SA-6412 and SA-6413 was completed. For the basic adhesive bonding screening tests, all electroprimer films were cured at 220F for 30 minutes, the temperature determined to provide completeness of cure in the MEK rub test reported in Phase 1.

The tests performed in the basic adhesive bending assessment were: (1) wedge crack extension at 120F, 95% R. H. (2) -65F tensile shear test and (3) -65F and ambient temperature T-peel. Specimens were prepared for evaluation of each of the new electroprimers. Test panel substrates of 7075-T6 bare aluminum alloy were 10-volt phosphoric acid anodized, electroprimed and the electroprimers cured at 220F for 30 minutes. The panels were then bonded with FM-73 adhesive in accordance with the manufacturer's instructions, and machined to test specimen configuration. Test results for the four electroprimers are presented in Tables 3, 4, and 5. Wedge crack extension ranged from 0.08 to 0.12 inch after 30 days exposure. The -65F tensile

TABLE 3. TENSILE SHEAR TEST * RESULTS OF SA-6410,
SA-6411, SA-6412 AND SA-6413 ELECTROPRIMERS
CURED AT 220F FOR 30 MINUTES

Electroprimer	Test Temperature (F)	Ultimate Load (psi)	Failure Mode
SA-6410-1	-65	8500	Cohesive**
SA-6410-2	-65	8440	Cohesive
SA-6410-3	-65	8300	Cohesive
SA-6410-4	-65	8430	Cohesive
SA-6410-5	-65	8600	Cohesive
	<u>Average</u>	<u>8455</u>	
SA-6411-1	-65	8620	Cohesive
SA-6411-2	-65	8380	Cohesive
SA-6411-3	-65	8285	Cohesive
SA-6411-4	-65	8565	Cohesive
SA-6411-5	-65	8970	Cohesive
	<u>Average</u>	<u>8565</u>	
SA-6412-1	-65	8630	Cohesive
SA-6412-2	-65	8760	Cohesive
SA-6412-3	-65	8550	Cohesive
SA-6412-4	-65	8160	Cohesive
SA-6412-5	-65	8520	Cohesive
	<u>Average</u>	<u>8525</u>	
SA-6413-1	-65	8000	Cohesive
SA-6413-2	-65	8050	Cohesive
SA-6413-3	-65	8220	Cohesive
SA-6413-4	-65	8300	Cohesive
SA-6413-5	-65	8300	Cohesive
	<u>Average</u>	<u>8175</u>	

* Standard thick adherend machined notch tensile shear specimen of 7075-T6 bare aluminum alloy, 10 volt phosphoric acid anodized, electroprimed with the indicated test electroprimer, and bonded with FM-73 adhesive cured at 250F/60 minutes.

** All failures were cohesive, within the FM-73 adhesive.

TABLE 4. T-PEEL TEST* RESULTS OF SA-6410, SA-6411, SA-6412 AND SA-6413 ELECTROPRIMERS CURED AT 220F FOR 30 MINUTES

Primer**	T-Peel Strength (pounds/inch)		Failure Mode
	Ambient	-65F	
SA-6410-1	18.0	9.0	Cohesive†
SA-6410-2	15.0	7.5	Cohesive
SA-6410-3	22.0	9.0	Cohesive
SA-6410-4	16.0	10.0	Cohesive
Average	18.0	8.9	
SA-6411-1	14.0	8.5	Cohesive
SA-6411-2	14.0	9.0	Cohesive
SA-6411-3	21.0	8.5	Cohesive
SA-6411-4	22.5	7.5	Cohesive
Average	18.0	8.4	
SA-6412-1	14.5	8.0	Cohesive
SA-6412-2	14.5	9.0	Cohesive
SA-6412-3	17.5	11.5	Cohesive
SA-6412-4	14.5	10.0	Cohesive
Average	15.2	9.6	
SA-6413-1	16.5	11.0	Cohesive
SA-6413-2	15.5	8.5	Cohesive
SA-6413-3	12.0	8.5	Cohesive
SA-6413-4	12.5	9.0	Cohesive
Average	14.1	9.3	
BR-127-1	13.0	5.5	Cohesive
BR-127-2	15.5	8.5	Cohesive
BR-127-3	14.5	8.0	Cohesive
BR-127-4	14.5	6.0	Cohesive
Average	14.4	7.0	

* 1-in. x 14-in. T-peel specimens of 7075-T6 bare aluminum alloy, 10 volt phosphoric acid anodized, electroprimed with the indicated test primer and bonded with FM-73 adhesive at 250F/60 minutes.

**Nominal primer thickness — electroprimers, 0.2 mil; BR-127, 0.1 mil.

†All failures were cohesive. within the FM-73 adhesive.

TABLE 5. WEDGE CRACK EXTENSION TEST* RESULTS
OF SA-6410, SA-6411, SA-6412 AND SA-6413 ELECTROPRIMERS
CURED AT 220F FOR 30 MINUTES**

Electroprimer	Average Crack Extension† (inches)				
	1 Day	7 Days	10 Days	14 Days	30 Days
SA-6410	0.12	0.12	0.12	0.12	0.12
SA-6411	0.11	0.11	0.11	0.11	0.11
SA-6412	0.10	0.11	0.11	0.11	0.11
SA-6413	0.08	0.08	0.08	0.08	0.08

*Standard 1 in. x 6 in. wedge crack extension specimens of 7075-T6 bare aluminum alloy, 10 volt phosphoric acid anodized, primed with the indicated test primer, and bonded with FM-73 adhesive cured at 250F/60 minutes.

**Reported results are average of five individual test specimens.

† Exposure conditions: 120F, 95% R. H.

shear values were highest (8565 psi) on SA-6411 and lowest in SA-6413 (8175 psi). All failures were cohesive. The T-peel strength at ambient temperature was highest on SA-6410 and SA-6411 (18 pounds/inch each), and at -65F was highest for SA-6412 (9.6 pounds/inch).

Upon completion of screening tests of the SA-6410, SA-6411, SA-6412 and SA-6413 electroprimers, a comparative rating scale was devised to facilitate selection of the electroprimer for the Phase 3 Primer Performance Assessment. A one-to-ten scale was established, with ten (10) being the best, and the electroprimers given a number rating in each screening test area. Results of the comparative rating are given in Table 6. The BR-127 corrosion inhibiting adhesive primer was also included for comparison purposes. The following is the rationale for rating given.

- 1) Cure - The cure objective was to develop an electroprimer with a cure of 250F, equivalent to the control baseline, BR-127. Since all four electroprimers exceeded the 250F cure objective, i.e., 30F below the requirement for the BR-127, they were rated a 10, as opposed to the BR-127 with the higher, less desirable cure temperature, which was rated an 8 in cure.

**TABLE 6. PERFORMANCE COMPARISON RATING OF SA-6410,
SA-6411, SA-6412 AND SA-6413 ELECTROPRIMERS AND BR-127
SPRAY PRIMER**

EVALUATION TEST	PRIMER RATING				
	SA-6410	SA-6411	SA-6412	SA-6413	BR-127
Cure	10	10	10	10	8
Primer Stability	8	10	10	10	6
Processing Characteristics	10	10	10	10	6
Crack Extension Wedge Test	8	9	9	10	10
-65F Tensile Shear Test	9	10	10	8	10
-65F T-Peel Test	9	8	10	9	7
Ambient Temp T-Peel Test	9	9	8	7	7
Fracture Modes of Tested Adhesive Bonded Specimens	8	10	10	8	10

- 2) Stability - The desired stability of the adhesive primer is that the material should be capable of reproducing constant composition, uniform films when stored for extended periods of time at ambient temperature. Electroprimer formulations SA-6411, SA-6412 and SA-6413 are completely stable in this respect, and thus were rated as 10. The SA-6410 electroprimer did show some signs of coagulation after a laboratory test equivalent to 8 months of production use and was therefore rated an 8. If the SA-6410 were in a production tank with a normal depletion and replenishment activity, it is doubtful that any signs of instability would be detected. In contrast, the BR-127, which contains a chromate inhibitor, can stratify or settle even under the rigorous agitation schemes currently employed. As a consequence, variances in the film composition can occur. Further, even if the sprayable BR-127

primer material were uniform, variations in application thickness, intrinsic to hand applied coatings, yield variances in the chromate content in areas of the aluminum substrate that are difficult to reach by spray coating. In addition, the BR-127 requires refrigerated storage and has a limited shelf life since the material is not stable in ambient longterm storage. Therefore, the BR-127 was rated 6 in stability.

- 3) Processing - The processing characteristics of the electroprimers are excellent. Different operators with a minimum of training will deposit a uniform, reproducible film with little effort. The SA-6410, SA-6411, SA-6412 and SA-6413 electroprimers are readily rinsed, removing the small amounts of electroprimer solution "drag out," and no preference can be given to any one of the four electroprimers. The four electroprimer solutions equally wet the immersed substrate and require the same low application voltage.

Comparatively, the processing requirements for the hand applied BR-127 are stringent. The cold storage material (normally in 5 gallon containers) is initially brought up to ambient temperature and agitated on a paint shaker to evenly distribute the contents, and then poured into a larger agitated storage tank for application. The spray equipment operator requires careful training and skill to meet the film application requirements of 0.1 - 0.3 mils. Further, careful cleaning and maintenance of the spray equipment is mandatory. Collectively, the processing requirements for the BR-127 are difficult and therefore BR-127 was rated a six in "Processing."

- 4) Wedge Crack Extension - All of the four electroprimers perform satisfactorily in the standard wedge crack extension test at the exposure conditions of 120F, 95% relative humidity. A small difference in the wedge crack opening after 30-day exposure, see Table 5, was adequate to differentially rate the electroprimers in this test area.
- 5) -65F Tensile Shear Strength - All four of the electroprimers perform satisfactorily in the -65F Tensile Shear Strength Test, all averaging over 8,000 psi, see Table 3. Assigning a value of ten (10) for 8500 psi average established assignment of the ratings listed in Table 6.

- 6) T-Peel Strength Test - All four of the electrophrimers and the BR-127 control primer perform satisfactorily in the -65F and the ambient temperature T-Peel strength test. In the -65F T-Peel test the ratings are equivalent to the T-Peel strength test result rounded off to the nearest whole number. In the ambient temperature T-Peel test, the rating is one half the peel strength result, i.e., a test result of 20 pounds/inch peel test result is rated a ten (10) in Table 6.
- 7) Fracture Modes - The assignment of ten (10) was made for 100% cohesive fracture (within the adhesive) in all the screening test specimens. Three primers, SA-6411, SA-6412 electrophrimers and the BR-127 spray primer met this requirement. The SA-6410 and SA-6413 electrophrimers showed intermittent partial adhesive failure (~10%) and were therefore assigned a rating of eight (8).

The electrophrimers SA-6410, SA-6411, SA-6412 and SA-6413 were all acceptable and met the contract goals. However, since some tank stability problems did arise with the SA-6410 formulation in the Northrop stability test cell, it was eliminated from the final candidate selection group. SA-6413 showed somewhat lower -65F tensile shear strength than SA-6411 and SA-6412 and therefore final selection was between these two formulations.

TABLE 7. COMPARATIVE SCREENING TEST RESULT AVERAGES ON ELECTROPRIMER FORMULATIONS SA-6411 AND SA-6412

	AVERAGE TEST RESULT	
	SA-6411	SA-6412
<u>Wedge Crack Extension (inch)</u>		
1-day, 120F/95% R. H.	0.11	0.10
30-day, 120F/95% R. H.	0.11	0.11
<u>Tensile Shear Strength (psi)</u>		
-65F	8565	8525
<u>T-Peel Strength (pounds/inch)</u>		
-65F	8.4	9.6
Ambient	18.0	15.2

Comparison of the screening test data on Formulations SA-6411 and SA-6412 shows both electrophrimers to be excellent adhesive bonding primer candidates and therefore both were evaluated in Phase 3.

PHASE 3 — ASSESS PRIMER PERFORMANCE

The objective of this phase was to verify paint systems compatibility with the electroprimers and evaluate the adhesive bond characteristics of the selected electroprimers, SA-6411 and SA-6412.

Summary

In the paint systems compatibility assessment, the SA-6411 and SA-6412 electroprimers were demonstrated to be compatible with the MIL-P-23377 primer and MIL-C-83286 top coat and equivalent in substrate protection properties to the MIL-P-23377 primer in the 1000 hour salt spray exposure and 1000 hour humidity resistance tests.

In the adhesive bond characteristics evaluation, the SA-6411 and SA-6412 electroprimers were demonstrated to be equivalent to the control spray primer, BR-127 in tensile shear strength properties, metal to metal T-peel strength properties and adhesively bonded joint durability.

After formula modifications and performance evaluations were complete, the laboratory designations of SA-6411 and SA-6412 were given the final formulation designation of AF-C-5050-11 and AF-C-5050-12 respectively.

Results and Discussion

1. Paint System Compatibility Assessment. Table 8 defines the test specimens and tests performed to demonstrate the compatibility of the SA-6411 and SA-6412 electroprimers with both the standard MIL-P-23377 catalyzed epoxy primer and the MIL-C-83286 aliphatic urethane top coat and to determine the environmental resistance of the various combinations.

Test results are given in Tables 9, 10, and 11.

- A. Flexibility. The Conical Mandrel Flexibility Test (FTMS 141, Method 6222), Table 8, was performed on 15 panels of 7075-T6 bare aluminum alloy which were 10 volt phosphoric acid anodized and electroprimed. After electropriming, one-third of the panels were spray primed with the MIL-P-23377 epoxy primer. Another set of five electroprimed specimens were primed with MIL-C-23377 epoxy primer and then sprayed with MIL-C-83286 aliphatic urethane topcoat. All of the test panels passed the flexibility test without loss of adhesion to the substrate or between the electroprimer and the spray applied MIL-C-23377 primer. Since the 7075-T6 aluminum alloy was used, approximately one-half of the panels were fractured in the 1/4-inch mandrel bend area without loss of adhesion interfacially or to the substrate (see Figure 1).

TABLE 8. PAINT SYSTEMS ASSESSMENT PLAN

Test	Test Specification	Primer		Top Coat MIL-C-83286	Number of Specimens	Comments
		Developed Electroprimer	MIL-P-23377			
Flexibility	FTMS 141	X			5	
	Method 6222	X	X		5	
		X	X	X	5	
Salt Spray (5% Fog)	FTMS 141	X			5	1000 hours Exposure to 5% salt fog at 95 F.
	Method 6061		X		5	
		X	X		5	
		X	X	X	5	
Humidity Exposure		X			5	1000 hours Exposure to 95-100% relative humidity at 140 F.
			X		5	
		X	X		5	
		X	X	X	5	
Note: All tests were conducted with 10 volt phosphoric acid anodized 7075-T6 bare aluminum alloy substrates.						

TABLE 9. PAINT SYSTEMS COMPATIBILITY, SA-6411 AND SA-6412
ELECTROPRIMERS, DETERMINED BY THE CONICAL MANDREL
FLEXIBILITY TEST (FTMS 141, METHOD 6222)

ELECTROPRIMER		SPRAY PRIMER	SPRAY TOPCOAT	NUMBER OF SPECIMENS	TEST RESULTS
SA-6411	SA-6412	MIL-P-23377	MIL-C-83286		
x				5	No evidence of loss of adhesion, chip- ping, cracking, or flaking of coatings when bent 180 de- grees over a con- ical mandrel in accordance with FTMS 141, Method 6222
x		x		5	
x		x	x	5	
	x			5	
	x	x		5	
	x	x	x	5	

NOTES: (1) Panels prepared with 10 volt phosphoric acid anodized 0.032 inch thick 7075-T6 bare aluminum alloy substrates.

(2) Average SA-6411 and SA-6412 electroprimer thickness was 0.0002 inch.

(3) Average MIL-P-23377 spray primer thickness was 0.0007 inch.

(4) Average MIL-C-83286 spray topcoat thickness was 0.0015 inch.

(5) Typical flexibility test specimens are shown in Figure 1.

TABLE 10. PAINT SYSTEM COMPATIBILITY, SA-6411 AND SA-6412 ELECTROPRIMERS, DETERMINED BY THE 1000 HOUR (FTMS 141, METHOD 6061) 5% SALT SPRAY EXPOSURE TEST

ELECTROPRIMER		SPRAY PRIMER	SPRAY TOPCOAT	NUMBER OF SPECIMENS	TEST RESULTS
SA-6411	SA-6412	MIL-P-23377	MIL-C-83286		
x				5	No evidence of corrosion, blisters, loss of adhesion or softening of the primer or top coat films was observed on any of these test panels.
		x		5	
x		x		5	
x		x	x	5	
	x			5	
	x	x		5	
	x	x	x	5	

NOTES: (1) Panels prepared with 10 volt phosphoric acid anodized 0.032 inch thick 7075-T6 bare aluminum alloy substrates.

(2) Average SA-6411 and SA-6412 primer thickness was 0.0002 inch.

(3) Average MIL-P-23377 spray primer thickness was 0.0007 inch.

(4) Average MIL-C-83286 spray topcoat thickness was 0.0015 inch.

(5) Typical salt spray test specimens are shown in Figure 2.

**TABLE 11. PAINT SYSTEMS COMPATIBILITY, SA-6411 AND SA-6412
ELECTROPRIMERS, DETERMINED BY THE 1000 HOUR HUMIDITY
EXPOSURE RESISTANCE TEST (FTMS 141, METHOD 6201)**

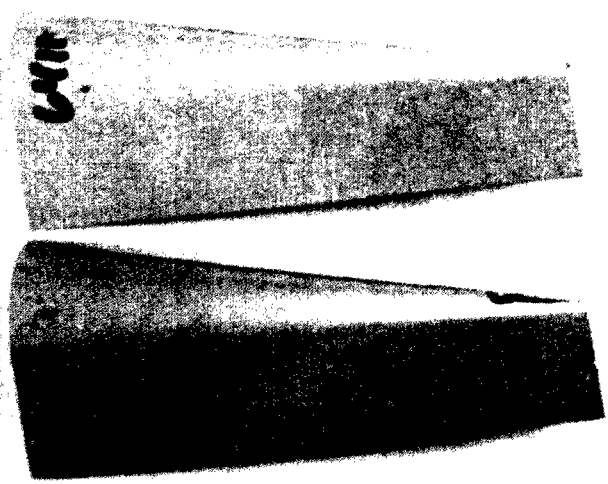
ELECTROPRIMER		SPRAY PRIMER	SPRAY TOPCOAT	NUMBER OF SPECIMENS	TEST RESULTS
SA-6411	SA-6412	MIL-P-23377	MIL-C-83286		
x				5	No film degrada- tion, softening, pinholes or corro- sion was observed on any of the test panels after 1000 hour exposure to 140F, 95% relative humidity exposure testing.
		x		5	
x		x		5	
x		x	x	5	
	x			5	
	x	x		5	
	x	x	x	5	

NOTES: (1) Panels prepared with 10 volt phosphoric acid anodized 0.032 inch thick 7075-T6 bare aluminum alloy substrates.

- (2) Average SA-6411 and SA-6412 primer thickness was 0.0002 inch.
- (3) Average MIL-P-23377 spray primer thickness was 0.0007 inch.
- (4) Average MIL-C-83286 spray topcoat thickness was 0.0015 inch.
- (5) Typical humidity exposure test specimens are shown in Figure 3.



SA 6411 PRIMER
+
MIL-P-23377 PRIMER
+
MIL-G-83286 TOPCOAT



SA 6411 PRIMER
+
MIL-P-23377 PRIMER

SA 6411 PRIMER

Figure 1. Flexibility Conical Mandrel Test Specimens, SA-6411 Electropimer,
(FTMS 141, (Method 6222)

The panel fracture is normal and was expected when using the 7075-T6 aluminum alloy in bending over the 1/4 inch mandrel. Normally the "O" condition material which would not fracture is used for the flexural tests, but in this program the 7075-T6 was exclusively used.

- B. Salt Spray Resistance. The 5 percent salt spray test (FTMS 141 Method 6061) was performed on the electrophrimers alone, and in combination with the MIL-P-23377 primer and MIL-C-83286 urethane topcoat as specified in Table 8. Test results are presented in Table 10, and representative specimens shown pictorially in Figure 2.

None of the electrophrimed or MIL-P-23377 control panels showed signs of corrosion after the 1000 hour exposure.

- C. Humidity Exposure Resistance. The 1000 hour exposure 140F, 95% humidity test was performed on the electrophrimers alone, and in combination with the MIL-P-23377 primer and MIL-C-83286 urethane topcoat as specified in Table 8. Test results are presented in Table 11 and representative specimens shown pictorially in Figure 3.

None of the electrophrimed or MIL-P-23377 control panels showed signs of degradation, softening or corrosion after the 1000-hour exposure.

2. Adhesive Bond Characteristics Evaluation. Table 12 defines the tests performed and the specimen configurations used to assess the performance of the SA-6411 and SA-6412 electrophrimers as adhesive bonding primers. The electrophrimers were compared to the control primer BR-127 in these tests. To ensure a valid comparative basis, all of the required test panels, electrophrimed and BR-127 control spray primed, were anodized simultaneously, bonded with the same lot and roll of FM-73 adhesive, and cured in a single lay-up. The bonded test panels were machined to test specimen configuration, and mechanical tested before and/or after environmental exposure as required by the test plan.

- A. Tensile Shear Strength Test. Table 13 gives the machined notch tensile shear strength test results obtained "as-fabricated" and after salt spray exposure using the SA-6411 and SA-6412 electrophrimers at test temperatures of -65F, ambient and 180F. The salt spray exposure was 1000 hours to 5 percent salt spray at 95F. Figure 4 shows typical fracture

SA 6411 PRIMER
+
MIL-P-23377 PRIMER
+
MIL-G-83286 TOPCOAT

SA 6411 PRIMER
+
MIL-P-23377 PRIMER

BR-127 CONTROL

SA 6411 PRIMER

PHOSPHORIC ACID
ANDDIZE 10 VOLT
7075-T6 BARE
1000 HOURS

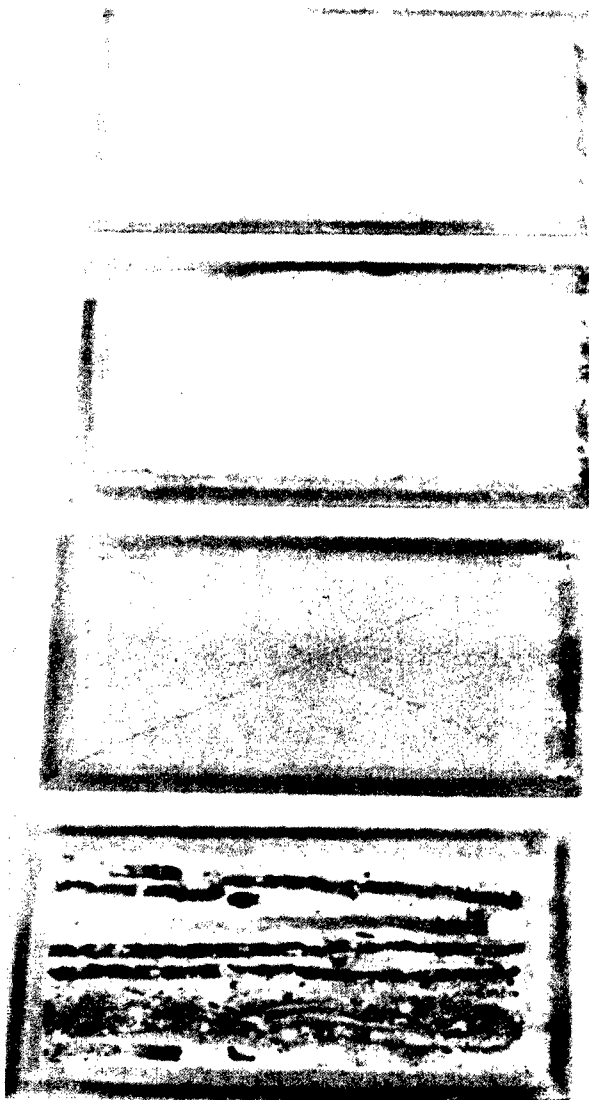
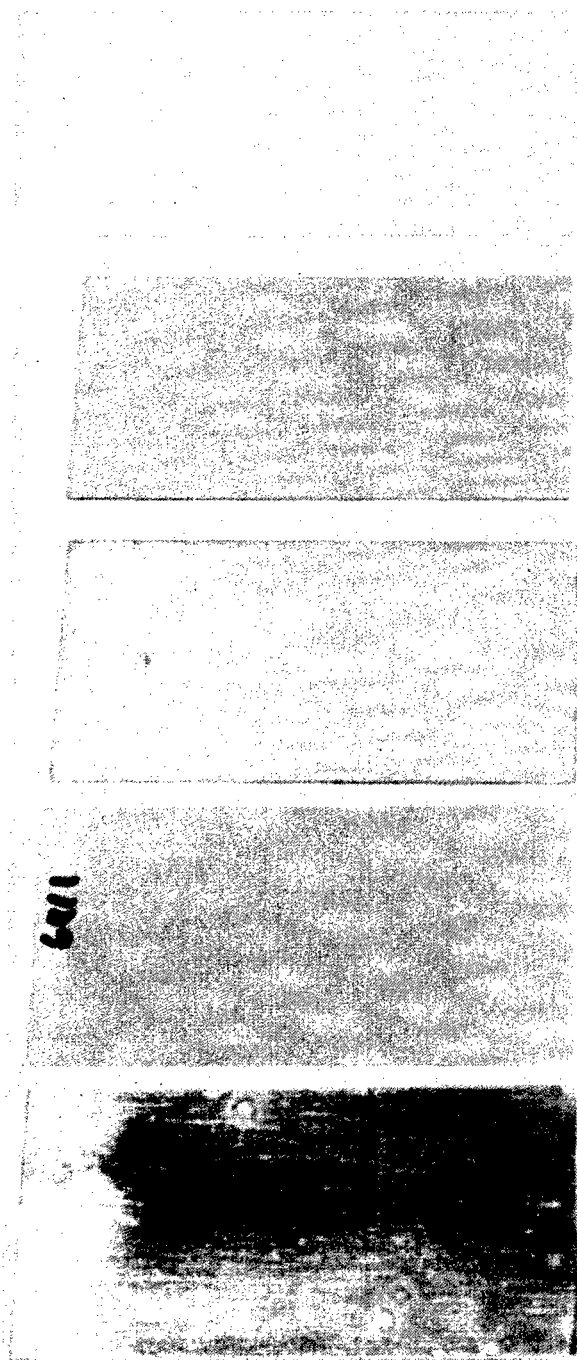


Figure 2. Salt Spray Exposure Test Specimens, (FTMS 141, Method 6061),
SA-6411 Electropimer



SA 6411 PRIMER
+
MIL-P-23377 PRIMER
+
MIL-G-83286 TOPCOAT

SA 6411 PRIMER
+
MIL-P-23377 PRIMER

BR-127 CONTROL

SA 6411 PRIMER

PHOSPHORIC ACID
ANDDIZE 10 VOLT
7075-T6 BARE
1000 HOURS

Figure 3. Humidity Exposure Resistance Test Specimens (1000 Hours at 140F/95% R. H.), SA-6411 Electropimer

TABLE 12. ADHESIVE BONDING ASSESSMENT PLAN

Test	Test Sequence	Test Specification	Test Temperature (F)			Environmental Exposure	Number of Specimens	Comments
			-65	Amb	180			
Tensile Lap-Shear	1	Machined Notch Tensile - Configuration in accordance with AFML TR-75-3 Figure 5	X			None	5	RT static test values to establish load requirements for stress durability test.
			X		None	5		
				X	None	5		
	2		X	X		1000 hours 5% Salt Spray, 95 F 1000 hours 5% Salt Spray, 95 F 1000 hours 5% Salt Spray, 95 F	5 5 5	Tensile lap-shear strength retention will be determined after 1000 hours environmental exposure.
Metal to Metal Peel	3	MMM-A-132	X	X		None None None	5 5 5	
Stress Durability	4	Ref: Mil-A-83377 Configuration in accordance with AFML TR-75-3, Figure 5	See environmental exposure			140 F, 95-100 Relative Humidity - Stress loaded to 40% RT ultimate lap shear tensile strength	10	Exposure time will be 1000 hours or failure, whichever occurs first. If specimens pass 1000 hours exposure, RT strength retention will be determined.
Notes: (1) All tests were conducted with 10 volt phosphoric acid anodized 7075-T6 bare aluminum alloy substrates, primed with the SA-6411 and SA-6412 electroprimers. (2) All test specimens were bonded with FM-73, 250F Curing adhesive. (3) Comparative baseline data for all of the above tests using BR-127 adhesive primer is available.								

TABLE 13. TENSILE SHEAR STRENGTH TEST RESULTS WITH FM-73 ADHESIVE OVER SA-6411 AND SA-6412 ELECTROPRIMERS AND BR-127 SPRAY PRIMER, DRY AND AFTER SALT SPRAY EXPOSURE

Test Temperature	Ultimate Tensile Strength (PSI)							
	SA-6411 Electroprimer			SA-6412 Electroprimer			BR-127 Spray Primer	
	As Fabricated	After 1000 Hrs 5% Salt Spray at 95F	% of Initial Strength Retained	As Fabricated	After 1000 Hrs 5% Salt Spray at 95F	% of Initial Strength Retained	As Fabricated	After 1000 Hrs 5% Salt Spray at 95F
-65F	8470	8440	100	9030	8820	100	8440	---
	8350	8220		8860	8800		8420	
	8850	8720		8380	8550		8480	
	8390	8610		8750	9080		8750	
	8740	8960		8760	8820		8600	
Ambient	Avg 8560	Avg 8590	96	Avg 8760	Avg 8810	97	Avg 8550	98
	5550	5200		5530	5580		5420	
	5960	5400		5420	5230		5120	
	5490	5460		5480	5420		5320	
	5300	5660		5380	5370			
180F	5550	5250	99	5500	5150	99		100
	Avg 5610	Avg 5390		Avg 5460	Avg 5310		Avg 5290	
	4540	4230		5030	4740		4850	
	4850	4610		4630	4640		4600	
	4180	4850		4560			4500	
	4600	4080		5130				
	4450	4610		4580				
	Avg 4520	Avg 4480		Avg 4790	Avg 4690		Avg 4650	

NOTES: (1) Specimen configuration: Machined Notch Tensile Specimen, Appendix D, Figure D-3.

(2) Average bond line thickness was 0.013 inch.

(3) Specimens prepared with 10 volt phosphoric acid anodized 7075-T6 bare aluminum alloy substrates.

(4) Average SA-6411 and SA-6412 electroprimer film thickness was 0.0002 inch.

(5) All failure modes were cohesive (within the adhesive) both "dry" and after salt spray exposure.

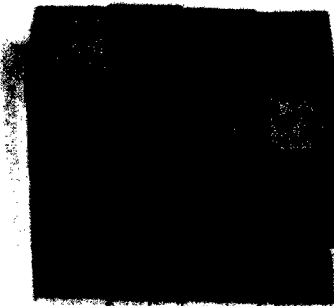
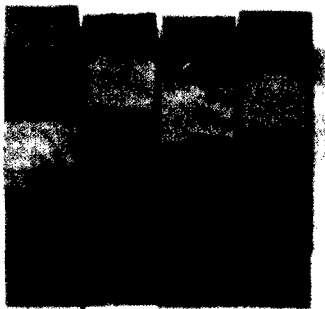
SA 6412
PRIMER



SA 6411
PRIMER



180°F



RT



-65°F

TENSILE SHEAR FM-73 FILM ADHESIVE

Figure 4. Tensile Shear Strength Test Specimens, SA-6411 and SA-6412
Electroprimers, at -65F, RT, and 180F

modes of the tensile test specimens. All failures were 100 percent cohesive. Results are equivalent to data obtained using the BR-127 control primer. The sample lot size was five specimens. Data indicate that the specimens made with the SA-6411 and SA-6412 electroprimers are equal in strength to those made with BR-127 and the salt spray exposure has essentially no degradative effect on the bonds made with the electroprimers.

- B. Metal/Metal T-Peel Strength Test. Table 14. gives the metal/metal T-Peel strength test results at -65F, ambient and 180F on 7075-T6 bare aluminum. All failures were 100 percent cohesive. Typical fracture modes are shown pictorially in Figure 5. The T-Peel strength for both the electroprimers at RT and 180F is somewhat higher than the BR-127. At -65F, the SA-6411 is equal to BR-127 and the SA-6412 is slightly lower. However, since all fracture modes were 100 percent cohesive, the electroprimers are considered to be equivalent to the BR-127 baseline control.
- C. Tensile Shear Stressed Durability Test. Table 15 gives the stressed durability test results on machined notch tensile shear specimens made using SA-6411 and SA-6412 electroprimers. Specimens were stressed to 40 percent of ambient ultimate strength and exposed for 1000 hours to 140F condensing humidity. No failures occurred during the 1000 hour exposure and room temperature residual strengths after the 1000 hour exposure were 100 percent of the initial control strengths. No degradation in strength of the bonds was caused by the stressed/humidity/temperature exposure. The SA-6411 and SA-6412 electroprimers performed equivalent to the control primer, BR-127, in these tests.

PHASE 4 — ASSESS COST/UNIFORMITY/REPRODUCIBILITY

Cost Assessment

The cost assessment had the following objectives:

- 1) Assess the adaptability of the contract SA-6411 and SA-6412 electroprimers to automated processing.
- 2) Estimate the present application cost of the BR-127 primer.
- 3) Estimate the costs of an automated application of the electroprimer and compare to the BR-127.

TABLE 14. METAL/METAL T-PEEL STRENGTH TEST RESULTS WITH FM-73 FILM ADHESIVE OVER SA-6411 AND SA-6412 ELECTROPRIMER AND BR-127 SPRAY PRIMER

Test Temperature (F)	Electroprimer				Control Primer	
	SA-6411		SA-6412		BR-127	
	Pounds/Inch Width	Failure Mode	Pounds/Inch Width	Failure Mode	Pounds/Inch Width	Failure Mode
-67	10.5	All	6.0	All	7.5	All
	7.5	Failures	5.5	Failures	8.0	Failures
	6.0	100%	6.0	100%	8.5	100%
	5.5	Cohesive	5.0	Cohesive	5.5	Cohesive
	Avg 7.1		Avg 5.6		Avg 7.4	
RT	16.0	All	14.5	All	14.5	All
	17.5	Failures	18.0	Failures	14.0	Failures
	19.0	100%	16.0	100%	16.0	100%
	18.0	Cohesive	18.5	Cohesive		Cohesive
	Avg 18.1		Avg 17.5		Avg 14.8	
180	40.0	All	31.0	All	20.0	All
	37.3	Failures	37.0	Failures	35.0	Failures
	34.5	100%	35.0	100%	29.0	100%
	34.0	Cohesive	36.0	Cohesive		Cohesive
	Avg 37.4		Avg 34.5		Avg 28.0	

NOTES: (1) Specimen configuration: T-Peel Test Specimen, Appendix D, Figure D-4.

(2) Average bond line thickness was 0.013 inch.

(3) Specimens prepared with 10 volt phosphoric acid anodized 7075-T6 bare aluminum substrates.

(4) Average SA-6411 and SA-6412 electroprimer film thickness was 0.0002 inch.

(5) Average BR-127 primer thickness was 0.0001 inch.

(6) All failure modes were cohesive (within the adhesive).

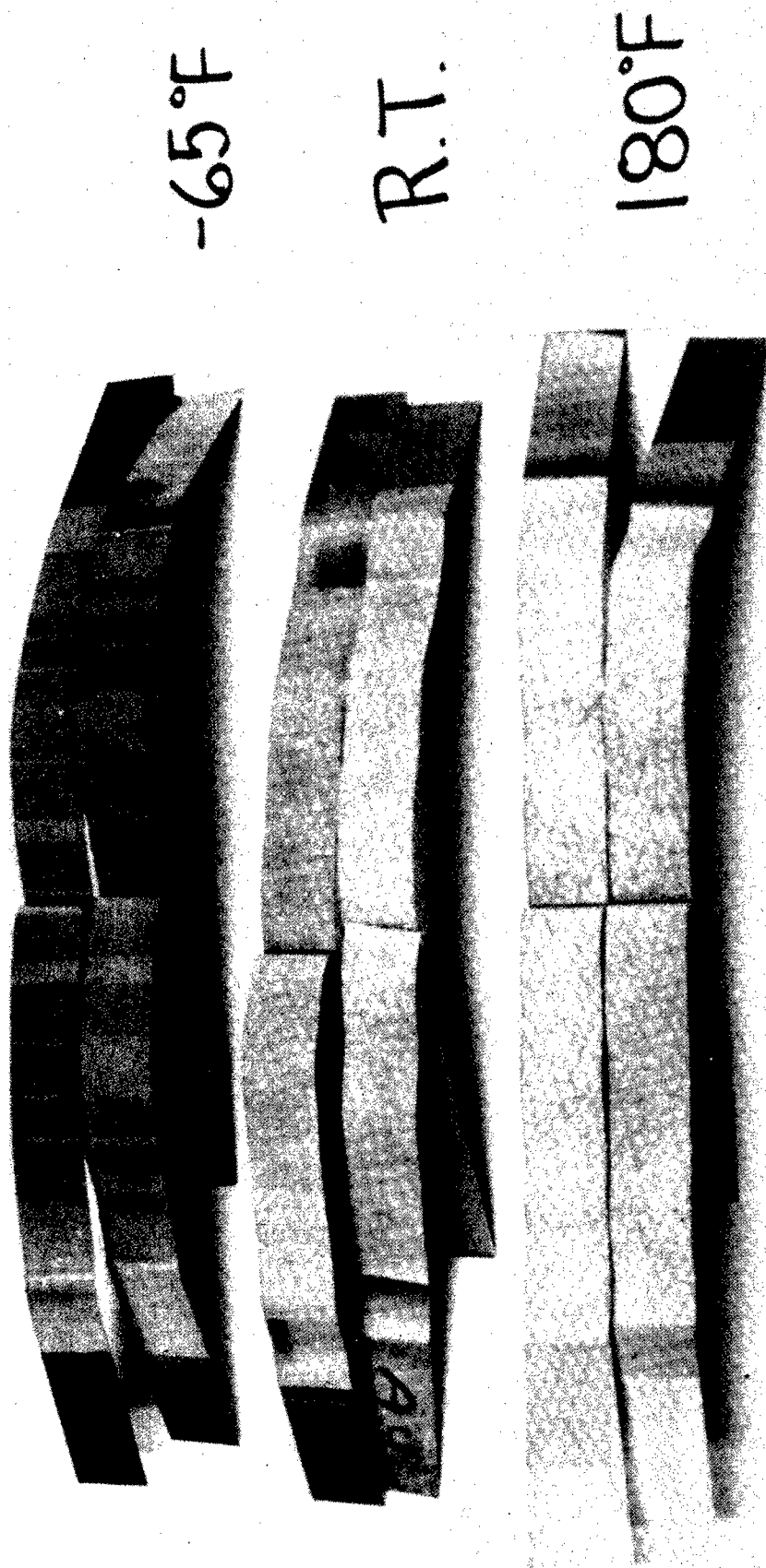


Figure 5. Metal/Metal T-Peel Strength Test Specimens, SA-6412 Electroprimer on 7075-T6 Bare Aluminum, at -65F, RT, and 180F

**TABLE 15. TENSILE SHEAR STRESSED DURABILITY TEST RESULTS
WITH FM-73 FILM ADHESIVE OVER SA-6411 AND SA-6412 ELECTROPRIMERS
AND BR-127 SPRAY PRIMER**

Electro- primer	*Average Initial Tensile Strength (psi)	Load (lbs)	Stress Exposure (Percent RT Ultimate)	Environ- mental Exposure Conditions	Time To Failure (Hrs)	Residual Strength (psi)	Percent Residual Strength	Failure Mode
SA-6411-1	5610	1120	40	140F, Condensing Humidity	No Failure in 1000 Hours	6150	108	All Failures 100% Cohesive
SA-6411-2	5610	1120	40			5820	102	
SA-6411-3	5610	1120	40			6110	107	
SA-6411-4	5390	1080	40			6580	122	
SA-6411-5	5390	1080	40			6720	125	
SA-6411-6	5390	1080	40			<u>6400</u>	<u>119</u>	
						Avg 6290	Avg 114	
SA-6412-1	5460	1090	40	140F, Condensing Humidity	No Failure in 1000 Hours	6150	109	All Failures 100% Cohesive
SA-6412-2	5460	1090	40			5900	106	
SA-6412-3	5460	1090	40			6100	108	
SA-6412-4	5310	1060	40			6060	114	
SA-6412-5	5310	1060	40			5970	112	
SA-6412-6	5310	1060	40			<u>6020</u>	<u>113</u>	
						Avg 6030	Avg 110	
BR-127-1	5290	1060	40	140F, Condensing Humidity	No Failure in 1000 Hours	6280	119	All Failures 100% Cohesive
BR-127-2	5290	1060	40			5920	112	
BR-127-2	5290	1060	40			<u>6120</u>	<u>116</u>	
						Avg 6170	Avg 118	

NOTES: (1) Specimen Configuration: Stressed Durability Tensile Shear Test Specimen, Appendix D, Figure D-2.

(2) Average bond line thickness was 0.013 inch.

(3) Specimens prepared with 10 volt phosphoric acid anodized 7075-T6 bare aluminum alloy substrates.

(4) Average SA-6411 and SA-6412 electroprimer film thickness was 0.0002 inch.

* Average of five specimens tested at RT, "as-fabricated," dry.

This study uses as a baseline a 1976 Northrop engineering assessment of the electroprime process which determined the feasibility and cost effectiveness of installing an automated electroprime line to prime aluminum detail parts for corrosion protection with and without subsequent topcoats. The engineering assessment recommended the procurement and installation of an electropriming facility with a projected savings of 2.0 million dollars based on a 7-year amortization period with a 2.2-year pay-back.

The recommended complete installation, all costs included, was estimated at \$622,000. The assessment was based on the flow of aluminum parts 24-inch wide by 48-inch long or smaller. Larger aluminum parts were not considered in the study. The selection of aluminum parts represents 83 percent of the Northrop parts using the NAI-1269* primer and approximated 46,000 parts per week. Parts handling methods for cleaning, alodining, and top coating were compared to those proposed for an electroprime facility. Labor content of the present and proposed methods were compared and a summary of the labor savings given. Material cost reductions made possible by the electroprime process were documented. The major material savings resulted from reduction in the amount of primer used, since electropriming can maintain a controlled film thickness of 0.0002 inch, and eliminates losses due to over-spray.

Figure 6 shows the proposed process sequence of the automated electropriming line for priming detail aluminum parts for corrosion protection. This line utilizes the Northrop NAI-1414 (Northrop Materials Specification) cathodically applied modified epoxy electroprimer for corrosion protection. It is chemically and functionally distinct from the modified epoxy electroprimers SA-6411 and SA-6412 and serves only as a corrosion inhibiting primer.

Variations of the sequence shown in Figure 6 are in use in the aircraft industry today. These variations in surface preparation include acidified and deionized rinses. The electropriming stage is a total immersion application requiring an approximate 60-second application time with a 2-3 minute rinse and a 30-minute curing cycle. To adapt the electroprimer for adhesive bonding requires the addition of a phosphoric acid anodizing capability shown by the dotted line in Figure 6.

The engineering study performed by Northrop compared the cost of handspraying a corrosion protection primer to automated application of an electroprimer which serves as the comparative basis for estimating the application costs of BR-127.

*Northrop Materials Specification, "Fluid Resistant Catalyzed Primer."

The recurring cost differential, or potential yearly savings, amounts to \$425,000 (see Table 16), based on a load of approximately 46,000 parts per week. Based on estimates used in the referenced study, approximately \$622,000 would be required to install an electropriming system capable of treating up to 46,000 parts per week. The maximum part size would be 48 inches in length and 24 inches in width.

In summary, a projected annual savings of \$425,000 (based on 1976 dollars) can be realized utilizing the contract developed electroprimer compared to the conventional hand sprayed BR-127. An investment of approximately \$622,000 would be required to implement a completely automated cathodic electropriming facility.

Uniformity and Reproducibility Assessments

To comparatively evaluate the hand-spray application method of priming versus the electropriming application method for uniformity and reproducibility, a fairly simple part configuration was designed. A sketch of the part is presented in Figure 7. Eight specimens of this configuration were fabricated. Four of the specimens were hand sprayed with BR-127 adhesive primer in a production priming facility on four different days, and four were electroprimed in the laboratory's 3-gallon electropriming cell. Results of this comparative study are presented in Table 17.

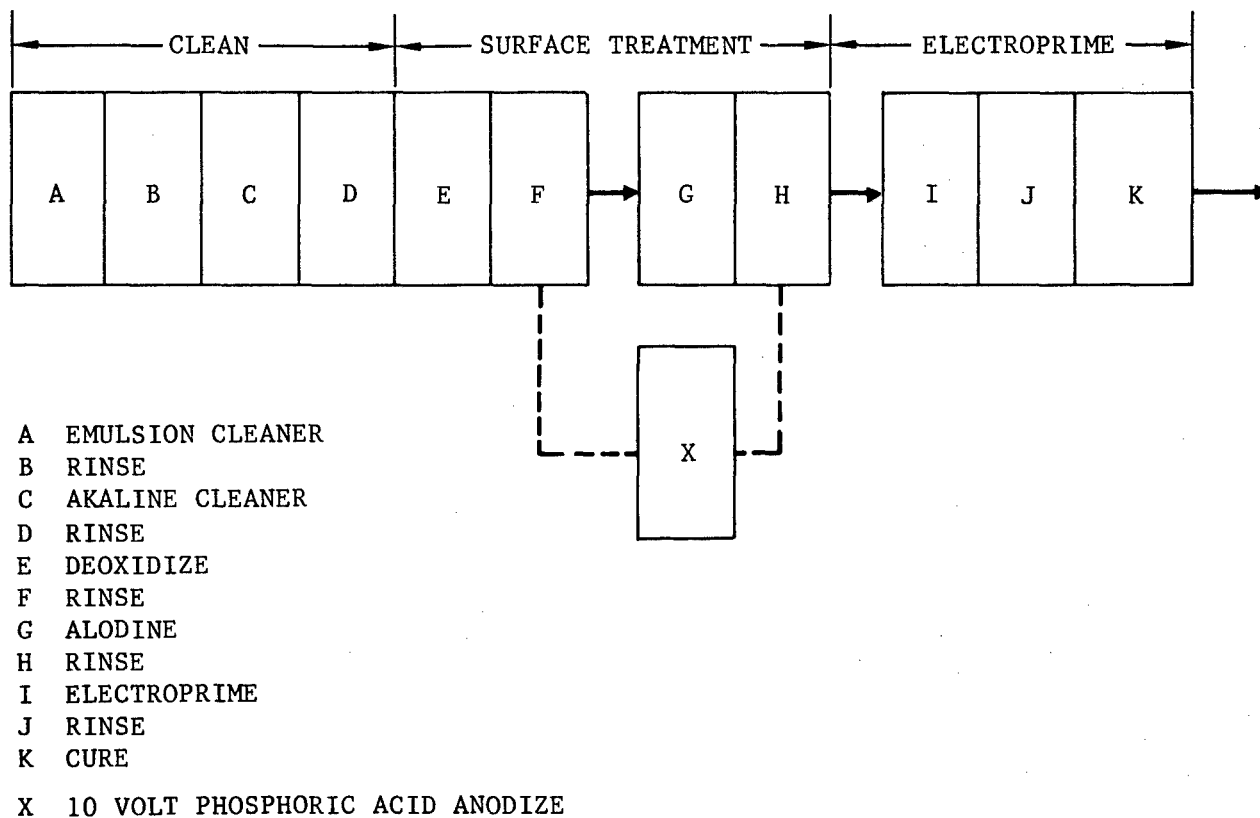
The test data show that all specimens meet the average adhesive primer film thickness requirement of 0.1 - 0.3 mil. However, out of 120 thickness determinations taken on the hand sprayed specimens, 28 individual readings were beyond the required 0.1 - 0.3 mil range (8 determinations below and 20 determinations above the designated range). All film thickness determinations on the electroprimed specimens fell well within the required range. The areas on hand sprayed substrates which are most likely to be out of the tolerance range are the edges and corners, areas A and C in Figure 7, whether the part be of flat stock or compound curvature. This is due to the airflow pattern of the sprayed material around the parts being coated. The film thickness is generally high in those areas close to the edges and minimum in interior angle areas. The electroprimer is far superior in reproducibility even though both methods (electropriming and hand spraying) are acceptable. The controlling factor for film thickness in the electropriming process is the applied potential. For this assessment, a 30 volt potential was used. The film can be reproduced by any operator using the 30 volt application potential.

The electroprimed process can be further controlled by "locking in" the 30 volt application potential on the control panel. In hand sprayed primers, day-to-day reproducibility is operator-dependent and is a developed art.

TABLE 16. RECURRING COST ESTIMATES* OF HANDSPRAYED BR-127
AND AUTOMATED ELECTROPRIMING

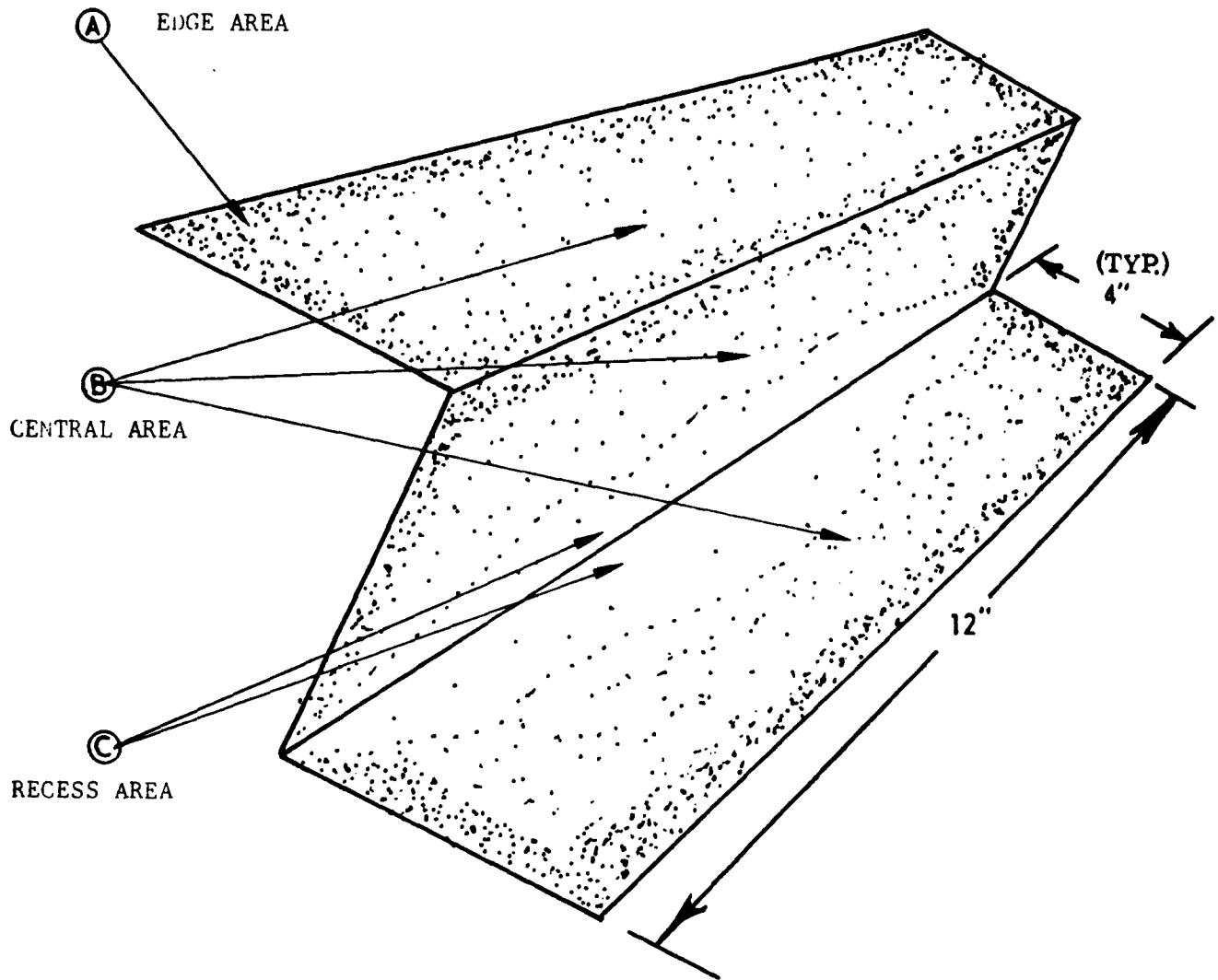
COST AREA	APPLICATION METHOD	
	BR-127 LINE (HANDSPRAYED)	ELECTROPRIME LINE (AUTOMATED)
Base Labor Costs	\$ 800,000	\$535,000
Base Material Costs	200,000	80,000
Base Energy Cost	70,000	30,000
Total Base Cost	\$1,070,000/Year	\$645,000/Year

*Assuming 46,000 parts per week primed.



NOTE: To utilize the above electroprime process line with the SA-6411 or SA-6412 electroprimer for adhesive bonding, tank G (alodine) must be replaced with tank X, (10 volt phosphoric acid anodize).

Figure 6. Proposed Northrop NAI-1414 Electroprime Process Line



ELECTROPRIME METHOD	HAND SPRAY METHOD
(A) Uniform Primer Applied	Excess Primer Applied
(B) Uniform Primer Applied	Average Primer Applied
(C) Uniform Primer Applied	Minimal Primer Applied

Figure 7. Specimen Configuration for Uniformity and Reproducibility Assessment

**TABLE 17. UNIFORMITY AND REPRODUCIBILITY ASSESSMENT
TEST RESULTS FOR HAND SPRAYED VERSUS
ELECTROPRIMED SUBSTRATES**

SPECIMEN	PRIMER	PRIMER THICKNESS (mil)			
		HIGH	LOW	RANGE	AVERAGE
<u>Hand Sprayed</u>					
1	BR-127	0.30	0.04	0.26	0.15
2	BR-127	0.28	0.05	0.23	0.17
3	BR-127	0.35	0.02	0.33	0.20
4	BR-127	0.35	0.02	0.33	0.20
<u>Electroprimed</u>					
1	SA-6411	0.21	0.13	0.08	0.16
2	SA-6411	0.19	0.12	0.07	0.15
3	SA-6411	0.19	0.12	0.07	0.15
4	SA-6411	0.22	0.13	0.09	0.16

NOTES: (1) Panels prepared with 10 volt phosphoric acid anodized 0.032 inch 7075-T6 bare aluminum alloy substrates.

(2) Primer thickness measurements were made with a Model EC-3-Ta Perma-scope, manufactured by Twin City Testing Corporation, Tonawanda, N. Y.

Specification thickness range for the BR-127 adhesive primer is 0.1 to 0.3 mil. The acceptable thickness range for the SA-6411 electroprimer has not been established, therefore a thickness approximately midway in BR-127 range was selected for the uniformity and reproducibility assessment. It is also the thickness used for the overall assessment tests in Phase 3 of the test program. The SA-6411 electroprimer can easily be deposited in the range of 0.1 to 0.8 mil, but there are indications that the adhesive bonding performance of the electroprimers may be thickness sensitive above 0.5 mil. (Reference Table E-10.)

PHASE 5 — ECOLOGICAL ASSESSMENT

The electropriming process is the most efficient method for applying primers relative to material usage. All of the priming material put into the electropriming process tank is utilized for coating the hardware. Even the small amount of "drag-out" from the priming tank is reclaimed for usage. This "drag-out" is thoroughly removed in the post electroprime rinse stage, and the rinse water is cycled through membrane filters to remove the priming material which is then pumped back into the electropriming tank. It is conservatively estimated that the electroprime process is 99% material efficient.

Comparatively, the current state-of-the-art method of handspraying primers is inefficient in that 50% of all material emanating from the spray gun is lost in overspray. Added to this loss is the solvent release from the material applied to the hardware which amounts to 50% of the applied material. The net result is that hand-sprayed primers are 25% efficient relative to material usage.

Based on the Northrop cost study discussed in Phase 4, the savings in materials using the electropriming process takes on real significance. In 1974, Northrop sprayed approximately 25,000 gallons of primer on hardware with a major dimension of 48 inches. At a 25% efficiency, 6,250 gallons were delivered with the hardware, and 18,750 gallons were lost in overspray and solvent evaporation during film cure. At an average of 10.5 pounds/gallon, 196,875 pounds or 98.5 tons of material were lost in the priming operation. In addition 5,500 gallons of clean-up solvent were used (primarily MEK). A grand total of pollutants in excess of 100 tons were added to the environment.

From an ecological standpoint, a very small percentage of material is expelled into the atmosphere by the electropriming process and, since the system is water-based, the atmospheric contamination by the process is insignificant. Further, the water base electroprimer contains no chromates which eliminates a material manufacturing problem and a users disposal problem.

AFML Contract Samples — Wedge Crack Extension Durability Test Specimens

At the request of the AFML project monitor, a wedge crack extension durability test in sea coast exposure was run in addition to the tests required and outlined in Table 6. Table 18 gives the wedge crack extension durability results on specimens made using the SA-6166, SA-6300, SA-6410, SA-6411, SA-6412, and SA-6413 electroprimers. The SA-6166 and SA-6300 electroprimers were developed early in the contract and have been exposed for a longer time than the SA-6410, SA-6411, SA-6412 and SA-6413 electroprimers. No crack growth (zero crack extension) was noted in any of the specimens after 120 days exposure to sea coast environmental conditions at El Segundo, California.

TABLE 18. AFML CONTRACT SAMPLES — WEDGE CRACK EXTENSION DURABILITY TEST RESULTS WITH FM-73 FILM ADHESIVE OVER SA-6166, SA-6300, SA-6410, SA-6411, SA-6412, AND SA-6413 ELECTROPRIMERS, SEA COAST EXPOSURE

ELECTROPRIMER	NUMBER OF SPECIMENS	WEDGE CRACK EXTENSION (INCHES) AT VARIOUS TIME INTERVALS (DAYS)						
		30	60	90	120	150	180	240
SA-6166	5	0	0	0	0	0	0	0
SA-6300	5	0	0	0	0	0	0	0
SA-6410	5	0	0	0	0	0	0	0
SA-6411	5	0	0	0	0	0	0	0
SA-6412	5	0	0	0	0	0	0	0
SA-6413	5	0	0	0	0	0	0	0

- NOTES: (1) Specimen Configuration — Standard Wedge Test Specimen, Appendix D, Figure D-1.
- (2) Average bond line thickness was 0.013 inch.
- (3) Specimens prepared with 10 volt phosphoric acid anodized 7075-T6 bare aluminum substrates.
- (4) Average SA-6411 and SA-6412 electroprimer film thickness was 0.0002 inch.

SECTION III
CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE WORK

CONCLUSIONS

- (1) The electroprimers SA-6411 (AF-C-5050-11) and SA-6412 (AF-C-5050-12) were developed that cure at 220F in 30 minutes.
- (2) The SA-6411 and SA-6412 electroprimers perform equivalent to the BR-127 control baseline in adhesive bonding of 7075-T6 aluminum in -65F, RT, and 180F tensile shear and T-Peel tests and in wedge crack extension tests on exposure to 120F/95% R. H.
- (3) The SA-6411 and SA-6412 electroprimers are compatible with the current state-of-the-art military paint primers (MIL-P-23377) and topcoats (MIL-C-83286).
- (4) The SA-6411 and SA-6412 electroprimers provide uniform ($\pm$.0001 inch thick), reproducible films on all surfaces and complex shapes including surfaces that are inaccessible to spray application.
- (5) The electropriming process is a cost effective process. Total priming is complete in 30 seconds at 30 volts.
- (6) The electroprimers developed are water base, nonchromated materials, and are ecologically preferred to solvent base primers.

RECOMMENDATIONS FOR FUTURE WORK

Based on the encouraging results of this test program, the following recommendations for future work are made:

- (1) Develop the manufacturing technology required for application of the electropriming process to aircraft fabrication, maintenance and repair.
- (2) Develop methods for electropriming honeycomb core to provide a complete corrosion resistant adhesive bonded aluminum structure.

- (3) Generate data base to characterize SA-6411 and SA-6412 electroprimers for use as primers for corrosion protection, paint bases, and adhesive bonding.
- (4) Develop electroprimers for 350F curing (250F service temperature) modified epoxy adhesives.
- (5) Develop field repair procedures for electropriming.

APPENDIX A

DEFINITION OF TERMS

CATALYST — A substance added to a reaction mixture to promote the chemical change, and to affect the rate of reaction. The catalyst can cause the reaction to be initiated at lower temperatures, lower pressures, or in shorter times. The catalyst is not consumed, is not a component of the chemical reaction (change) and does not form an integral part of the reaction products.

COALESCENCE (FILM) — The ability of the deposited resin to flow after deposition and provide a continuous, uniform film.

COALESCING SOLVENT — An organic solvent, soluble in the organic phase of the electroprime bath, which provides film coalescence. The coalescing solvent evaporates from the film during cure, and therefore is not an integral part of the cured system.

CROSSLINKER — A chemically reactive monomer which, in the presence of the resin monomer under reactive conditions (temperature, etc.), will combine with the monomer to interlink carbon chains ("crosslink") and form a macromolecule (polymer). Thus, the crosslinker is a partner in the reaction and is an integral part of the product formed.

APPENDIX B

MECHANISM OF FILM FORMATION

AND SCHEMATIC DIAGRAM OF CATHODIC ELECTROPRIMING

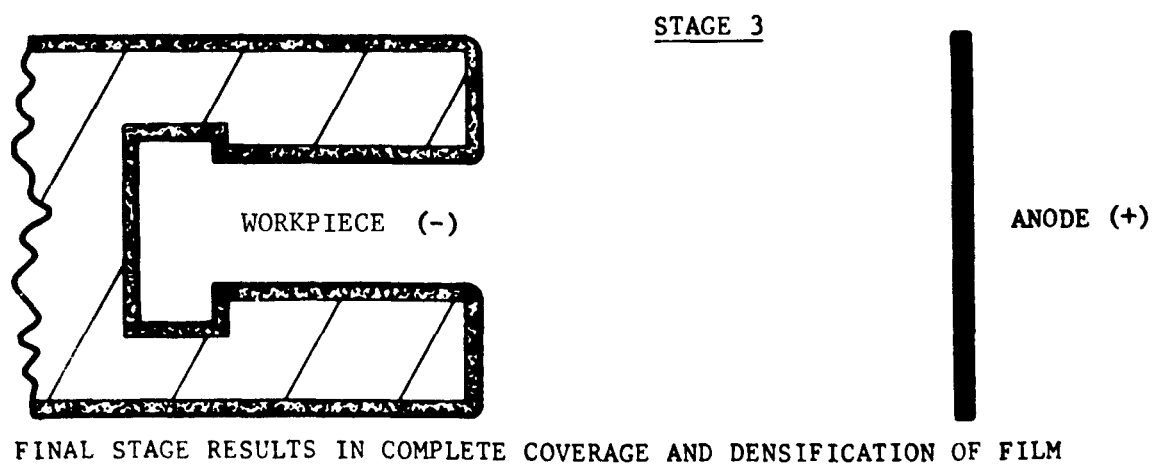
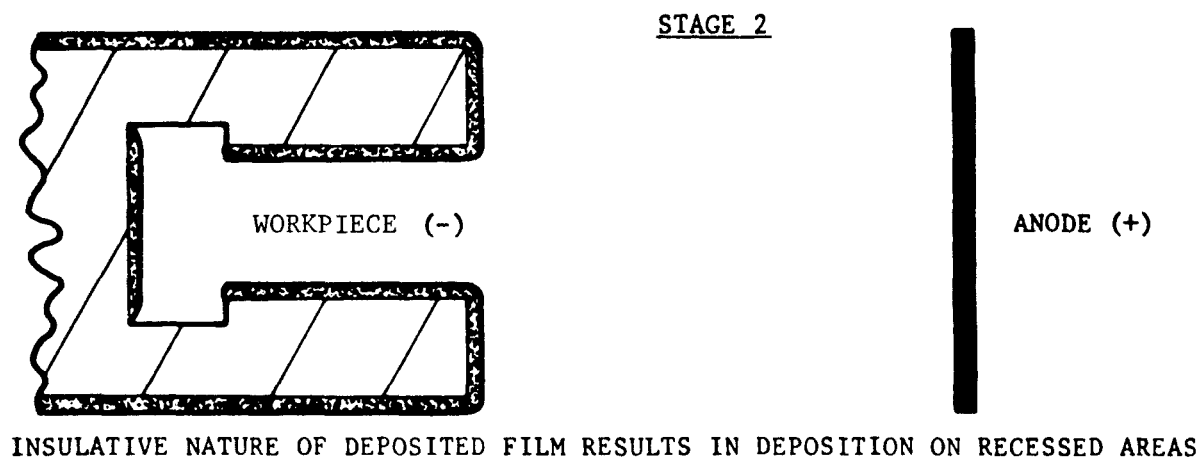
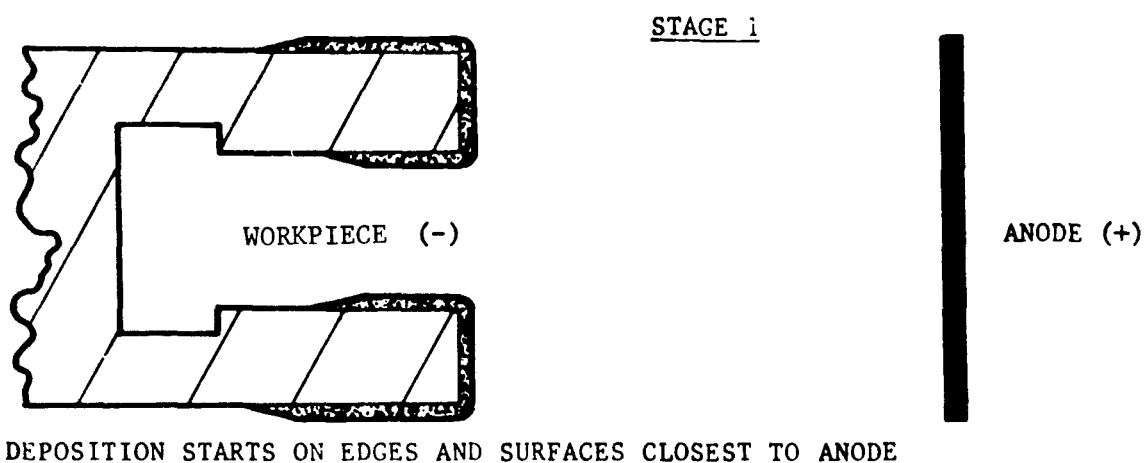
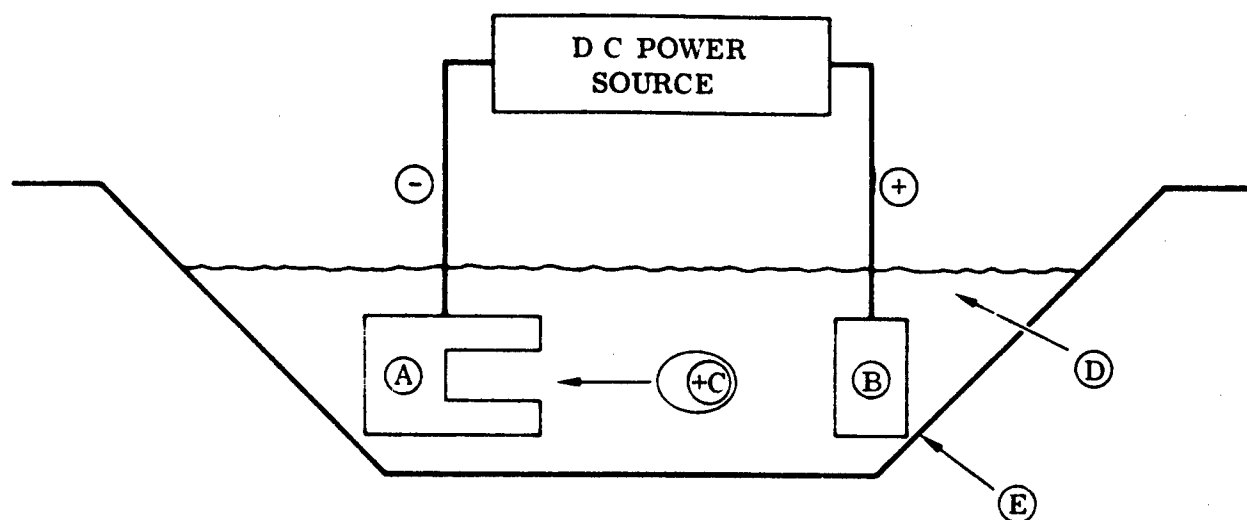


Figure B-1. Mechanism of Film Formation on Irregular Surfaces



- (A)- WORKPIECE - CATHODE (-)
- (B)- AUXILIARY - ANODE (+)
- (C)- ELECTROPRIME RESIN
- (D)- WATER DISPERSION OF RESIN SYSTEM
- (E)- ELECTROPRIMING TANK

Figure B-2. Schematic Diagram of Cathodic Electropriming

APPENDIX C

CURE SCREENING TESTS

MESERAN EVALUATION — The Meseran cure test unit senses radioactive carbon.

The panels are electroprimed and cured. An indentation in the panel is made to accommodate a sample of volatile radioactive solvent. A stream of nitrogen is passed over the solvent and a counter/detector registers the time of dissipation of the solvent. The time of solvent dissipation is inversely proportional to completeness of cure of the resin; zero time is 100% cure.

MEK RUB TEST — The MEK rub test is accomplished by saturating (dripping) a piece of cheesecloth with MEK and vigorously rubbing the primer film with an approximate 3 inch forward and reverse stroke to determine if breakthrough or removal of the film can be achieved. One forward and reverse rub is counted as one stroke. "Pass" condition is defined as no breakthrough of the film in 100 strokes. Slight discoloration of the cheesecloth is not considered as film failure.

APPENDIX D

TEST SPECIMEN CONFIGURATIONS AND ADHESIVE ADHESIVE BONDING LAY-UP AND CURE CONTROL

SPECIMEN LAY-UP PROCEDURE FOR ADHESIVE BONDING

The primed and cured panels were assembled into pairs using one layer of FM-73-15, 0.085 psf film adhesive applied to one faying surface of one panel for each pair. The faying surfaces of each pair were mated carefully to avoid entrapment of air in the bondline. Care was taken to insure that the paired adherends were matched and square, i.e., the edges were aligned without overlaps. Thermocouples were installed into the bondline and taped to prevent pull out. One layer of nonporous Teflon release film (Armalon) was placed over the assembled panels. Three layers of vacuum transfer cloth were applied in the same manner. The assembled panels were placed into a nylon vacuum bag with a vacuum source and sealed. The vacuum bag was leak checked before autoclave cure.

ADHESIVE CURE CONTROL FOR BONDED SPECIMENS

All adhesive cures of test specimens were accomplished in a 5 foot diameter autoclave equipped with Research Inc. Data Trak programmers. The Data Trak programmers provide automatic temperature and pressure control. A programmed standard heat up rate of 3-5°F/minute was used for all adhesive cures. All adhesive bonds were maintained at the required adhesive cure temperature for 90 minutes with 40 psi augmented pressure, and the vacuum bag vented to atmosphere. The cool down rate to 150°F was 8-10 °F/minute before venting augmented pressure. The programmed Data Trak cure cycle was used on all contract adhesive cures to insure uniformity of the bonding process throughout the work effort.

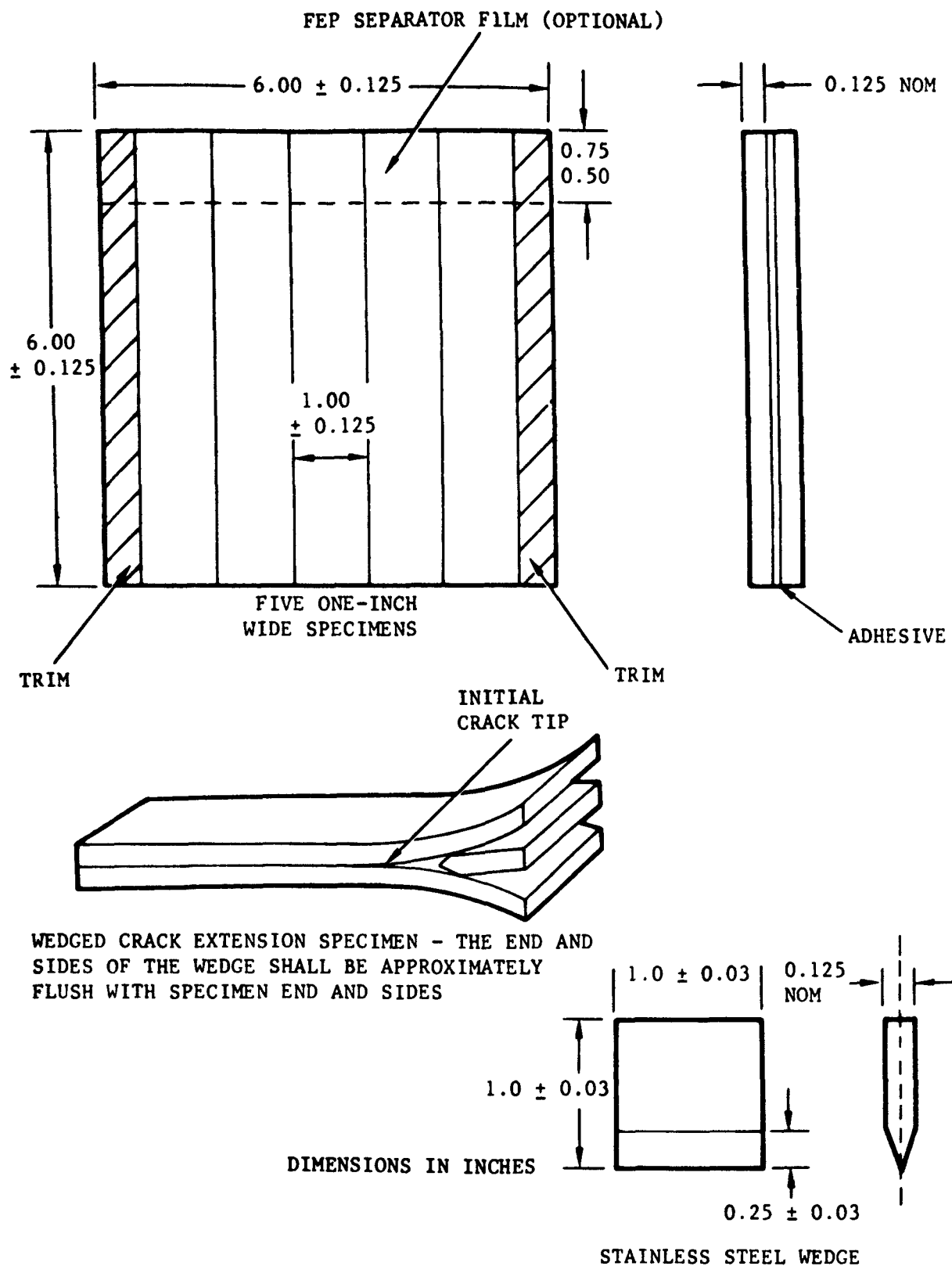
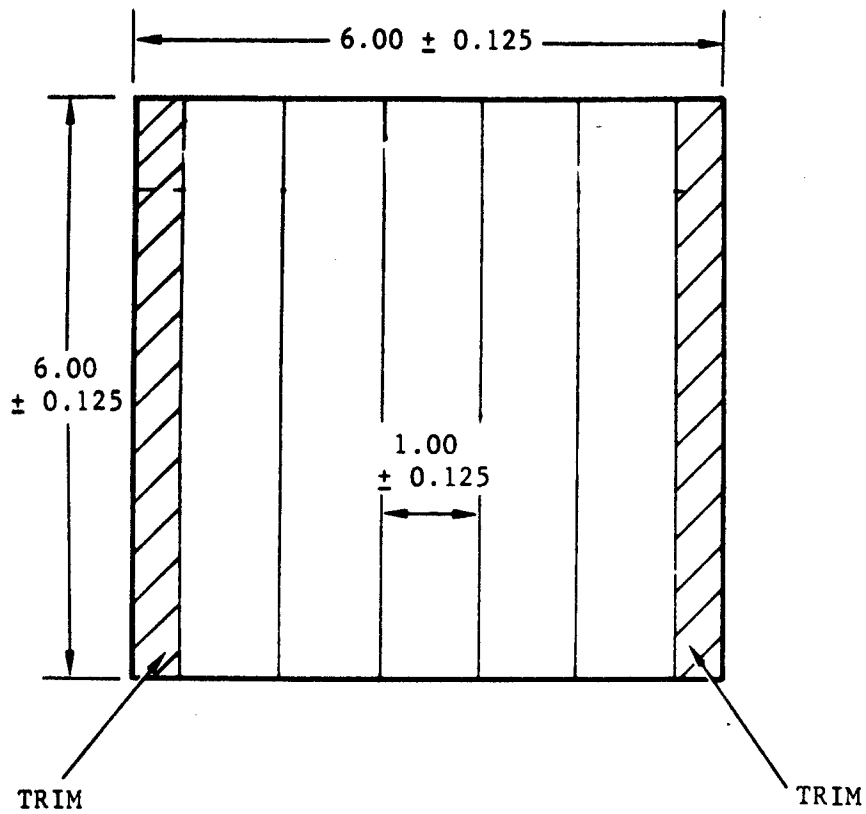


Figure D-1. Standard Wedge Test Panel and Coupon



DIMENSIONS IN INCHES

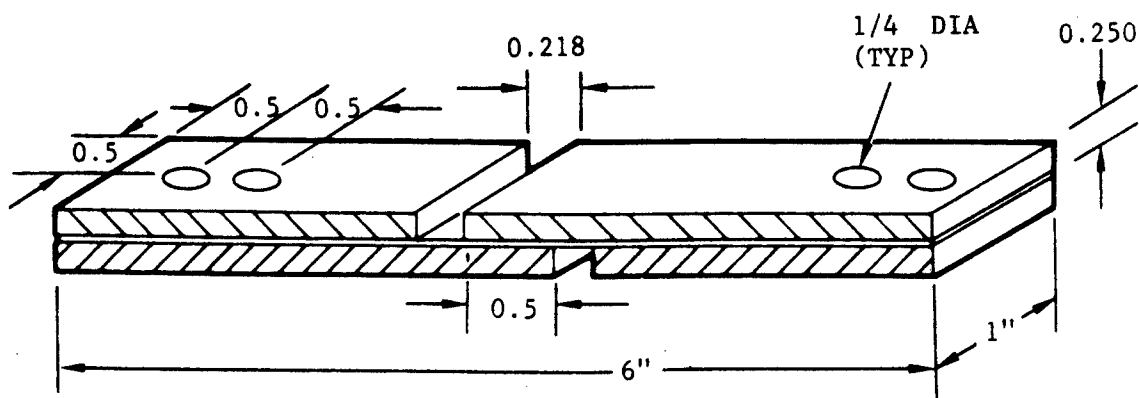


Figure D-2. Thick Adherend Tensile Shear Specimen

APPENDIX E

DETAILS OF PHASE 1 AND PHASE 2 DEVELOPMENTS

This section contains the development work performed in Phases 1 and 2 which lead to the selection of the SA-6411 and SA-6412 electroprimers for evaluation in the remaining phases of the contract. Only the data on the final series, SA-6410 through SA-6413, are presented in Section 2 of this report. All other prior development work under this contract is presented in this Appendix.

PHASE 1 — DEVELOP 250F CURE ELECTROPRIMER

Formulate and Compound Candidate Crosslinkers

In formulating the 250F curing modified epoxy electroprimer, several technical aspects were considered:

1. For an established base resin system, a specific crosslinker may be identified which can provide the required 250F cure response. However, some polymerization will occur in the ED bath and will produce deposited resin films with an increasing polymer/monomer species ratio as the ED bath ages. This premature partial polymerization of the most reactive functional groups will produce a deposited resin film requiring higher temperatures to complete the polymerization of the secondary reactive functional groups. Since the original total functionality available is diminished, the crosslink mechanism and resultant polymer structure of the film will change, resulting in film properties different than the original 250F curing ideal resin/crosslinker system.
2. For an established base resin system, a specific class of crosslinker may be identified which yields polymerization at temperatures below 250 F. The reactive groups of the crosslinker may be built to mate with the base resin functionality to minimize premature crosslinking, or balanced in the crosslinker to allow for some polymerization of the resin in the ED bath without affecting the minimum cure temperature or film performance properties.
3. The reactive functionality of the base resin may be built to mate with a specific crosslinker to provide polymerization with acceptable stability at the desired temperature without altering the resulting film properties.

4. The base resin reactive functionality and the crosslinker functionality may be built and mated to provide the required polymerization temperature response with allowance for partial prepolymerization.
5. The base resin/crosslinker ratio may be varied to increase cure stability and the system may be modified to maintain a constant cured polymer structure, i.e., identical film properties.
6. Further, a catalyst can be used with a stable, balanced resin/crosslinker system, with a higher than desired polymerization temperature, to lower the cure temperature to the desired range.

These aspects, as well as others which surfaced during the initial development as explained below, were given due consideration in the formulation of the 250F curing modified epoxy electroprimer.

Eleven acceptable resin formulations were developed for evaluation. The eleven resin formulations are presented in Table E-1.

Screen Formulated Crosslinkers

Initially, two screening test methods were utilized, the Meseran cure evaluation* and the MEK rub test⁽¹⁾, to evaluate the degree of cure. Later, adhesive bonding tests were used to optimize the cure for those formulations which demonstrated acceptable tank stability. MEK rub test results for the eleven formulations are presented in Table E-2.

Four crosslinkers, Cr A, Cr B, Cr C, and Cr D and modifications Cr B Mod. and Cr C Mod. were formulated and compounded into electropriming solutions (see Table E-1). Cure temperature tests on the initial three formulations indicated that a 250F curing modified epoxy electroprimer was a practical goal.

SA-6029 Formulation

Formulation SA-6029 is completely cured after exposure to 225F for 30 minutes, as measured by the Meseran evaluation, and MEK rub test. Cure temperatures less than 225F were not evaluated by the MEK rub test; however, the Meseran evaluation indicated that cure of SA-6029 is initiated in the 180F to 200F range.

*See Appendix C for test description.

TABLE E-1. FORMULATIONS OF CANDIDATE ELECTROPRIMER RESINS

Formulation Sequence	Formulation Identification	Base Resin ⁽²⁾	Crosslinker	Pigment	Coalescing Solvent
Reference	C-5301	Modified Epoxy	Cr X ⁽¹⁾	(3)	Co A ⁽⁴⁾
1	SA-5641 ⁽⁷⁾	Modified Epoxy	Cr A ⁽¹⁾	None	Co A
2A	SA-6029 ⁽⁸⁾	Modified Epoxy	Cr B ⁽¹⁾	None	Co B ⁽⁵⁾
2B	SA-6029M ⁽⁹⁾	Modified Epoxy	Cr B	None	Co A + Co B
3	SA-6082 ⁽¹⁰⁾	Modified Epoxy	Cr C ⁽¹⁾	None	Co B
4A	SA-6106 ⁽¹⁰⁾	Modified Epoxy	Cr C	None	Co C ⁽⁶⁾
4B	SA-6106M ⁽¹¹⁾	Modified Epoxy	Cr C	None	Co C
5	SA-6166 ⁽¹²⁾	Modified Epoxy	Cr B Mod.	None	Co C
6	SA-6167 ⁽¹³⁾	Modified Epoxy	Cr A Mod.	None	Co C
7	SA-6300 ⁽¹⁴⁾	Modified Epoxy	Cr D ⁽¹⁾	None	Co C
8	SA-6410 ⁽¹⁵⁾	Modified Epoxy	Cr B Mod	TiO ₂ & Clay	Co C
9	SA-6411 ⁽¹⁶⁾	Modified Epoxy	Cr D	TiO ₂ & Clay	Co C
10	SA-6412 ⁽¹⁷⁾	Modified Epoxy	Cr B Mod + Cr D	None	Co C
11	SA-6413 ⁽¹⁸⁾	Modified Epoxy	Cr B Mod + Cr D	TiO ₂ & Clay	Co C

NOTES:

- (1) Sherwin-Williams experimental crosslinker.
- (2) All formulations are made with the C-5301 modified epoxy resin.
- (3) NALZIN SC-1, SiO₂/TiO₂/SC-1, Product of National Lead Company.
- (4) Co A = "Isophorone" Coalescing Solvent (3,5,5-trimethyl-2-cyclohexen-1-one).
- (5) Co B = "Butylate" Coalescing Solvent (n-butyl acetate).
- (6) Co C = "Cellate" Coalescing Solvent (Cellusolve Acetate).
- (7) SA-5641 is the first modification of the C-5301 electroprimer and utilizes a new crosslinker which lowered the cure temperature from 325F/60 minutes to 290F/30 minutes.
- (8) SA-6029 is the first experimental formulation with crosslinker B and coalescing solvent B.
- (9) SA-6029M is SA-6029 with coalescing solvent, Co A, added.
- (10) SA-6082 and SA-6106 are similar to C-5301 but have different resin/crosslinker ratios and different coalescing solvents.
- (11) SA-6106M contains an elastomer which aids in film coalescence.
- (12) SA-6166 is similar to SA-6029 except the crosslinker B has a built-in flexibilizer, and the coalescing solvent Cellusolve Acetate is used.
- (13) SA-6167 is similar to SA-5461 except the crosslinker has been modified and contains an elastomer which also aids in film coalescence.
- (14) SA-6300 is the first experimental formulation utilizing crosslinker Cr D.
- (15) SA-6410 is the SA-6166 with sufficient inert filler ingredient (TiO₂ and clay) to reduce the cured primer film gloss.
- (16) SA-6411 is SA-6300 with sufficient inert filler to define any effect of the inert filler on adhesive bonding properties.
- (17) SA-6412 is the base resin system of SA-6166 and SA-6300 with a blend of the SA-6166 and SA-6300 crosslinkers.
- (18) SA-6413 is the SA-6412 system with sufficient inert filler to maintain low gloss in the cured electroprimer film.

**TABLE E-2. MEK RUB TEST RESULTS OF CANDIDATE ELECTROPRIMERS
CURED 30 MINUTES AT VARIOUS FILM CURE TEMPERATURES**

Formulation Identification	Cure Temperature, F				
	225	250	275	290	300
C-5301	NT ⁽¹⁾	NT	NT	NT	Fail
SA-5641	Fail	Fail	Fail ⁽²⁾	Pass	Pass
SA-6029 ⁽⁶⁾	Pass	Pass	Pass	NT	Pass
SA-6029M	Fail	Fail	Pass	NT	Pass
SA-6082	NT	NT	Fail	Pass	Pass ⁽³⁾
SA-6106	NT	Fail	Pass ⁽⁴⁾	Pass	Pass
SA-6106M	NT	Fail	Pass ⁽⁴⁾	Pass ⁽⁵⁾	Pass
SA-6166	Fail	Pass	NT	NT	NT
SA-6167	Fail	Pass	NT	NT	NT
SA-6300	Fail	Fail	Pass	Pass	Pass
SA-6410	Pass ⁽⁶⁾	Pass	NT	NT	NT
SA-6411	Pass ⁽⁶⁾	Pass	NT	NT	NT
SA-6412	Pass ⁽⁶⁾	Pass	NT	NT	NT
SA-6413	Pass ⁽⁶⁾	Pass	NT	NT	NT

(1) NT = Not Tested

(2) Meseran evaluation indicates cure develops at this temperature.

(3) Passes 250 rub cycles (discontinued).

(4) 60 minute cure at indicated cure temperature.

(5) Passes 200 rub cycles (discontinued).

(6) Passes 250 rub cycles. Will also pass 250 rub cycles at a cure temperature of 220F, for 30 minutes.

Wedge crack extension tests* were performed with the SA-6029 electroprimer cured at 225F, 245F, 275F, and 295F. Test substrates of 7075-T6 bare aluminum alloy were prepared by 10 volt phosphoric acid anodizing prior to electropriming and bonded with FM-73 adhesive. Test specimens were exposed to 120F, 95% R. H. up to 504 hours. Results of wedge crack extension tests are presented in Table E-3 and presented graphically in Figure E-1. Discernible from the test data and the graphical presentation is the very slow, continuous crack extension. Usually crack extension tests yield results of near zero extension after 24 hours exposure, as displayed by the BR-127 control in this test, or a very rapid growth as may be a result from inadequate surface treatment prior to priming. Since the test results were unexpected, a SEM analysis was performed on the failure area of one crack extension test specimen.

Figure E-2 shows the failed test specimen with the area selected for SEM analysis. Figure E-3 shows the analysis area viewed normal to the crack propagation direction at 10,000 magnification. Figure E-4 shows the substrate and oxide condition viewed parallel to the crack propagation direction at 20,000 magnification. Figure E-4 shows the electroprimer/oxide interface has changed, compared to a control anodize surface (Figure E-6), and failure has taken place between the anodize surface and the electroprimer. The interface change is probably the hydration of the anodize oxide, and the rate of crack propagation is dependent on the susceptibility of the interface to hydration under the test exposure conditions of 120F, 95% R.H. Since the crack extension wedge test is a good indicator of adhesive bond durability, the study indicates that the primer/oxide interface susceptibility to hydration or change should be lowered to increase adhesive bond durability. Candidate Phase I electroprimers were formulated to reduce the susceptibility of the interface to change.

Effect of Coalescing Solvents on Cure Temperature

During a curing experiment, some of the panels electroprimed with C-5301 were inadvertently given an extended dwell time between primer application and elevated temperature cure. These panels were found to perform superior in the MEK rub test compared to those given a normal 1-5 minute "dwell" time. Further tests showed that long dwell periods, prior to cure, reduced the cure temperature of the film to 290F, substantially lower than the original 325-345F.

*See Appendix D for test specimen configuration.

**TABLE E-3. WEDGE CRACK EXTENSION TEST RESULTS* OF SA-6029
ELECTROPRIMER CURED AT VARIOUS TEMPERATURES**

Primer	Primer Cure Temp (F)	Exposure Time** (Hours)	Average Crack Extension† (Inches)
SA 6029	225	1	0.04
SA 6029	245	1	0.03
SA 6029	275	1	0.06
SA 6029	295	1	0.06
BR 127	250	1	0.02
SA 6029	225	24	0.08
SA 6029	245	24	0.06
SA 6029	275	24	0.07
SA 6029	295	24	0.09
BR 127	250	24	0.06
SA 6029	225	336	0.33
SA 6029	245	336	0.26
SA 6029	275	336	0.41
SA 6029	295	336	0.34
BR 127	250	336	0.06
SA 6029	225	504	0.41
SA 6029	245	504	0.36
SA 6029	275	504	0.60
SA 6029	290	504	0.62
BR 127	250	504	0.07

* Standard wedge test configuration, i. e., 1" x 6" x 0.125" adherends of 7075-T6 bare aluminum alloy surface treated with 10-volt phosphoric acid anodize and adhesively bonded with FM-73 adhesive cured at 250 F for 60 minutes.

** Exposure conditions — 120 F, 95+% R. H.

† Reported results are averages of five specimens.

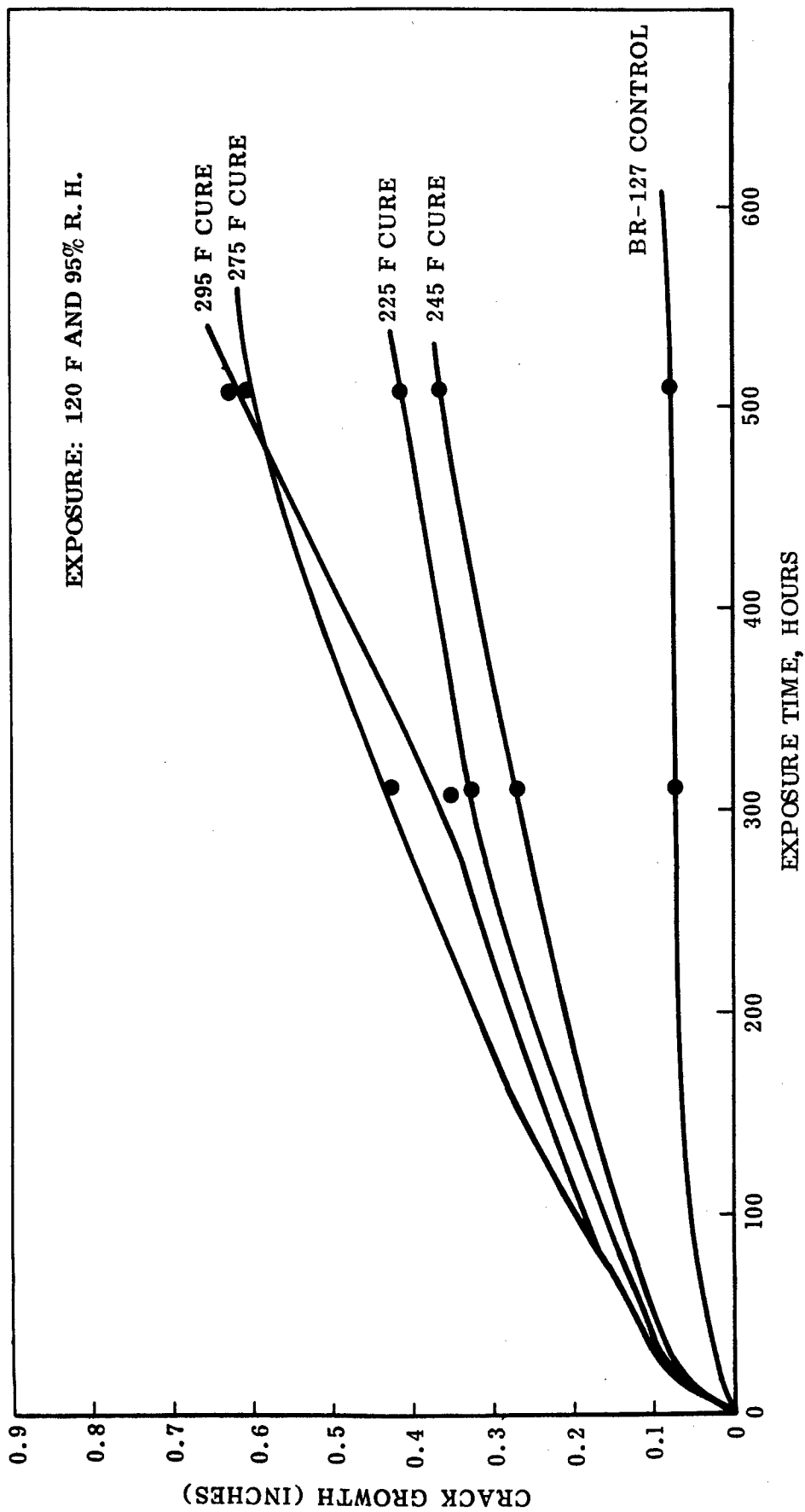


Figure E-1. Wedge Crack Extension Test Results of SA-6029 Electroprimer
Cured at Various Temperatures

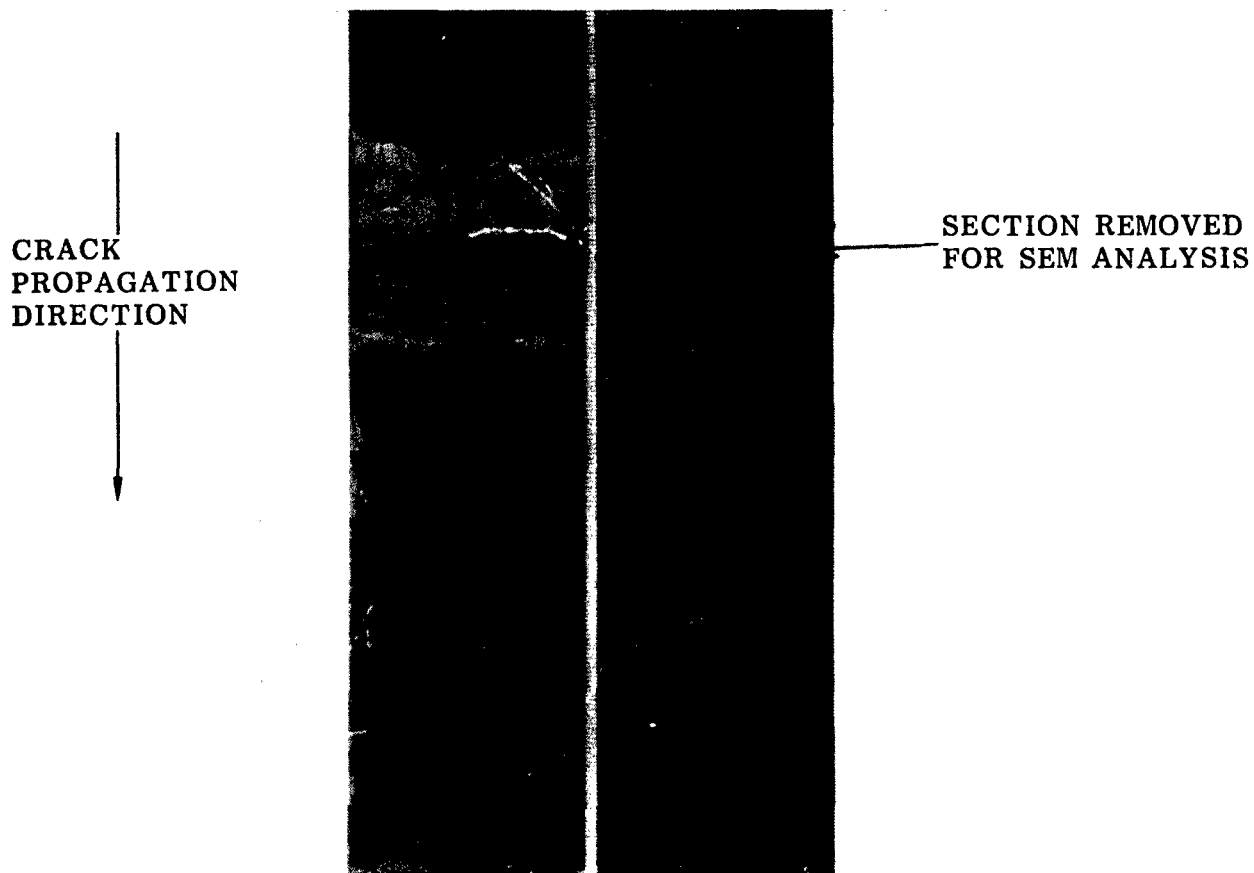
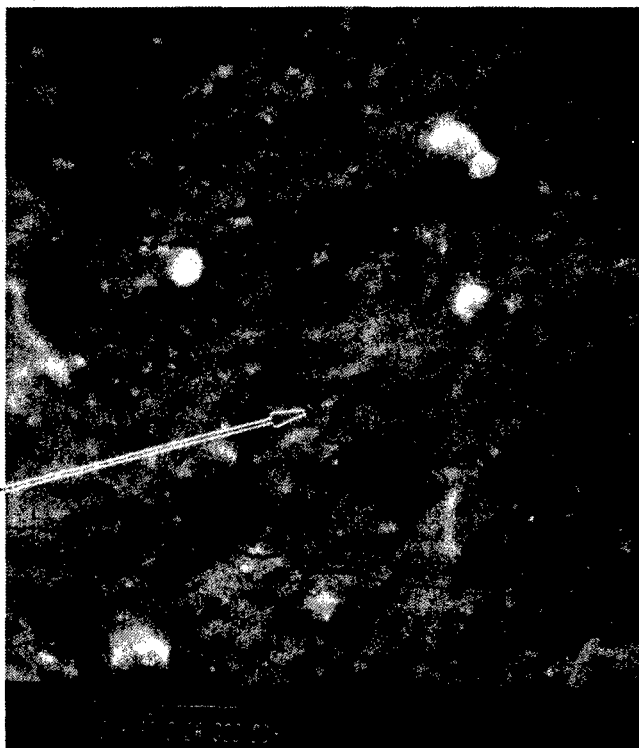


Figure E-2. Fractured Wedge Crack Extension Specimen, 7075-T6 Bare Aluminum, 10 Volt Phosphoric Acid Anodized, Electroprimed with SA-6029 and Bonded with FM-73 Adhesive

Figure E-3. Wedge Crack Extension Failure Area, Normal to Crack Propagation Direction

Aluminum Oxide in Failure Area



10,000X

Figure E-4. Oxide Layers in Wedge Crack Extension Failure Area, Parallel to Crack Extension Direction

Hydrated Aluminum Oxide

Anodize Oxide

Aluminum Substrate



20,000X

These results suggested that coalescing solvents with excessively high boiling points may be retained in the deposited film, retarding crosslinking and thereby requiring unnecessarily high curing temperatures.

The electrodeposition application parameters of the electropriming process were varied to establish and control coalescing solvent levels and to define the acceptability of a candidate coalescing solvent. The coalescing solvent must be soluble in the resin system and, ideally, insoluble in the water phase of the electropriming bath. An acceptable coalescing solvent will provide resin flow resulting in a continuous film as the film builds on the conductive substrate. This acts as a barrier that insulates the conductor that is being coated. An unacceptable solvent, or an incorrect level of coalescing solvent will not produce a continuous film and will permit the continuous passage of current. Although a thicker film will be produced in this latter case, the film will be porous. Figure E-5A is a plot of the voltage and current levels produced by an acceptable coalescing solvent at correct concentration. Figure E-5B shows the results when coalescing solvent is in an incorrect concentration permitting a diminishing current passage through the deposited film. Figure E-5C shows the voltage and current response when an incorrect coalescing solvent is used permitting a continuous passage of current. Voltage and current measurement have been used extensively to guide electroprimer formulation. Initially, a nominal potential is applied to the cathode (workpiece), approximately 50 volts, and the test coalescing solvent is added slowly, while monitoring the current curve. When the current falls sharply to zero, effective film coalescence has occurred.

SA-6082 and SA-6106 Formulations

Based on these results, the C-5301 electroprimer was reformulated to produce electroprimer formulations SA-6082 and SA-6106. Several of the higher boiling solvents (over 350F) in the C-5301 primer formulation were replaced with more volatile, lower boiling solvents.

Additionally, the base resin/crosslinker ratios were modified. It was believed that these changes would produce a solvent resistant coating curing below 300F from the identical resin-crosslinker system of the C-5301 electroprimer which had developed full cure at 325F. Indeed, coatings deposited from these reformulations (SA-6082 and SA-6106) exhibit excellent resistance to the MEK rub test at cure cycles of 275F for 60 minutes or 290F for 30 minutes.

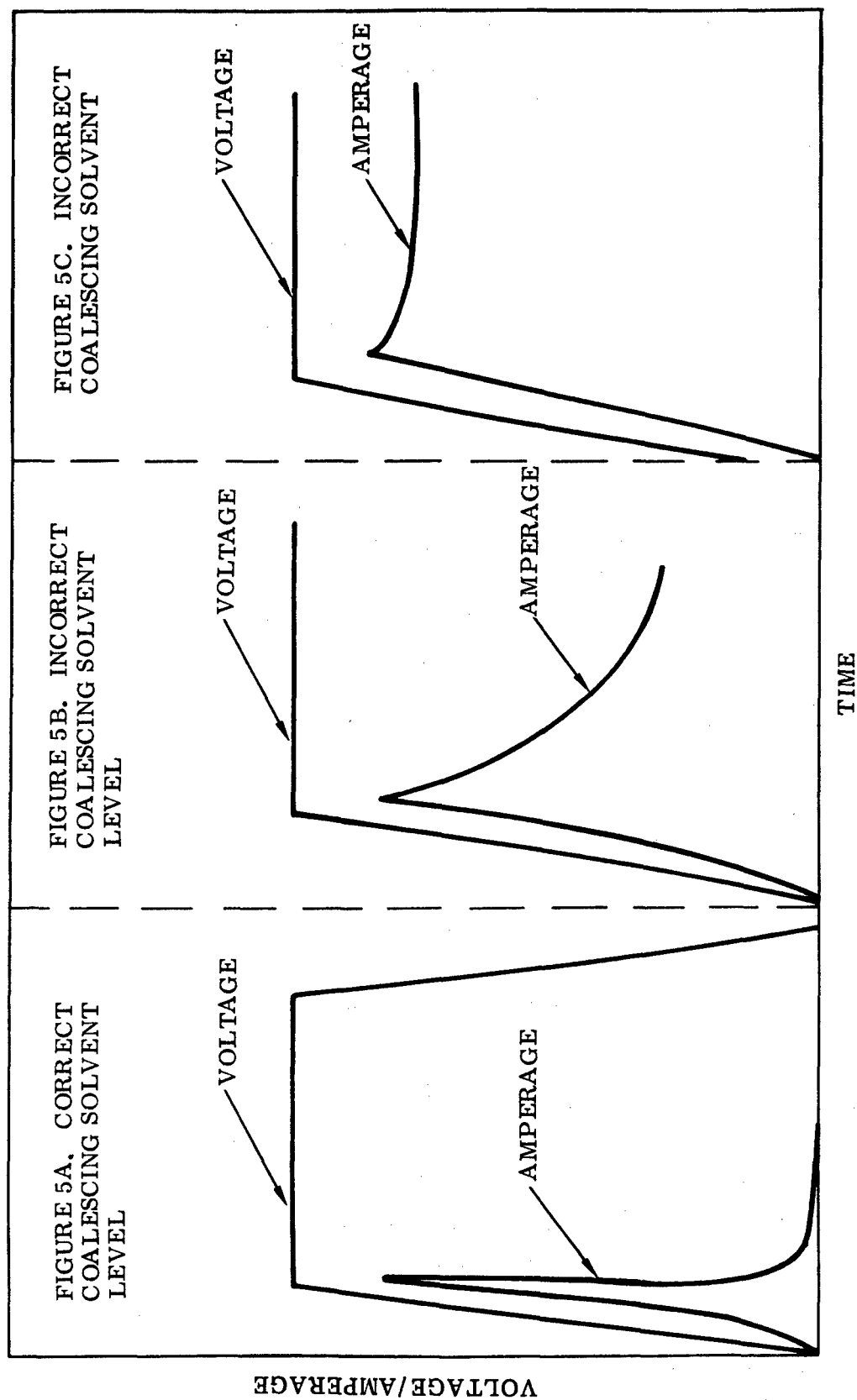


Figure E-5. Effect of Coalescing Solvent on Voltage and Current Levels in Depositing an Electropimer

The SA-6082 contains the coalescing solvent n-butyl acetate. This coalescing solvent was determined to be compatible with the electroprimer formulation, but the volatility was excessive and required frequent replenishment to maintain adequate film coalescence. This condition was attributed to the incomplete solubility of the n-butyl acetate in the base resin system. The SA-6106 formulation contains cellusolve acetate. It was found to be completely stable and did not require the maintenance additions of solvent. Therefore, the SA-6082 formulation with the n-butyl acetate was eliminated from further development.

The coalescing solvent, cellusolve acetate was found acceptable for low temperature cure development and appears to be near the optimum for this contract effort.

SA-6106M Formulation

The SA-6106 formulation was modified with the flexibilizer PCP-0300* which initial tests indicated aided in the formation of a uniform film deposit. However, it was also determined that addition of the PCP-0300 to the SA6106 increased the application voltage required from 30 volts to 80 volts to form the uniform film. Since the higher application voltage is undesirable from a power usage standpoint, the SA-6101M was not considered for further investigation.

SA-6167 Formulation

The SA-6167 formulation contains a modification of the crosslinker A to lower the cure temperature of the basic C-5301 electroprimer formulation. The SA-6167 also contains the PCP-0300 flexibilizer, and the low boiling cellusolve acetate coalescing solvent. The SA-6167 formulation cures at 230F in 30 minutes as verified by wedge crack extension tests (see Table E-7 and Figure E-27).

SA-6300 Formulation

Formulation SA-6300 was formulated with CrD, the fourth crosslinker developed for this program. The SA-6300 was evaluated for cure response by electropriming specimens of 7075-T6 bare aluminum and curing the applied film at various temperatures from 220F to 275F. The specimens were then MEK rub tested.** Results of the rub test are presented in Table E-4.

*PCP 0300 is a low M.W. (~500), triol flexibilizer compound made by Union Carbide Company. This is a polycaprolactone distributed under the trade designation NAIC polyol PCP-0300.

**See Appendix C for test description.

TABLE E-4. CURE EVALUATION OF SA-6300
BY THE MEK RUB TEST

Cure Temperature (° F)	Rub Test Result
220	Electroprimer Film Readily Removed in Three Rub Cycles
235	Electroprimer Film Penetrated at 200 Rub Cycles
250	Electroprimer Film Penetrated at 250 Rub Cycles
275	Electroprimer Film Not Penetrated with 325 Rub Cycles

Note: Normally, when penetration of the electroprime film is not achieved in 100 MEK rub cycles, the film is considered passing (completely cured), and the higher temperature cures need not be tested. However, since the rub cloth was discolored at 100 rub cycles on the specimen cured at 235F, the higher cure temperatures for SA-6300 were evaluated.

Based on the MEK rub test results, the 275F primer cure temperature was selected for wedge crack extension test specimen preparation. This test is performed to verify that complete cure of the electroprimer film has been achieved. If the wedge crack does not grow in excess of 0.2 inch after 30 days exposure to 120F, 95% R. H., the electroprime film is considered to be completely cured. The wedge crack extension specimens of 7075-T6 bare aluminum were 10 volt phosphoric acid anodized, electroprimed at 30 volts for 30 seconds, and the primer cured at 275F for 30 minutes. The wedge specimens were then adhesively bonded with FM-73 adhesive; the adhesive was cured in an autoclave at 250F for 60 minutes under 40 psi pressure.

Results of the wedge crack extension tests with the SA-6300 electroprimer cured at 275F for 30 minutes are presented in Table E-5. Data verify that cure is complete at 275F in 30 minutes. Bonding properties of SA-6300, discussed in Phase 2, were excellent.

TABLE E-5. WEDGE TEST RESULTS⁽¹⁾ OF SA-6300
ELECTROPRIMER CURED AT 275F/30 MINUTES

Exposure Time ⁽²⁾ (Days)	Wedge Crack Extension ⁽³⁾ (Inches)
1	0.04
4	0.07
10	0.10
60	0.10

(1) Specimens bonded with FM-73 adhesive; cured for one hour at 250F.

(2) Exposure conditions: 120F, 95% R. H.

(3) Reported results are averages of five individual specimens.

PHASE 2 — DEVELOP -65F ADHESIVE BOND PROPERTIES

Effect of Inert Filler

The C-5301 electroprimer developed under Air Force Contract F33615-76-C-5301, provided high mechanical strength properties; however, the -65 F adhesive bond properties were somewhat lower than desired. In Phase II of this program the -65 F adhesive bond properties of the cathodically applied modified epoxy electroprimer were improved to acceptable levels. Since low temperature adhesive bond properties characteristically reveal weaknesses in surface preparation, this area of investigation was pursued first to determine if the anodize surface changes during cathodic electropriming.

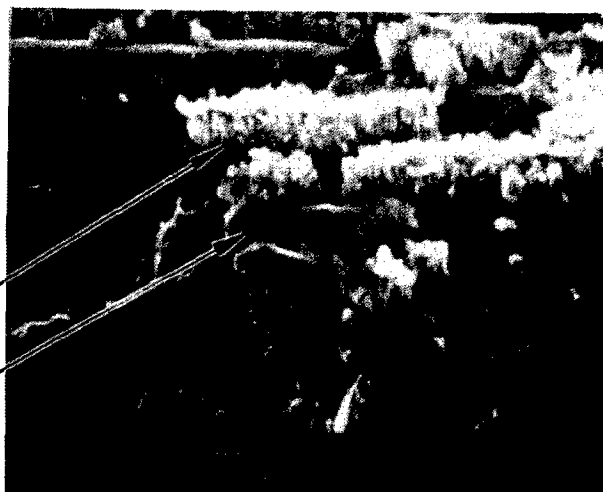
The anodize/electroprimer interface was investigated utilizing cathodic deposition potentials of 10 volts, 15 volts, 20 volts, 25 volts, and 40 volts. SEM analysis of the anodize/electroprimer interface, including oxide thickness measurements, revealed no changes in the anodize oxide thickness or character. These results are presented pictorially in Figures E-6 through E-11.

The C-5301 electroprimer contains a substantial percentage of inert fillers to provide rigidity and toughness to the cured resin film. Since the epoxy resin system is intrinsically a rigid resin system, inert filler makes the film brittle. This, in part, contributed to the low mechanical test results at -65F. Three methods were used to increase the flexibility of the electroprimer film: (1) reduce or eliminate the inert component, (2) add a flexibilizer to the electroprimer formulation, and (3) build a flexibilizer into the crosslinker or base resin backbone structure. In formulation SA-6029 (Table E-1) the inert fillers are eliminated. Formulations SA-6106M and

Figure E-6. Oxide Layers
on 10 Volt Phosphoric
Acid Anodize Surface
Treated 7075-T6 Bare
Aluminum Alloy

Anodize Oxide

Aluminum
Substrate



CONTROL

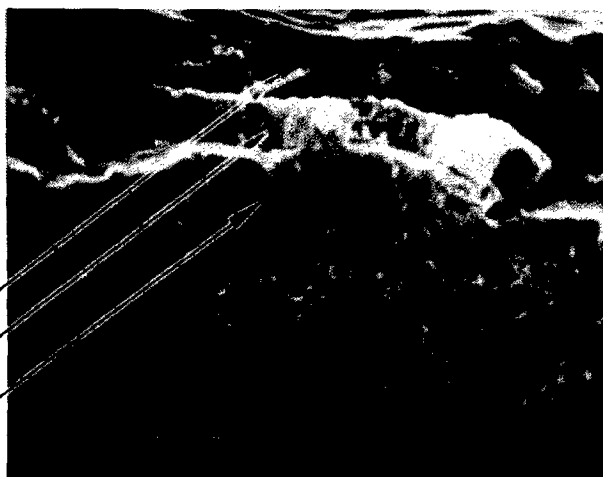
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Figure E-7. Electroprime
Resin on Oxide Layers of
10 Volt Phosphoric Acid
Anodize, Cathodically
Electroprimed at 10 Volts

Electroprimer

Anodize Oxide

Aluminum
Substrate



10 VOLTS

10,000X

Figure E-8. Electroprime
Resin on Oxide Layers of
10 Volt Phosphoric Acid
Anodize, Cathodically
Electroprimed at 15 Volts

Electroprimer

Anodize Oxide

Aluminum
Substrate



15 VOLTS

10,000X

Figure E-9. Electroprime Resin on Oxide Layers of 10 Volt Phosphoric Acid Anodize, Cathodically Electroprimed at 20 Volts

Electroprimer

Anodize Oxide

Aluminum Substrate



20 VOLTS

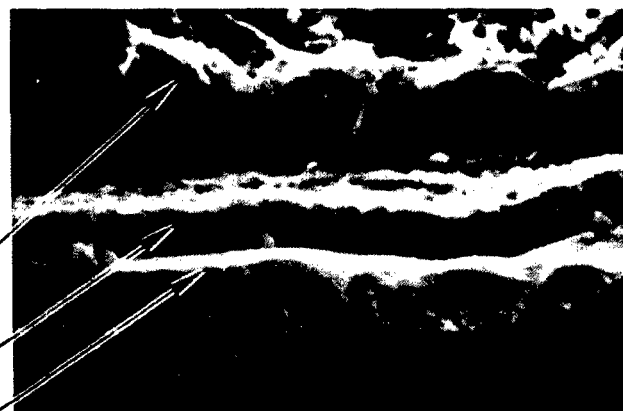
10,000X

Figure E-10. Electroprime Resin on Oxide Layers of 10 Volt Phosphoric Acid Anodize, Cathodically Electroprimed at 25 Volts

Electroprimer

Anodize Oxide

Aluminum Substrate



25 VOLTS

10,000X

Figure E-11. Electroprime Resin on Oxide Layers of 10 Volt Phosphoric Acid Anodize, Cathodically Electroprimed at 40 Volts

Electroprimer

Anodize Oxide

Aluminum Substrate



40 VOLTS

10,000X

SA-6167 contain the flexibilizer PCP 0300*, which reacts chemically during cure to become part of the resin polymer. Formulation SA-6166 incorporates a flexibilizing unit in the crosslinker to provide the required flexibility to the cured resin polymer.

SA-6029 Formulation

Formulation 6029 was the first low-temperature curing (235F) modified epoxy electroprimer that was tested for -65F adhesive bond strength. It is the C-5301 formulation with the inert fillers taken out. Thick adherend notched tensile shear test properties at -65F, ambient, and 180F were performed on the SA-6029 formulation. Four sets of 7075-T6 bare aluminum alloy adherents were 10 volt phosphoric acid anodized and then electroprimed at 30 volts for 30 seconds. One set of the electroprimed panels was cured at 245F, 275F, and 295F and the fourth set was primed with BR-127 to serve as controls. The panels were adhesively bonded with FM-73 adhesive and machined to test configuration**. The results of the tensile tests are presented in Table E-6.

The experimental formulation SA-6029 cures 100F to 120F below the C-5301 electroprimer developed under contract F33615-75-C-5301. Further, at -65F the tensile shear strength is about 2,000 psi higher than the C-5301 with greatly reduced scatter in the tensile test results. The test results are equivalent at primer cure temperatures of 245F, 275F and 295F. Although tensile specimens were not prepared with electroprimed panels cured at 225F, results of the wedge tests (Table E-2) show complete primer cure was developed at 225F, and tensile test results were expected to be equivalent to those on specimens made with the higher primer cure temperatures.

Initial Failure Analysis on SA-6029, -65F Tensile Shear Specimens

Fracture analysis of the failed -65F tensile shear specimens, Figure E-12, suggest a 50% cohesive/50% adhesive failure. However, SEM photographs at 4,000X and 10,000X taken normal to failure area reveal that the "apparent" adhesive failure area is completely covered with electroprimer (Figures E-13 and E-14). The 10 volt phosphoric acid anodize oxide is not detectable in these photographs taken normal to the failure area. Specimens were also machined out of a fracture area in which failure was

*PCP 0300 is a low M.W. (500), triol flexibilizer compound made by Union Carbide Company. This is a polycaprolactone distributed under the trade designation NAIC polyol PCP-0300.

**See Appendix D.

TABLE E-6.
TENSILE SHEAR TEST⁽¹⁾ RESULTS OF SA-6029
ELECTROPRIMER CURED AT VARIOUS TEMPERATURES

Primer	Primer Cure Temp (F)	Tensile Test Temp (F)	Ultimate Strength (psi)	Failure Mode
SA 6029	275	180	4420	100% Cohesive
SA 6029	275	180	4290	100% Cohesive
SA 6029	275	180	4120	100% Cohesive
SA 6029	275	180	4070	100% Cohesive
SA 6029	275	180	4200	100% Cohesive
BR 127	250	180	4270	100% Cohesive
BR 127	250	180	3860	100% Cohesive
BR 127	250	180	4350	100% Cohesive
SA 6029	245	AMB	5290	100% Cohesive
SA 6029	245	AMB	5300	100% Cohesive
SA 6029	275	AMB	5240	100% Cohesive
SA 6029	275	AMB	5240	100% Cohesive
SA 6029	275	AMB	5200	100% Cohesive
SA 6029	275	AMB	5220	100% Cohesive
SA 6029	295	AMB	5250	100% Cohesive
SA 6029	295	AMB	5340	100% Cohesive
BR 127	250	AMB	5240	100% Cohesive
BR 127	250	AMB	5440	100% Cohesive
BR 127	250	AMB	5250	100% Cohesive
SA 6029	245	-67	7940	100% Cohesive
SA 6029	245	-67	7980	100% Cohesive
SA 6029	275	-67	8000	100% Cohesive
SA 6029	275	-67	8140	100% Cohesive
SA 6029	275	-67	7600	100% Cohesive
SA 6029	275	-67	7280	100% Cohesive
SA 6029	275	-67	8300	100% Cohesive
SA 6029	295	-67	7940	100% Cohesive
SA 6029	295	-67	8300	100% Cohesive
SA 6029	295	-67	8200	100% Cohesive
BR 127	250	-67	8180	100% Cohesive
BR 127	250	-67	8250	100% Cohesive
BR 127	250	-67	8050	100% Cohesive

(1) Thick adherend machined notch tensile specimen configuration with 10 volt phosphoric acid anodized 7075-T6 bare aluminum substrates.

- NOTES: A. The BR 127 control primer average thickness was 0.10 mil.
 B. The SA 6029 electroprimer film thickness was 0.18 mil.
 C. All specimens bonded with FM-73 adhesive cured at 250 F for 60 minutes.
 D. Average adhesive bondline thickness was 8 mil.

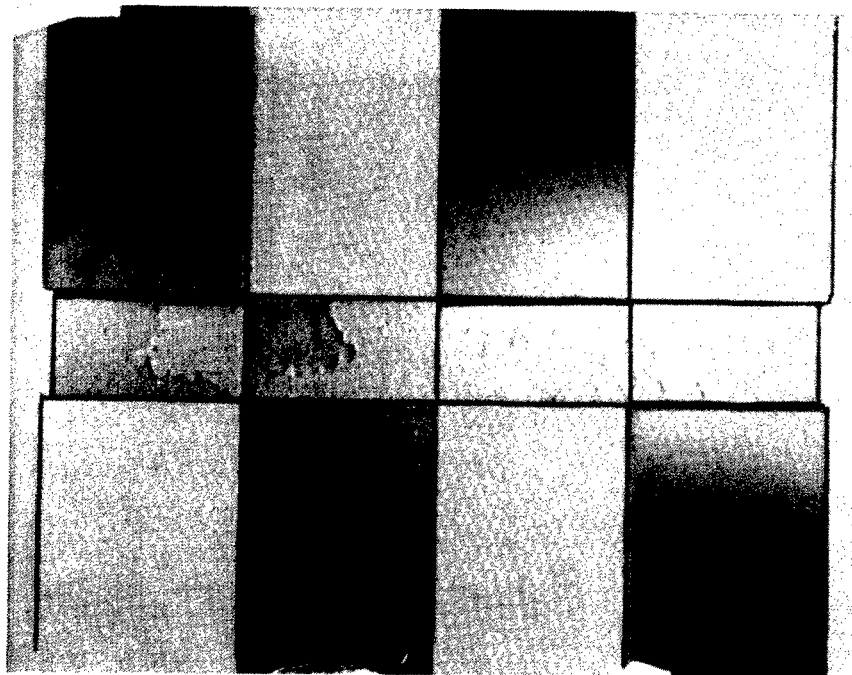
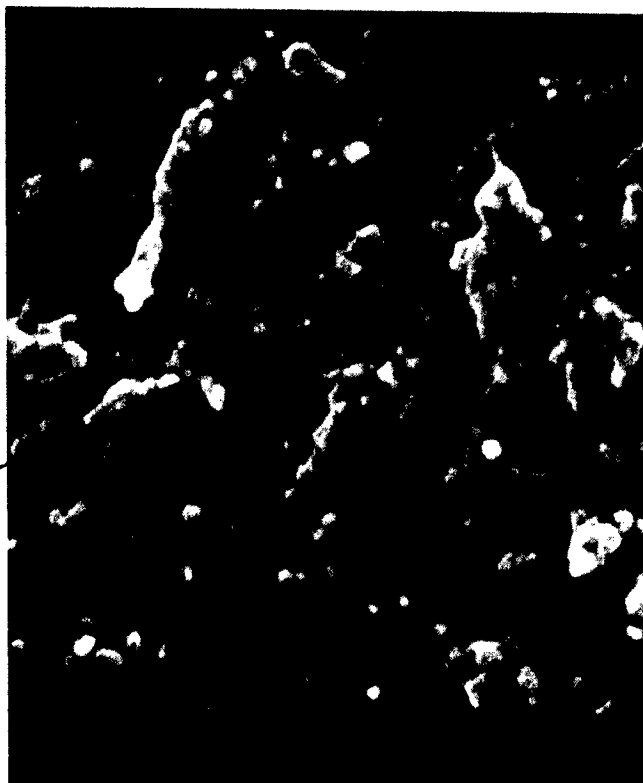


Figure E-12. Typical Failed -65F Tested Tensile Shear Specimens of 10 Volt Phosphoric Acid Anodized 7075-T6 Bare Aluminum, Electroprimed with SA-6029 and Bonded with FM-73 Adhesive

Figure E-13. SA-6029 Electroprimer
on Apparent Adhesive Failure Area of
Fractured -65F Tensile Shear Specimen
E-3 Viewed Normal to Tensile Strain

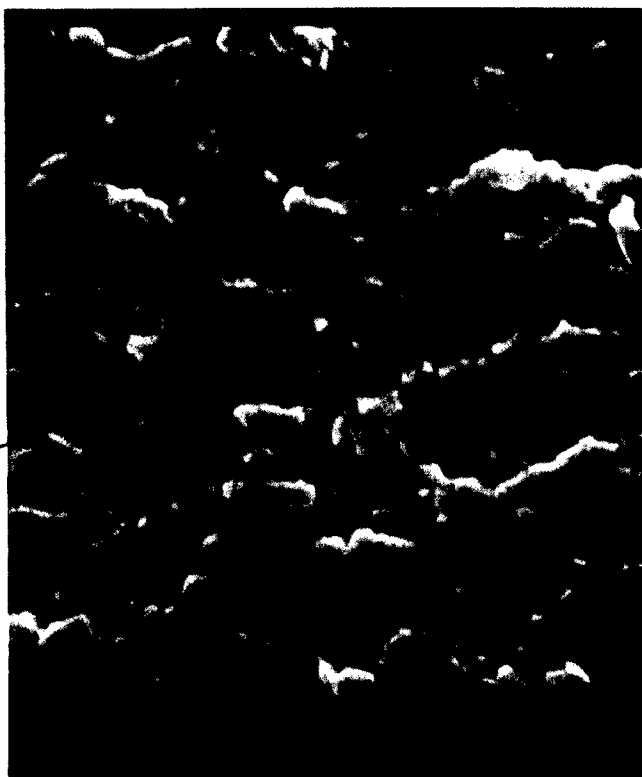
SA-6029 Electroprimer
(Entire Surface)



10,000X

Figure E-14. SA-6029 Electroprimer
on Apparent Adhesive Failure Area of
Fractured -65F Tensile Shear Specimen
B-2 Viewed Normal to Tensile Strain

SA-6029 Electroprimer
(Entire Surface)



10,000X

apparently adhesive. These were examined with the SEM viewing parallel to the tensile loading. The results, Figures E-15 through E-18, clearly establish that the fracture occurs through and in the electroprimer resin. Figure E-18 is particularly interesting in that it shows the anodic oxide/primer transition zone. A distinct bulk area of oxide below the bulk primer deposit does not exist, but rather a transition area of oxide and primer which shows the compatibility and intermingling of the two phases. This intermingling of the two phases leads one to speculate that stronger mechanical bonds may be produced by electroprimers than by conventional hand sprayed adhesive bonding primers which show very little intermingling of phases.

A review of the wedge test data on exposure to 120F/95% R. H. and -65F lap shear tensile test data on the SA-6029 electroprimer (Tables E-3 and E-6) indicated three deficiencies: (1) a slow crack growth in the wedge test, even though the crack length is small (about 0.4 in. in 21 days), (2) scatter in the -65F tensile test data greater than preferred, and (3) an unacceptable failure mode in the -65F tensile specimens, approximately 50% adhesive and 50% cohesive. The cause of these deficiencies had to be determined before reformulation for improvement of the base electroprimer resin system could be continued. Probable causes considered were incompatibility between the electroprimer and the adhesive, interfacial incompatibility between the 10 volt phosphoric acid anodized surface and the electroprimer, and incomplete primer cure.

Failure Analysis on SA-6029 Wedge Test Specimens

Fracture analysis of the SA-6029 primed wedge test specimens was performed and indicated the failure area was between the primer and the substrate. SEM analyses were performed to determine whether the failure was in the oxide or in the bond between the primer and oxide. This fracture analysis was performed in the following manner. Strips 1/8-inch wide were sectioned from the fractured wedge test specimen in a direction perpendicular to the crack propagation direction. This gave the 1-inch x 1/8-inch specimens defined in Figure E-19, Areas A and B on side 1 and Area C on side 2. Each specimen was then held at the 1-inch dimension extremities with pliers and repeatedly bent until the specimen broke or fractured near the center. The broken specimen (now halved) was mounted vertically for SEM analysis to permit examination from the substrate to the specimen surface as shown in Figure E-20.

The area designated A in Figure E-19 is about 0.5-inch from the crack tip. The SEM photograph of this is shown in Figure E-21. Analysis shows a bulky hydrated oxide layer on top of the normal 10-volt anodize oxide. This type of hydrated oxide was

Figure E-15. SA-6029 Electroprimer
on 10 Volt Phosphoric Acid Anodize
Oxide Layers of Fractured -65F
Tensile Shear Specimen E-3 in Apparent
Adhesive Failure Area

Electroprimer

Anodize Oxide

Aluminum
Substrate



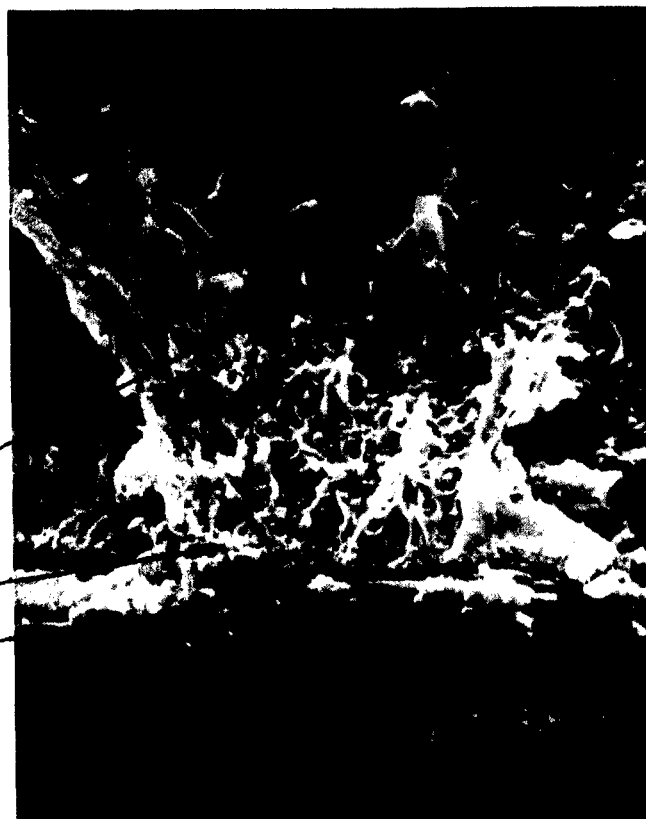
10,000X

Figure E-16. SA-6029 Electroprimer
on 10 Volt Phosphoric Acid Anodize
Oxide Layers of Fractured -65F
Tensile Shear Specimen B-2 in
Apparent Adhesive Failure Area,
4,000X

Electroprimer

Anodize Oxide

Aluminum
Substrate



4,000X

Figure E-17. SA-6029 Electroprimer on 10 Volt Phosphoric Acid Anodize Oxide Layers of Fractured -65F Tensile Shear Specimen B-2 in Apparent Adhesive Failure Area, 10,000X

Electroprimer
Anodize Oxide
Aluminum
Substrate



10,000X

Figure E-18. SA-6029 Electroprimer on 10 Volt Phosphoric Acid Anodize Oxide Layers of Fractured -65F Tensile Shear Specimen B-2 in Apparent Adhesive Failure Area, 20,000X

Electroprimer
Anodize Oxide
Aluminum
Substrate

Oxide Primer
Transition Zone



20,000X

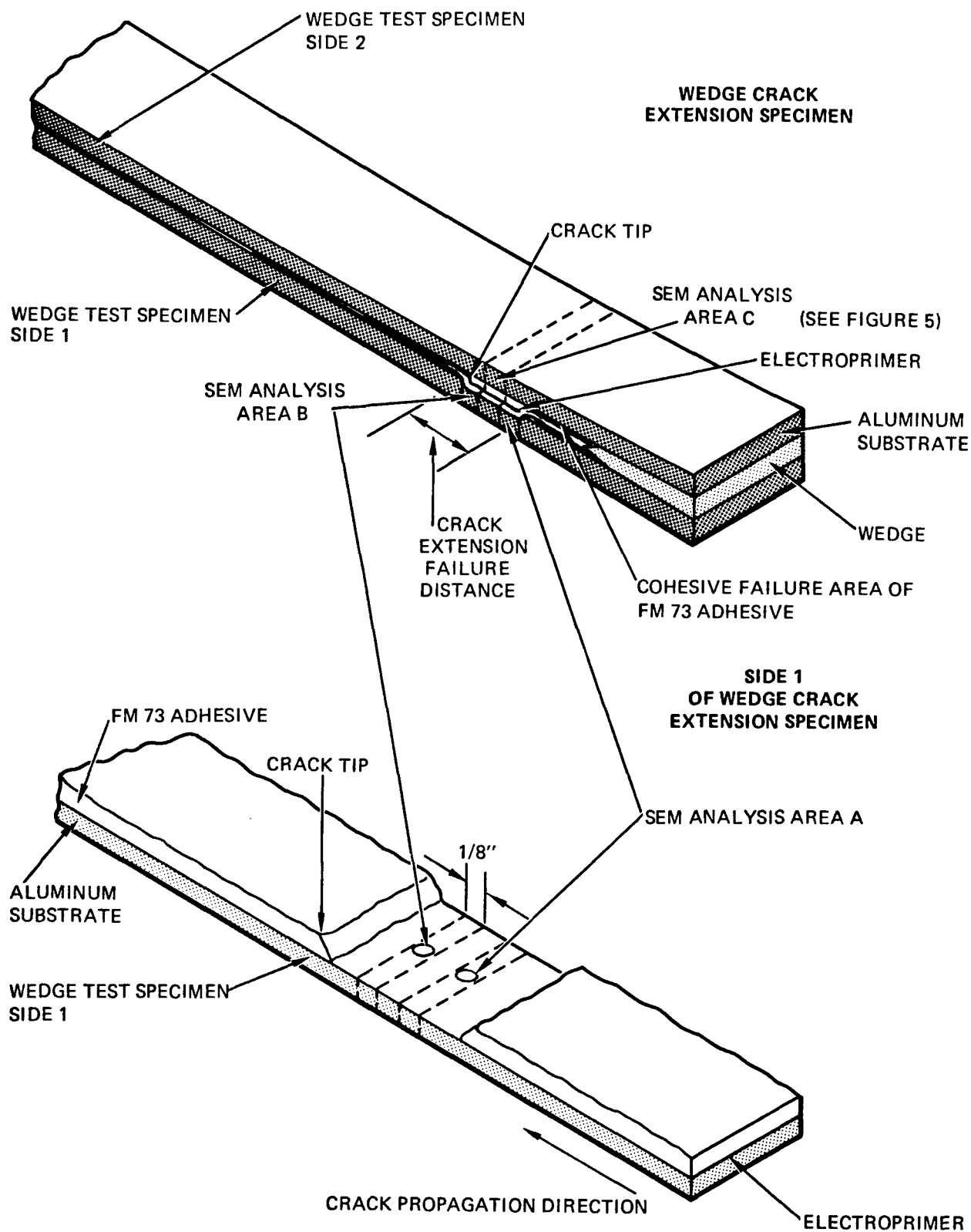


Figure E-19. Definition of Fracture Analysis Areas in the Wedge Crack Extension Specimen and Detail of Area A&B, Side 1

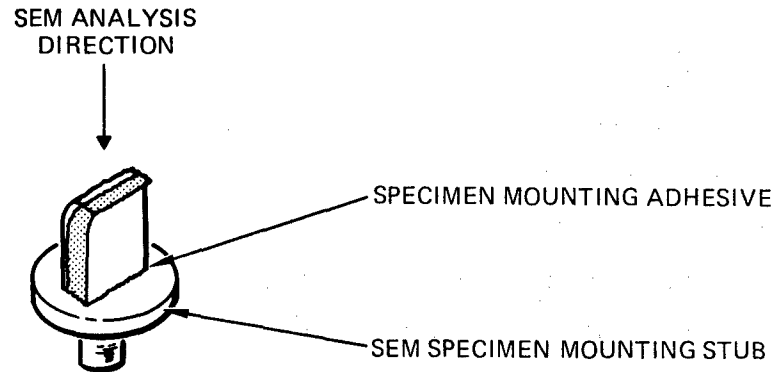


Figure E-20. Specimen Mount for SEM Analysis

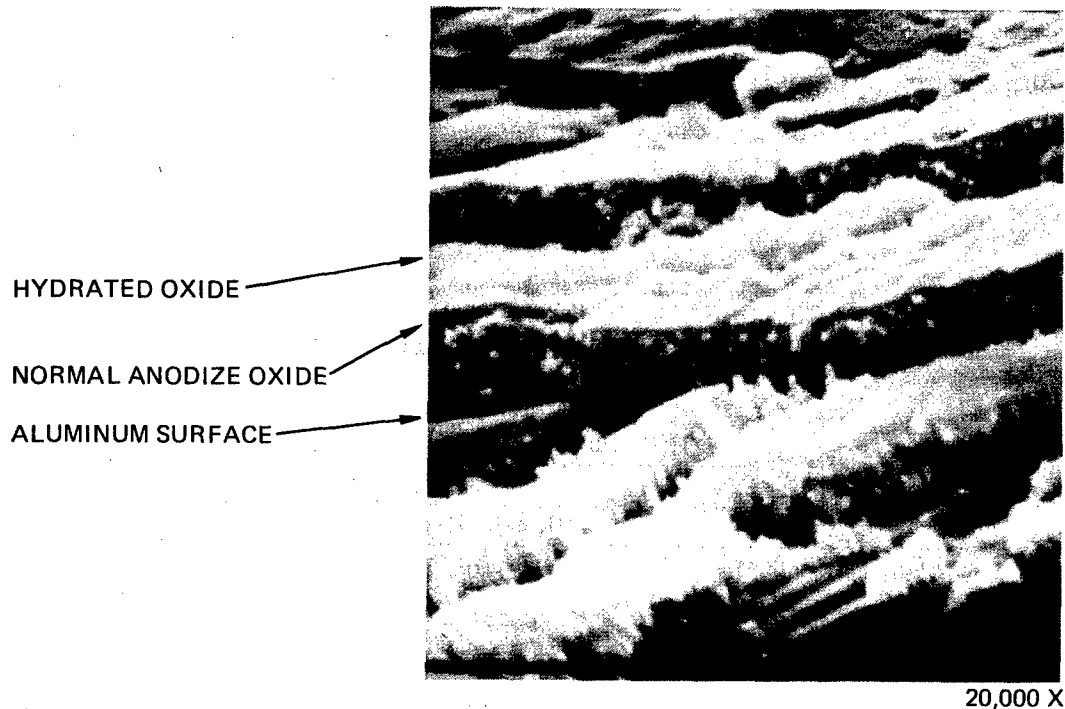


Figure E-21. SEM Photograph of Aluminum Oxide Layers on Wedge Test Specimen, Area A, Figure E-19

expected to be visible on any 10-volt anodize surface that had been exposed to 120F/95% R.H. However, the hydrated oxide on the failed wedge specimen appeared to be partially pulled off of the substrate as if the anodized oxide layer was being weakened by hydration and this hydration was causing the bond failure in the primer/substrate area.

To confirm that hydration was taking place on the SA-6029 primed wedge specimens, a SEM analysis was also made in the fracture area close to the location of the

crack tip. This is Area B in Figure E-19. This area should show less hydration than the Area A because it was exposed to high humidity for less time than Area A. The SEM analysis of Area B (see Figure E-22), the area near the crack tip, revealed a lesser quantity of hydrated anodized oxide than that in Area A, as expected. The hydrated oxide is, however, readily discernible and indicates that the failure may be caused by the progressing hydration of the oxide beneath the primer. This analysis proved only that hydration of the oxide is occurring and the quantity of hydrated oxide increases with the time of exposure of the oxide to the high humidity. This did not prove that hydration occurred before bond failure or crack extension.

If hydration of the anodized oxide was causing bond failure and crack extension, then it must have occurred before bond failure or crack extension. The weakened hydrated oxide should be visible on both parts of the failed wedge test specimen, on the anodized aluminum surface where we had already found it, and also on the opposite exposed primed surface of the wedge test specimen. If failure occurred in the hydrated oxide, about half of the oxide should be on the primer and the other half on the opposite metal surface. A SEM analysis was performed to verify this. The specimen is shown in Figures E-19 and E-23 as Area C on Side 2 of the wedge test specimen.

The 1 x 1/8-in. test specimen was sectioned from the wedge test specimen and mounted to permit SEM examination parallel to the crack propagation direction. The SEM photograph (Figure E-24) clearly shows the bulk hydrated oxide layer on top of the primer. The primer in this photograph is below the oxide and appears dark due to being out of focus.

These analyses provided us with two data points: first, in the wedge test with SA-6029 electroprimer, the failure area is in the 10 volt phosphoric acid anodize oxide; and second, the mechanism of failure is hydration of the oxide which weakened the oxide.

Final Failure Analysis on SA-6029 -65F Tensile Shear Specimens

Three possible paths for moisture to get to the oxide layer were considered. First, the cured epoxy primer could have a high moisture diffusion rate or be porous; second, something in the primer could provide the moisture path; and, third, a unknown layer between the primer and the anodize oxide could be permitting moisture to get into the oxide layer. Fracture analysis of the failed -65F lap shear tensile specimens provided the answer. The coalescing solvent was remaining in the primer and providing the path for moisture to get to the anodize oxide layer. The -65F lap shear tensile specimen failure analysis and results are given below.

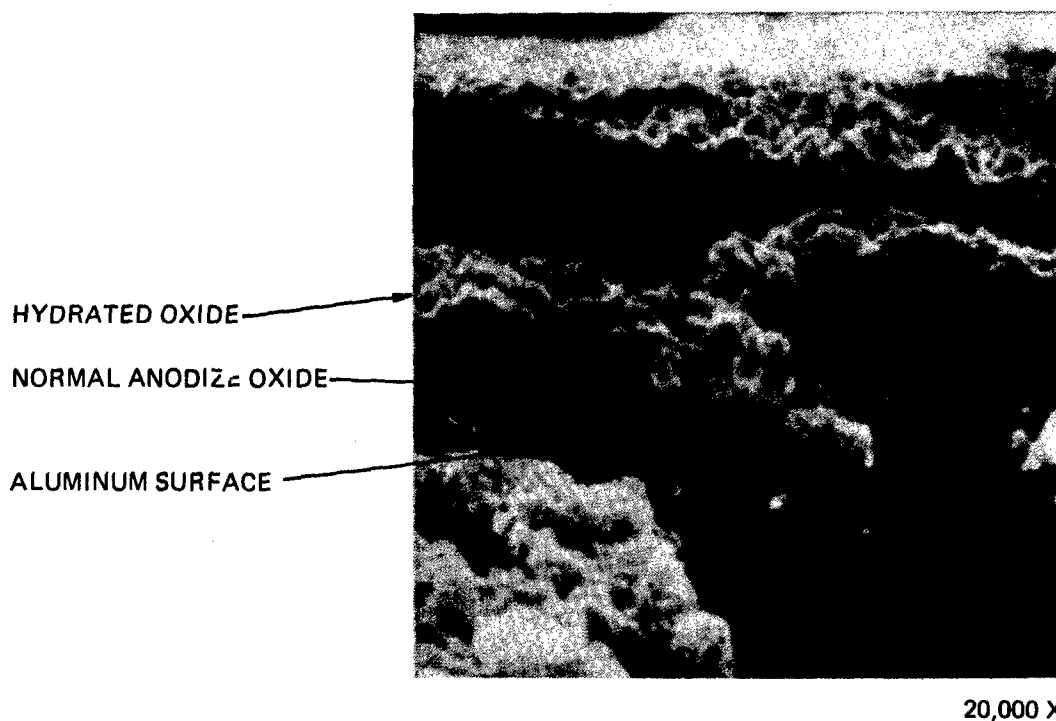


Figure E-22. SEM Photograph of Aluminum Oxide Layers on Wedge Test Specimen, Area B, Figure E-19

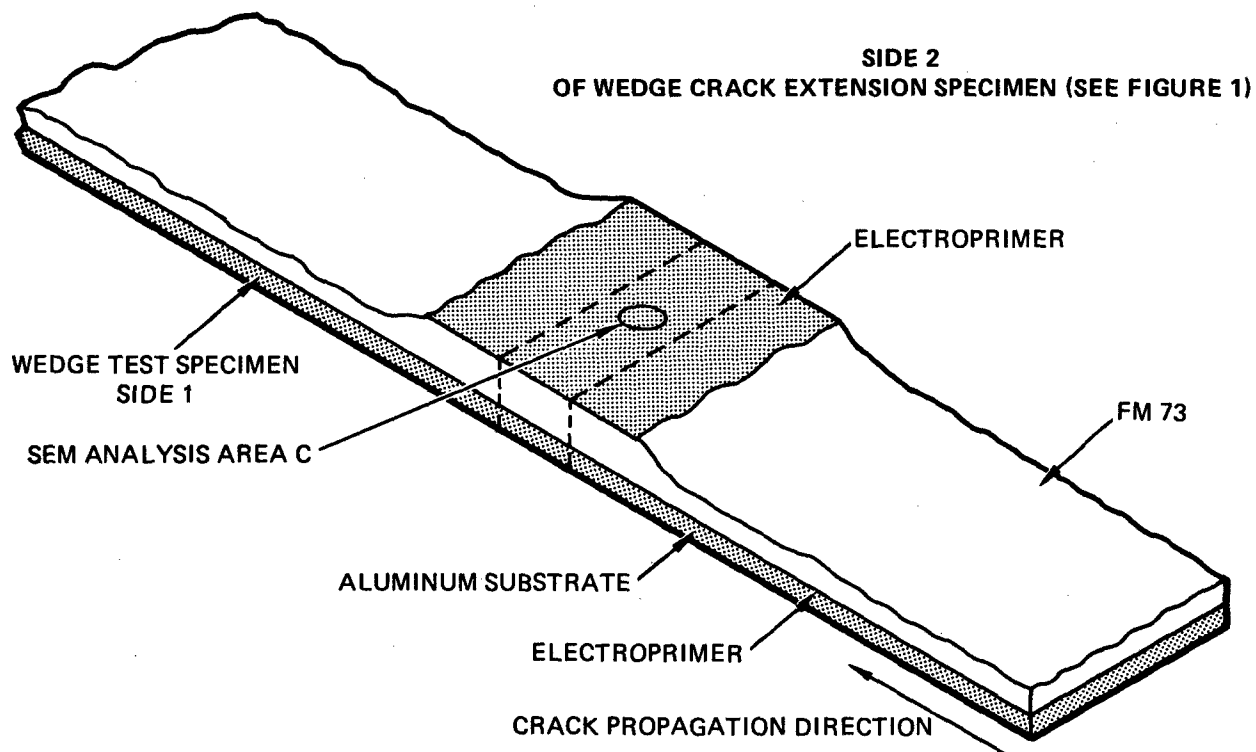


Figure E-23. Detail of Area C, Side 2, Wedge Crack Extension Specimen

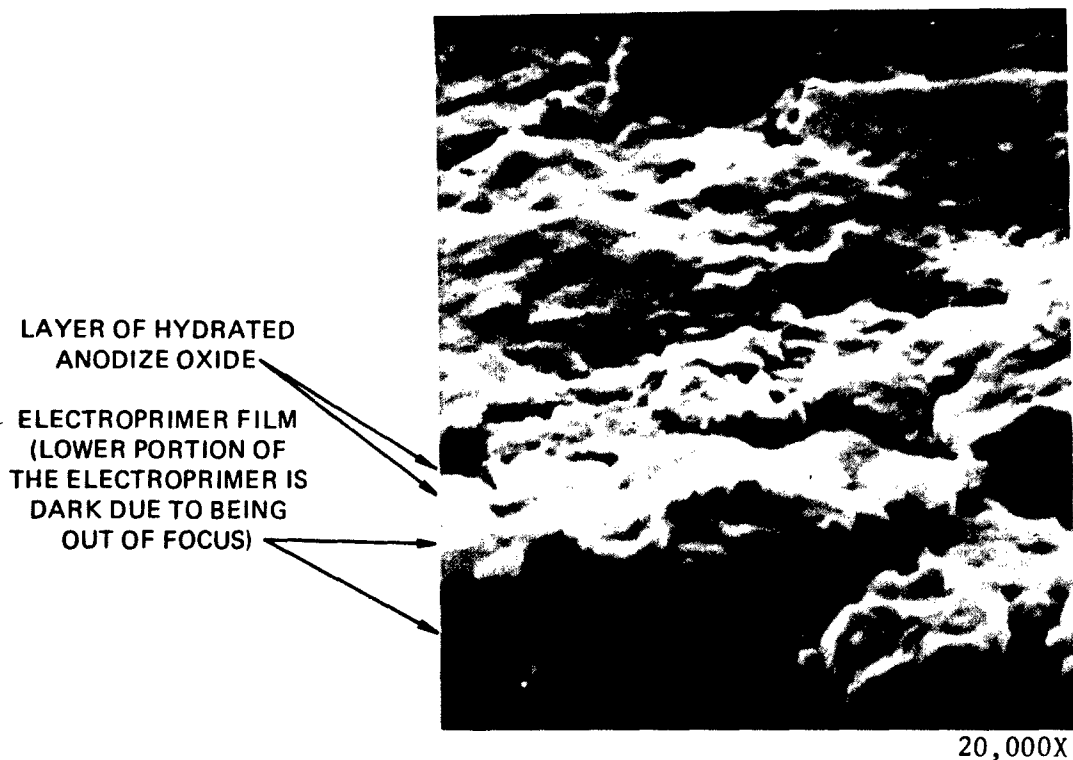


Figure E-24. SEM Photograph of Hydrated Aluminum Oxide Layers on SA-6029 Electrophimer (Area C, Figure E-23)

Fracture analysis of the -65F lap shear tensile specimens previously reported (Figures E-12 through E-18) shows the adhesive failure area is completely covered with an organic layer on top of the oxide layer. Thickness measurements of this organic layer establish it as the primer layer because the thickness is less than the applied electrophimer film thickness. If it were thicker than the electrodeposited prime layer, it would have to contain FM-73 adhesive used in making the test specimen. Therefore, it is concluded that failure in these -65F lap shear specimens is occurring within the primer and not at the oxide/primer or primer/adhesive interfaces or within the oxide layer. This implied that something was wrong with the electrophimer formulation but did not indicate the modification necessary for correcting it.

To continue the investigation, a lap shear tensile test panel was prepared with the electrophimer film cured at 235F but adhesive was not put on the panel. A SEM examination specimen was sectioned from the panel as shown in Figure E-25.

SEM examination of the specimen was made from the aluminum alloy substrates, through the 10-volt phosphoric acid anodize oxide, and through the electrophimer film. Figure E-26 shows the typical area examined. In the figure, the anodize oxide has two

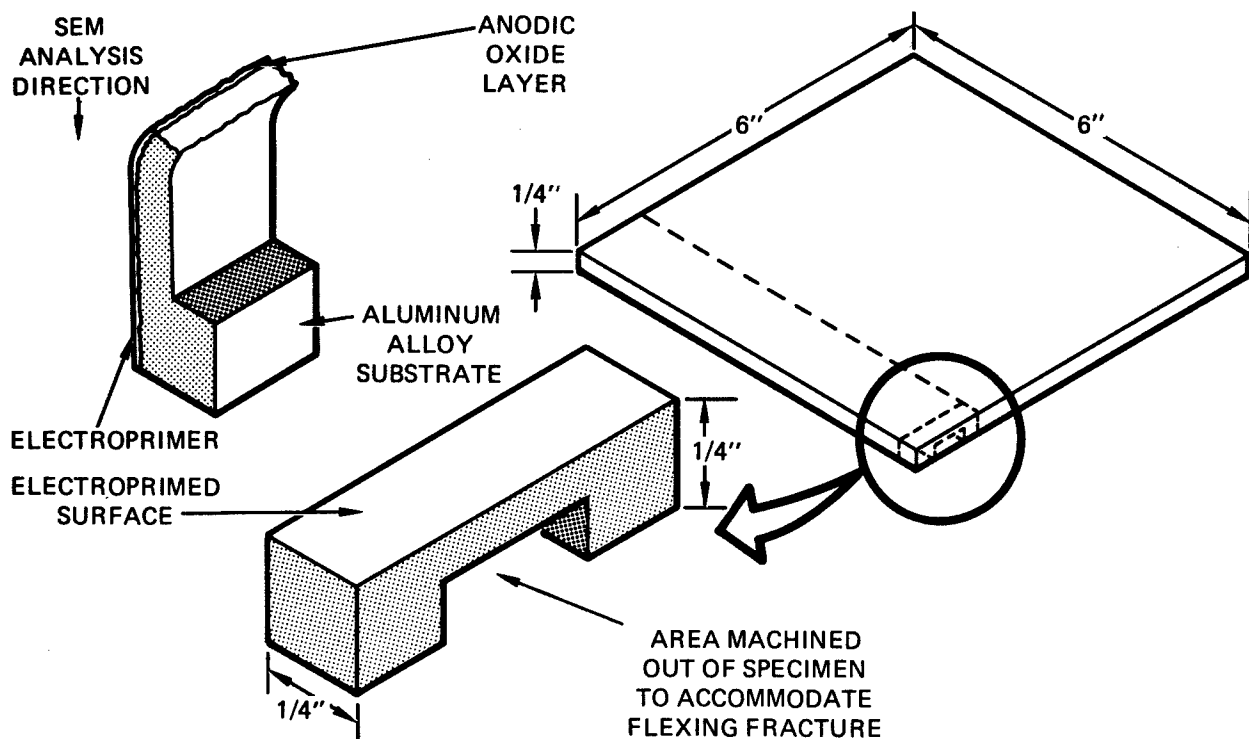


Figure E-25. SEM Specimen Preparation from Electroprimed Tensile Panel

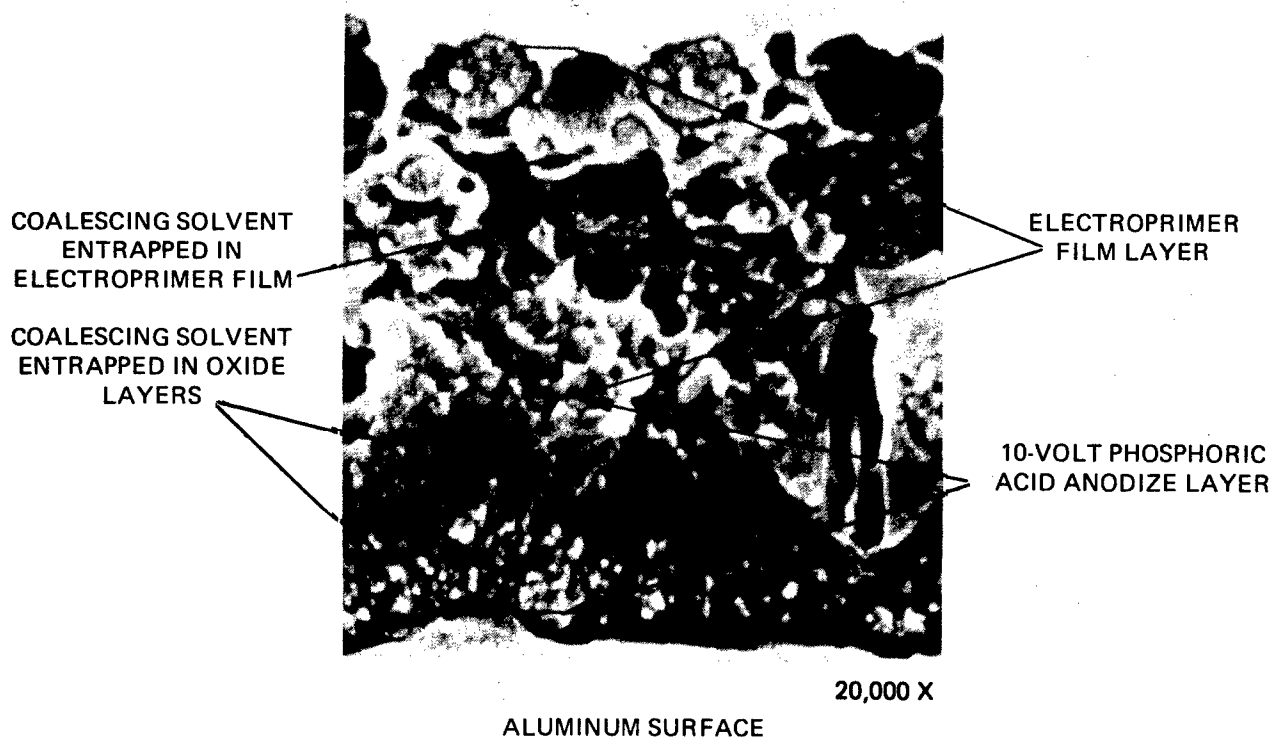


Figure E-26. SEM Photograph of Coalescing Solvent Entrapped in Both 10 Volt Phosphoric Acid Anodize Oxide and in Electroprimer Film

shades; the upper layer is less porous and darker in shade than the lower more porous layer. This is similar to a sealed sulfuric acid anodize surface treatment where the sealed oxide pores appear darker than the underlying unsealed oxide pores. Further, the electroprimer film in Figure E-26 appears "sponge-like," a condition that had not been noticed to any significant degree before. The electroprimer film has small "globules" of something in it. The only second phase material that could be in the primer is the coalescing solvent that should have been removed during the cure of the primer.

Conclusions on Failure Analysis of SA-6029 Specimens

Retained coalescing solvent in the primer film could explain the peculiar wedge test results and the -65F lap shear failure mode. The test panels for all tests were cured below 300F, a temperature below that required for complete removal of the isophorone coalescing solvent. In Figure E-26, the coalescing solvent remains in the anodize oxide giving it the appearance of a sealed oxide as well as in the bulk electroprimer film. The hydrophillic nature of the coalescing solvent provides the moisture path for hydration of the anodic oxide in the high humidity wedge tests. In the -65F lap shear tensile tests, the coalescing solvent in the bulk primer weakens the primer, and results in failure within the primer layer. Therefore, if the coalescing solvent can be removed from the primer film, the wedge crack propagation should be diminished and the failure mode in the -65F lap shear tensile tests should become cohesive with a reduction in data scatter.

SA-6166 and SA-6167 Formulations

Formulations SA-6166 and SA-6167 were prepared replacing the high boiling isophorone coalescing solvent with a much lower boiling coalescing solvent, cellusolve acetate. These two formulations have crosslinkers which have been modified to increase the elasticity of the cured film, to promote cohesive failure (within the adhesive) at -65F temperature test. The SA-6166 contains a modification of crosslinker B, and the SA-6167 contains a modification of crosslinker A.

Wedge test results at 120F/95% R. H. using these two modified formulations are presented in Table E-7 and are shown graphically in Figure E-27. Crack propagation has been arrested and crack extension is equivalent to the BR-127 baseline primer. In the -65F lap shear tensile test, the mode of failure has become mainly cohesive (see Figure E-28). The scatter in -65F strength is significantly diminished; the lowest

TABLE E-7. WEDGE CRACK EXTENSION RESULTS⁽¹⁾ USING LOW BOILING COALESCING SOLVENT – CELLUSOLVE ACETATE, SA-6166 AND SA-6167 ELECTROPRIMERS

Formulation Identification	Primer Cure Temperature ⁽²⁾ (F)	Average ⁽³⁾ Crack Extension (Inches)			
		Exposure Time to 120F/95% R. H.			
		24 Hour	96 Hour	336 Hour	504 Hour
SA-6166	230	0.05	0.06	0.06	0.06
SA-6166	245	0.05	0.06	0.06	0.06
SA-6167	230	0.05	0.06	0.06	0.06
SA-6167	245	0.04	0.05	0.05	0.06
BR-127	250	0.04	0.05	0.06	0.06
Control					

NOTES:

- (1) Standard wedge test specimen, see Appendix A, 10-volt phosphoric acid anodized 7075-T6 bare aluminum substrate bonded with FM-73 adhesive cured 1 hour at 250F.
- (2) All primers cured 30 minutes at specified temperature.
- (3) Results are the average of five test specimens.

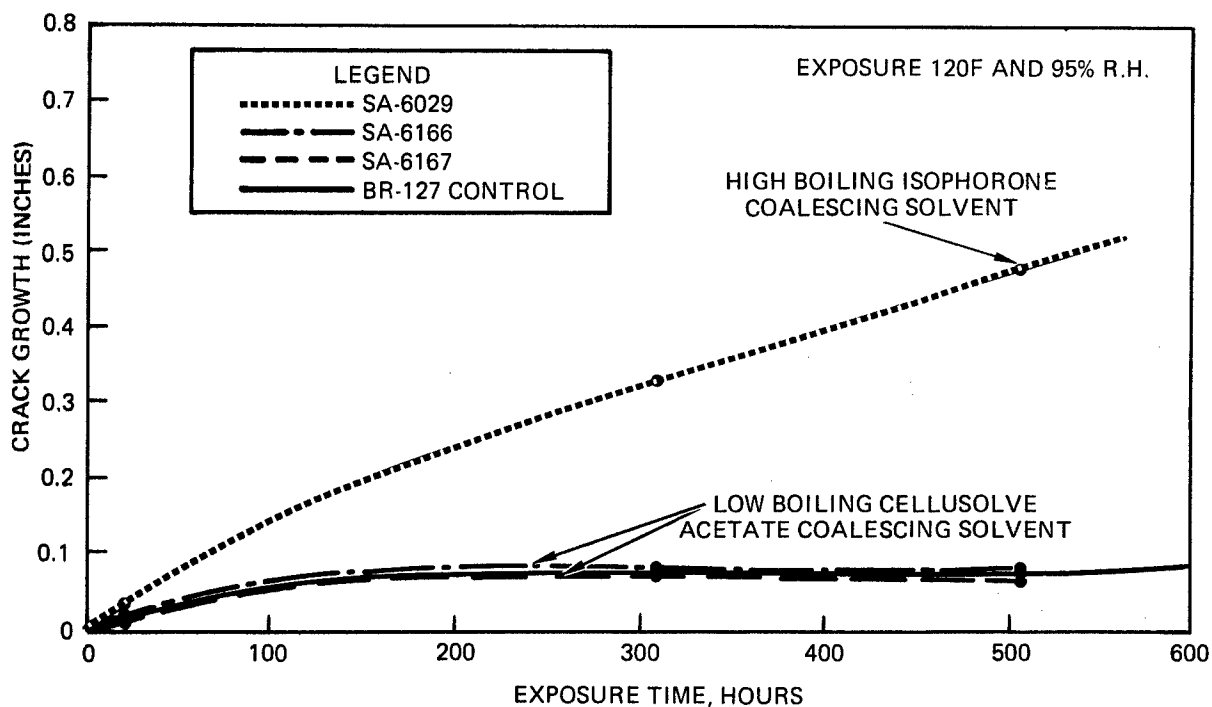
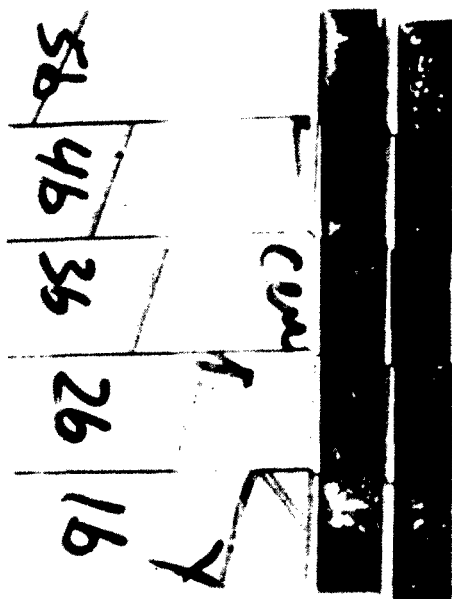
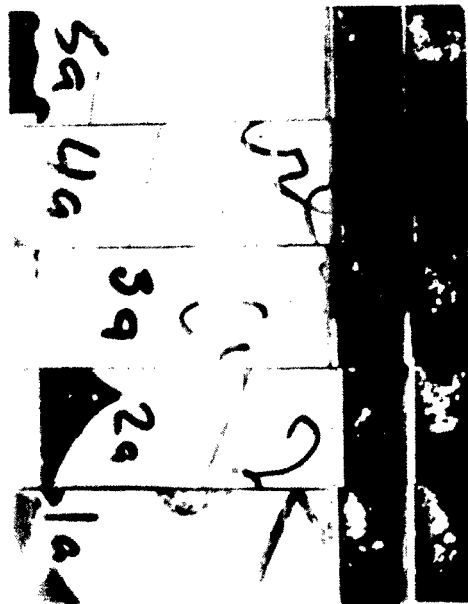


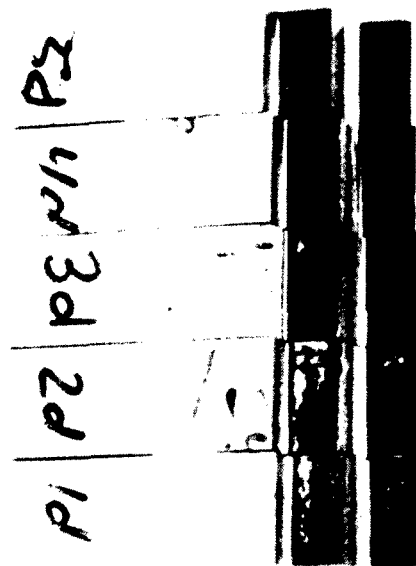
Figure E-27. Wedge Crack Extension Test Results of SA-6029, SA-6166 and SA-6167 Electroprimers



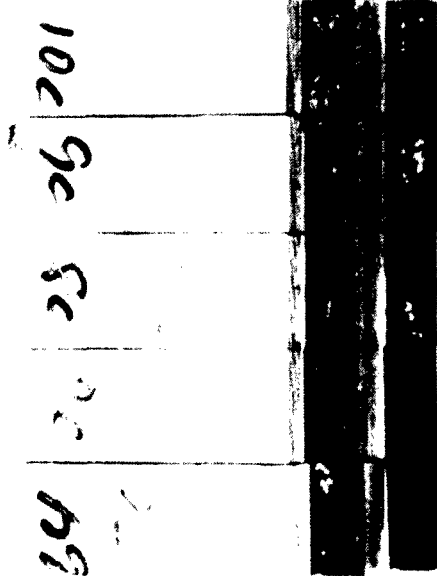
245F PRIMER CURE



230F PRIMER CURE



SA-6166



SA-6167

Figure E-28. Photograph Showing Failure Mode in -65 F Tensile Shear Specimens Made with Electroprimers Containing Cellulose Acetate Coalescing Solvent

tensile shear result of 36 specimens was 7920 psi with an overall average of 8290 psi (Table E-8).

The conclusion from this analysis was that the base electroprimer does not require reformulation. Complete solvent removal must be achieved during the cure of the electroprimer film and this can be accomplished by replacing the high boiling coalescing solvent with one that is completely eliminated by cure in the range of 235-250F.

Cocure of SA-6166

Northrop observed a small amount of primer to adhesive failure in the ruptured -65F tensile specimens of SA-6166 and SA-6167. An improved bond could be achieved between electroprimer and adhesive if the electroprimer and adhesive were cocured, i. e., both cured at the same time and temperature. Since the uncured electroprimer film contains a trace of water and a small percentage of coalescing solvent, the initial answer to the feasibility of cocuring is "no"; these volatile components will cause voids in the bond line. However, another possibility was suggested. The electroprimer film could be "B" staged to remove all traces of water and solvent, the adhesive applied, and then cure of the primer film could be accomplished during the adhesive film cure. This was tried and the results were surprisingly good. The cocure test was accomplished by electropriming two sets of 10-volt phosphoric acid anodized thick adherend* tensile test substrates. The electroprimer (SA-6166) was completely cured at 235F for 30 minutes on one set of panels. The second set was dried and B-staged for 30 minutes at 200F for solvent removal. Based on MEK and Meseran cure tests, it was known that some cross-linking or "B" staging of the SA-6166 primer does occur at 200F. Both sets of test panels were then layed-up with FM-73 adhesive, vacuum bagged and autoclave cured with the established cure cycle for the FM-73 adhesive system, one hour at 250F (see Appendix D for adhesive layup, bonding and cure control). The two sets of panels were then machined to standard 1/2-in. overlap specimens⁽¹⁾ and tensile tested at -65F. The average tensile strength is 120 psi higher for the cocured specimens, but the major improvement was the mode of failure which increased from approximately 75% cohesive to approximately 95% cohesive. This change in mode of failure was a very significant improvement (see Table E-9).

*See Appendix D for test specimen configuration.

TABLE E-8. THE -65F TENSILE SHEAR TEST RESULTS USING LOW BOILING COALESCING SOLVENT CELLUSOLVE ACETATE IN SA-6166 AND SA-6167 ELECTROPRIMERS

Primer Identification	Ultimate Tensile Shear Strength at -65F (psi)	
	Primer Cure	
	30 Minutes at 235F	30 Minutes at 245F
SA-6166	8090	8240
	8040	8560
	8320	7920
	7980	8130
	8640	9300
	8600	7880
	8490	8280
	8720	8240
	<u>8420</u>	<u> </u>
	Average 8360	8190
SA-6167	8400	8580
	8080	8250
	8260	8600
	8080	8500
	8240	7920
	7980	8490
	8270	8400
	8320	8140
	7980	8350
	<u> </u>	<u>8120</u>
	Average 8280	8340

NOTES:

- (1) Thick adherend machined notch tensile specimen (see Appendix D)
10-volt phosphoric acid anodized 7075-T6 bare aluminum substrates
bonded with FM-73 adhesive, cured 1 hour at 250F.
- A. The electroprimer film thickness was 0.1 mil.
- B. Average adhesive bondline thickness was 8 mil.

TABLE E-9. -65F TENSILE SHEAR STRENGTH TEST⁽¹⁾
 RESULT COMPARING COCURED⁽²⁾ VERSUS PRECURED⁽³⁾
 SA-6166 ELECTROPRIMER

PRECURED SA-6166 ELECTROPRIMER		COCURED SA-6166 ELECTROPRIMER	
Ultimate Strength (psi)	Failure Mode (% Cohesive)	Ultimate Strength (psi)	Failure Mode (% Cohesive)
7690	90	7920	95
8040	70	8000	95
7990	60	8480	95
8350	70	8210	95
7910	90	7920	95
<u> </u>	<u> </u>	<u> </u>	<u> </u>
Avg 7990	Avg 75	Avg 8110	Avg 95

(1) Specimen Configuration: Machined Notch Tensile Specimen, Appendix D,
 Figure D-2.

(2) SA-6166 B-staged 30 minutes at 200F, then cocured with the FM-73 adhesive at
 250F for 60 minutes.

(3) Standard 235F for 30 minute SA-6166 electroprimer cure, then bonded with FM-73
 and cured at 250F for 60 minutes.

Effect of Electrophimer Film Thickness on -65F Tensile Properties
(SA-6166 Formulation)

Another series of tests was performed to ascertain whether the electrophimer film thickness affected -65F tensile properties. Two sets of thick adherend tensile specimens* were 10-volt phosphoric acid anodized. One set was electrophimered to the nominal 0.2-mil thickness and the second set electrophimered to a 0.6-mil film thickness with electrophimer SA-6166. The electrophimer was cured for one hour at 245F. The electrophimered panels were then bonded* with FM-73 and machined to test configuration*. The -65F tensile test results, presented in Table E-10, show that the 0.6-mil primer thickness produced bonds of slightly lower average tensile strength, and slightly increased data scatter in the individual values. Only five specimens of each primer thickness were tested. The data suggested that the electrophimer is thickness sensitive; the thinner primer film tends toward higher lap shear tensile strength. This trend corresponds to the effect of primer thickness observed on the control primer, BR-127.

TABLE E-10. EFFECT OF SA-6166 ELECTROPRIMER FILM THICKNESS
ON -65F TENSILE SHEAR STRENGTH

Primer Identification	Ultimate Tensile Shear Strength at -65F (psi)	
	Film Thickness	
	0.2 Mils	0.65 Mils
SA-6166	7940	7110
	7830	6550
	8170	7660
	8340	7450
	<u>7930</u>	<u>8170</u>
	Average 7940	7410

NOTES:

- (1) Thick adherend machined notch tensile specimen, see Appendix D, 10 volt phosphoric acid anodized 7075-T6 bare aluminum substrates bonded with FM-73 adhesive, cured 1 hour at 250F.
- (2) Electrophimer cured at 245F for 30 minutes.

*See Appendix D for test specimen configuration.

A series of tests was performed to determine the effect of corrosion inhibiting fillers on primers. Strontium chromate is used in BR-127 as a corrosion inhibiting filler. Standard chromated BR-127 was compared to nonchromated BR-127 using the standard wedge crack extension test.*

A quart container of the BR-127 was rigorously shaken to evenly disperse the chromate constituent and was immediately divided into two equal parts. One of the two containers was centrifuged which readily separated the chromate fillers. The clear primer solution was then decanted for application as the nonchromated BR-127 primer. Two sets of wedge crack extension test panels were given a 10 volt phosphoric acid anodize surface treatment. One set was primed with standard chromated BR-127 primer, and the second set was primed with the nonchromated (centrifuged) BR-127. The primer in both cases was applied to a dry film thickness of 0.1 mil. The panels were then bonded with FM-73⁽¹⁾ and machined to test configuration⁽¹⁾ and exposed to the test environment of 120F, 95+% R.H. Since both sets of specimens, chromated and nonchromated primers, did not propagate a crack in seven days exposure, the specimens were subjected to 180F, 95+% R.H. In this environment, after 72 hours exposure, the average crack extension was approximately the same (0.6 in.) for the chromated and nonchromated BR-127, and the failure mode was approximately 50% within the adhesive and 50% between the adhesive and BR-127 primer. These results were unexpected and did not differentiate between the chromated and nonchromated primers.

Two factors may have prevented a good differentiation between the chromated and nonchromated BR-127 primer. First, some of the chromate may have been completely dissolved or colloiddally suspended in our "nonchromated primer"; and, second, recent data on other related programs indicate that the difference between a primed and an unprimed 10 volt phosphoric acid anodized surface can be observed only after very long time exposure.

*See Appendix D for test specimen configuration.

A critical factor involved in considering chromates as inhibitors in electropriming formulations is solubility. If the chromate additive is soluble to any significant degree, the conductivity of the electropriming bath will be disrupted and the primer will not deposit out of the bath. However, if the chromate is insoluble in water, it will be ineffective in inhibiting corrosion when exposed to moisture.

Inhibitors both chromated and non-chromated were considered for electropriming. However, no electroprime formulations were made with corrosion inhibitors because they were not required to achieve the contract goals.

Flexibilizing Agents

Another task in Phase II of this contract was the development of improved -65F adhesive bonding properties using flexibilizing agents*. The PCP-0300** flexibilizer was investigated as an additive to diminish the rigidity of the modified epoxy electro-resin at -65F. The PCP-0300 flexibilizer was selected based on its functionality and reactivity with the base resin functional groups. The flexibilizer is chemically bound in the polymer resin system during cure and thus eliminates potential stratification problems. The -65F lap shear tensile test was initially used to differentiate between increasing levels of the PCP-0300 to establish the optimum concentration of PCP-0300 to use. However, all the -65F tensile shear test results for the electroprimers were excellent (above 8,000 psi average) for increasing concentrations of PCP-0300 up to 60 ml/gallon. Since a definition of improved -65F adhesive bonding properties attributable to the PCP-0300 could not be made, the flexibilizer was not considered for further development work.

SA-6300 Formulation

The SA-6300 formulation was developed utilizing a new crosslinker, Cr D. An assessment of the basic adhesive bonding performance of SA-6300 was performed with an electroprime film cure of 275F. Panels of 7075-T6 bare aluminum were used to provide machine notched tensile specimens and T-Peel specimens were 10 volt phosphoric acid anodized, electroprimed and the electroprimer cured at 275F for 30 minutes. The electroprimed panels were adhesively bonded with FM-73 adhesive, cured for 60 minutes at 250F and machined to test specimen configuration. Results of the

*See Appendix A — Definition of Terms.

**PCP 0300 is a low M. W. (~500), triol flexibilizer compound made by Union Carbide Company. This is a polycaprolactone distributed under the trade designation NAIC polyol PCP-0300.

-65F machined notch tensile shear test are presented in Table E-11. The -65F and ambient temperature T-peel test results are given in Table E-12. The -65F and ambient temperature T-peel strengths are 9 and 16 pounds/inch, which is one pound/inch below the BR-127 control primer.

Cocure of SA-6300 Formulation

Since the 275F electroprimer cure temperature is above the required 250F cure goal of the contract electroprimer, a second set of tensile shear test panels were prepared in the following manner. After 10 volt anodizing and electropriming with the SA-6300, the electroprimer was "B-staged" at 220F for 30 minutes and then layed-up with FM-73 adhesive. The electroprimer was then cocured with the adhesive at 250F for 60 minutes. The -65F tensile shear test results (of the cocured SA-6300 electroprimer) are presented in Table E-13.

Although the -65F tensile test results with the B-staged SA-6300 electroprimer were somewhat lower (8750 psi) than the 275F cured SA-6300 electroprimer (9150 psi), the results were excellent compared to the other candidate electroprimers and above the baseline BR-127 control primer (8250 psi). Also, since the fracture in the tensile shear specimens was totally cohesive (within the adhesive) it was concluded that the SA-6300 is completely cured after exposure to 250F for 60 minutes.

Further, wedge crack extension specimens prepared in the same manner as above with the SA-6300 electroprimer "B-staged" at 220F for 30 minutes and cocured with the adhesive at 250F for 60 minutes, produced an average crack extension of less than 0.10 in. after 30-day exposure to 120F, 95% R.H. These wedge crack extension test results also verify the completeness of cure of the SA-6300 electroprimer exposed to 250F for 60 minutes.

SA-6410 to SA-6413 Formulation

The SA-6300 formulation lead to the development of the SA-6410 to 6413 series from which the two contract electroprimers, SA-6411 and SA-6412, were selected for more complete evaluation. Data on the SA-6410 to SA-6413 series are given in Section II of this report.

**TABLE E-11. TENSILE SHEAR TEST * RESULTS OF SA-6300
CURED AT 275F FOR 30 MINUTES**

Specimen Identification	Test Temperature (F)	Ultimate Load (psi)	Failure Mode
SA-6300-1	-65	9240	Cohesive**
SA-6300-2	-65	9260	Cohesive
SA-6300-3	-65	9120	Cohesive
SA-6300-4	-65	9160	Cohesive
SA-6300-5	-65	8980	Cohesive
Average		9150	

*Standard thick adherend machined notch tensile shear specimen of 7075-T6 bare aluminum alloy, 10 volt phosphoric acid anodized, SA-6300 electroprimed, and bonded with FM-73 adhesive cured at 250F/60 minutes.

**All failures were cohesive, within the FM-73 adhesive.

**TABLE E-12. T-PEEL TEST RESULTS OF SA-6300 ELECTROPRIMER
CURED AT 275F FOR 30 MINUTES***

Primer**	Test Temperature (F)	Average [†] T-Peel Strength (Pounds/Inch)	Failure Mode
SA-6300	-65	9	100% Cohesive [‡]
BR-127	-65	10	100% Cohesive
SA-6300	Ambient	16	100% Cohesive
BR-127	Ambient	17	100% Cohesive

*1 in. x 14 in. T-peel specimens of 7075-T6 bare aluminum alloy, 10 volt phosphoric acid anodize, primed with test primer and bonded with FM-73 adhesive cured at 250F/60 minutes.

**Nominal primer thickness; SA-6300 electroprimer 0.1 mil, BR-127 0.1 mil.

[†]Reported T-peel strength is the average of three individual values.

[‡]All failures were cohesive, within the FM-73 adhesive.

**TABLE E-13. TENSILE SHEAR TEST * RESULTS OF
B-STAGED SA-6300 ELECTROPRIMER COCURED WITH
FM-73 ADHESIVE AT 250F FOR 60 MINUTES**

Specimen Identification	Test Temperature (°F)	Ultimate Load (psi)	Failure Mode
SA-6300B-1	-65	8700	Cohesive**
SA-6300B-2	-65	8700	Cohesive
SA-6300B-3	-65	8900	Cohesive
SA-6300B-4	-65	8700	Cohesive
SA-6300B-5	-65	8760	Cohesive
Average 8750			

*Standard thick adherend machined notch tensile shear specimen of 7075-T6 bare aluminum alloy, 10 volt phosphoric acid anodized, SA-6300 electroprimed (cured 30 minutes at 220F) and bonded with FM-73 adhesive cured at 250F/60 minutes.

**All failures were cohesive, within the FM-73 adhesive.

APPENDIX F

DETAILS OF SURFACE PREPARATION AND MATERIAL AND PROCESS CONTROLS FOR ELECTROPRIMING FOR ADHESIVE BONDING

Sequence	Operation	Solution	Control and Maintenance
1	Vapor Degrease 3-5 minutes in Vapor Zone	1, 1, 1 Trichloethane Inhibited	pH 6.5 minimum
2	Alkaline Clean 15 minutes	Turco 42155 Alkaline Cleaner	6-8 ounces/gallon, 155+5F
3	Rinse 5 minutes	Tap water	120+10F
4	Deoxidize 7-8 minutes	Amchem 7 Nitric Acid	2.7-3.3 ounces per gallon 8-16 percent by volume Ambient temperature
5	Spray Rinse 5 minutes	Deionized water Rinse	Resistance: >1 megohm Ambient temperature
6	Anodize 20 minutes at 10 volts	Phosphoric Acid	13-16 ounces/gallon 74+5F
7	Spray Rinse 5 minutes	Deionized water Rinse	Resistance: >1 megohm Ambient temperature
8	30 volts 30 seconds	Sherwin-Williams Powerclad Electro- primer AF-C-5050-11	pH - 6.2 to 6.6 Conductivity - 900 ohms % solids - 9 to 10 Ambient temperature
9	Spray Rinse 5 minutes	Deionized water Rinse	Resistance: >1 megohm Ambient temperature
10	Cure 220F, 30 minutes	Recirculating Air Oven	None