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DEVELOPMENT OF IMPROVED LACV-30 PROPELLER BLADE COATINGS
FOR PROTECTION AGAINST SAND AND RAIN EROSION AND MARINE
ENVIRONMENT CORROSION

Glenn A. Malone
Bell Aerospace Textron
Post Office Box 1
Buffalo, New York 14240

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) An investigation was conducted of candidate systems offering potential erosion and corrosion protection when applied as coatings to Aluminum 7075 alloy propeller blades used to propel air cushioned vehicles operating in severe environments such as offshore and marine beach logistics missions. Blade lifespans are significantly abbreviated by erosion from sand and water impingement. This work focused on special hard anodized and hard nickel electroplated coatings as candidate protective systems with sand/rain erosion		

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20. Abstract (continued)

Testing to evaluate their merits. Attributes of the coating systems developed and studied included: *For (1)*

For hard nickel plated coatings → Ways and means to produce and control deposit hardness for optimum erosion resistance, methods of bonding to blades for high integrity adhesion, and inclusion of sacrificial corrosion protection electroplates in the coating systems (zinc and zinc-nickel alloy). *For (2)*

For hard anodized coatings → Incorporation of dry film lubricant systems on sealed hardcoats of various anodic coating thicknesses to enhance erosion performance.

Results of these studies indicated that anodized coatings did not provide suitable erosion protection to Aluminum 7075 in sand/rain environments, even with dry film lubricant supplemental films. Electroplated hard nickel coatings, Vickers hardnesses in the range of 380 to 440, appeared better for combined sand/rain erosion resistance based on comparisons with prior work. Dilute phosphoric anodizing the aluminum substrates led to excellent bonds and improved corrosion resistance when subsequently plated with ductile nickel from a low pH bath, followed by hard nickel electroplate. Electrodeposited sacrificial corrosion coatings degraded the overall coating bond integrity.

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SUMMARY

The propeller blades of air cushioned vehicles operating in coastal waters and over beaches are subject to extensive and rapid erosion from sand and water droplet impingement. The damage arises due to the high velocity (900 ft/sec) that is experienced at the propeller blade tip, and this is where erosion is most severe and rapid. The logical solution to this problem is to apply some type of coating, or covering, to the erosion sensitive areas which will have greater resistance to damage than the aluminum blade alloy. One such coating, which has received considerable interest, is electroplated hard nickel.

Successful application of hard nickel electroplate on air cushioned vehicle propeller blades has been reported for craft operated in primarily rainfield type environments. Previous work at Bell Aerospace Textron has demonstrated excellent water droplet erosion resistance with hard nickel during tests in a rain/sand erosion generation facility. Sand poses another problem in that impact velocity required to exceed the damage threshold is lower than for water droplets. Experience has shown that electroplated hard nickel performs best in a rainfield erosion mode when its hardness is high. A lower hardness deposit shows improved performance in sand erosion tests.

The current study demonstrates means of producing electrodeposited nickel with intermediate hardness levels suitable for both sand and rain erosion protection. The necessary process to accomplish this objective was developed and demonstrated by sand/rain erosion testing of Aluminum 7075 substrates coated with plated nickel having a Vickers hardness in the range of 380 to 440, the hardness region suggested by prior work as affording the optimum sand/rain combination protection. Suitable nickel deposits in this hardness range were achieved by use of low hardening agent concentrations in the plating bath and controlling the deposition parameters, bath temperature and current density, within specific limits. The conditions necessary for producing a wide range of specific nickel hardnesses were developed and demonstrated. Deposit compressive stresses, favorable to improved coating fatigue life, were characterized over a wide range of plating conditions. Mechanical properties for such deposits were also determined.

Since integrity of any coating applied to a propeller blade subject to high centrifugal forces during operation depends upon obtaining good bond strength to the substrate, an evaluation of the processes used to obtain this adhesion was conducted. Although the double zincating procedure produced excellent bonds on Aluminum 7075 samples, the extremely short zincate solution immersion times needed were not practical for full sized blades. It was also learned that zincate type bonds can be unreliable on Aluminum 7075 alloy due to the zinc segregation susceptibility of this material. The use of dilute phosphoric acid anodizing of Aluminum 7075 proved to be a preferred bond preparation method since excellent bond strengths could be achieved with better control.

Because the blades are used on craft operating in marine environments, and any applied erosion control coating is subject to penetration to expose the aluminum substrate, the problem of galvanic corrosion was addressed. Zinc and zinc-nickel alloy electrodeposits were applied as sacrificial intermediate coatings between the hard nickel and the anodized, or zincated, aluminum substrates. Both materials proved unsatisfactory; the zinc underwent rapid lateral corrosion which undermined the hard nickel, while the zinc-nickel alloy was fragmented by brittleness which led to galvanic pathways between the nickel and aluminum. The successful approach proved to be electrodeposition of ductile nickel from a low pH bath to bond to, and seal, the phosphoric anodized film. This was followed by hard nickel coating. This technique proved outstanding based on 336 hour salt fog exposure results.

Application of a dry film lubricant (thermosetting resin base) to relatively thick proprietary hard anodized systems appeared to be a viable alternative to hard nickel plating propeller blades. This also provided a comparison erosion control system for measuring the performance of hard nickel in the subsequent sand/rain erosion tests. Hard anodized coatings in the range of 0.002 to 0.004 inch thickness were produced on shot peened Aluminum 7075 surfaces and dry film coated. Sand and rain erosion performances of this material were poor, requiring only about one quarter of the time as hard nickel to sand erode a fixed volume of coating. Rainfield erosion performance of the hard anodized coatings was very poor, while performance of hard nickel was excellent.

Erosion tests, particularly in rain, revealed that the hard nickel performance was strongly influenced by the degree of surface smoothness in the "as deposited" condition. Any surface irregularities, such as slightly nodular growth, resulted in a shortening of the incubation period required to induce preliminary pitting.

From the encouraging results of this program, it appears that the next logical phase of propeller blade protection study -- that of coating full sized blades for field service evaluation -- should be considered.

PREFACE

Erosion studies of hard nickel electrodeposited coatings, for potential application as protective systems for air cushioned vehicles, was initiated at Bell Aerospace Textron by Mr. I. C. Snell in 1977. A large measure of the success realized in the program reported herein is due to his contributions in the areas of erosion testing and evaluation of the many specimens involved in the rain and sand studies.

The coordination of special hard anodizing work through commercial vendors was performed by Mr. H. A. Tripp, Chief, Electroforming Operations. He was also the author of Section V of this report. Within the Electroforming Operations Group, Mr. A. S. West performed much of the test specimen preparation and processing work. Metallurgical assistance was furnished by Mr. H. Kammerer.

The author wishes to express thanks to Messrs. H. J. Wittrock, Kaiser Aluminum Center for Technology (retired) and D. E. Thomas, National Bureau of Standards, for their helpful suggestions regarding dilute phosphoric anodizing of Aluminum 7075-T651. Permission to reproduce hard nickel performance diagrams from a recent paper presented at the March 1983 electroforming symposium in Los Angeles is gratefully given to the American Electroplaters' Society.

Finally, a special acknowledgement is given to Mr. Dario Emeric, U.S. Army-MERADCOM Materials Technology Laboratory, whose interest throughout the course of work was most encouraging.

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SECTION I

INTRODUCTION

The United States Army Mobility Equipment Research and Development Command (U.S. Army-MERADCOM) is committed to the evaluation and implementation of high mobility, rapid deployment transportation systems for military tactical and logistics applications. Military acceptance of such systems requires that they be capable of performing in a multitude of environmental scenarios. One such system, a thirty ton capacity air cushioned lighter (LACV-30), is currently under study based on its ability to deploy cargo from marine vessels onto, and over, beach surfaces at rapid speeds. Figure 1 illustrates a LACV-30 in operation.

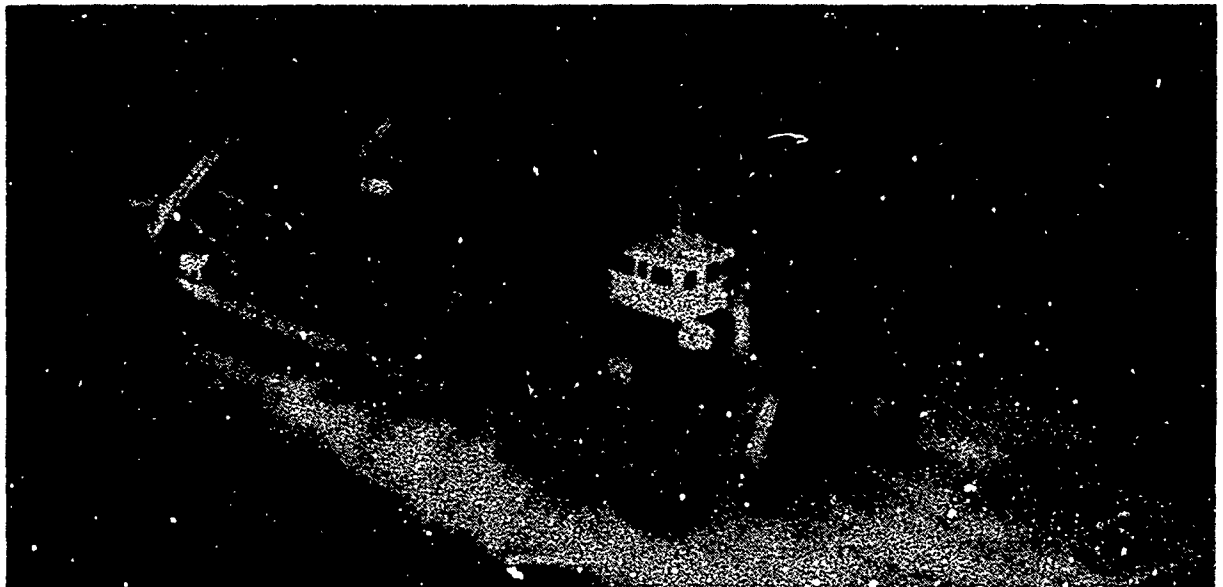


Figure 1. Amphibious Lighter LACV-30

The craft is propelled by two turbo-prop power plants at the stern end. Each propeller is composed of three variable pitch blades. The blades are very similar to Aluminum 7075-T6 in composition and material properties. The peripheral speed of the blade tip at normal full engine power is in the neighborhood of 900 feet per second. At such velocity, the erosion effects of water droplets and sand are very significant. In actual experience, rapid erosion wear of blades has resulted in a major impact on the LACV-30 test and evaluation program due to replacement blade costs, blade spares availability, and craft down-time for blade maintenance. Since the vehicle operates in a marine environment, erosion roughening of the blades probably accelerates intergranular corrosion damage.

As a result of the serious nature of these erosion and corrosion problems, a research and development program was initiated to provide

blade coatings which would indicate a prolonged blade life based on sample test results from service simulating environments. Electro-deposited hard nickel (EDHN) and molybdenum disulfide (epoxy base) sealed proprietary hard anodic films were the erosion resistant coatings selected for development and evaluation. The EDHN selection was based on encouraging results obtained from prior erosion studies performed at Bell Aerospace Textron and at the Air Force Materials Laboratory. The thick hard anodic coatings were selected for their reportedly good weathering performance -- which, when combined with the molybdenum disulfide lubricant seal, would be expected to provide good wear life and corrosion protection.

In the current program, three general problem areas were addressed to provide a hard nickel coating system exhibiting:

- (1) Optimum reproducible hardness in the outer electrodeposited nickel coating for resistance to both sand and rain erosion. This hardness had previously been defined as 400 to 450 Vickers Hardness Number (VHN).
- (2) High integrity bonding characteristics to the Aluminum 7075 alloy comprising the propeller blade. Bond strengths exceeding 137.9 MPa (20 ksi) were sought.
- (3) Good corrosion resistance in marine type environments where unexpected penetration, or localized disruption, of the hard nickel coating can lead to high galvanic cell potentials -- with rapid corrosion of the aluminum substrate and loss of adhesion at the bondline. A decrease in corrosion rate of three-fold was sought as compared to the corrosion performance of hard nickel bonded directly to the Aluminum 7075 alloy.

In that portion of the work involving hard anodizing for resistance to rain and sand erosion, specimens of Aluminum 7075 were to be shot peened, hard anodized by two different proprietary processes, sealed, and subsequently coated with a resin base molybdenum disulfide film to determine:

- (1) The effect of hard anodic film thickness on erosion performance.
- (2) The comparative performance with EDHN.
- (3) The value of the resin based lubricant films on erosion wear.

The total program was divided into discrete segments to investigate hardness control in EDHN, bonding characterization to Aluminum 7075 surfaces, corrosion protection intermediate coatings, fabrication of EDHN and hard anodic coated Aluminum 7075 specimens, and sand and rain erosion testing.

SECTION II

PRODUCING NICKEL COATINGS OF SUITABLE HARDNESS FOR BOTH SAND AND RAIN EROSION RESISTANCE

Background

Prior work by J. H. Weaver⁽¹⁾ has shown that electrodeposited nickel (EDN) coatings afford a marked improvement in erosion protection over most other coating materials. Weaver evaluated both hard and soft EDN on various substrate materials. He concluded that:

- (1) Both hard and soft EDN performed well in rain erosion environments.
- (2) Hard EDN was superior to soft EDN on glass-epoxy surfaces in a sand erosion environment -- based on limited data.
- (3) Thicker EDN coatings are required for sand protection than for rain.
- (4) Adhesion of the EDN coating to the substrate material is more critical to good sand erosion performance than to rain performance.

It should be noted that soft EDN coatings in this study had Vickers Hardness Numbers (VHN's) in the range of 230 to 271, while hard EDN coatings ranged from 454 to 542.

G. F. Schmitt, Jr.⁽²⁾ described the use of EDN coatings for helicopter main rotor blade protection in rain and sand environments. The EDN coating was applied either as an electroformed sheath adhesively bonded or fastened to the aluminum rotor blade or it was plated onto a stainless steel sheath which was fastened to the rotor leading edge.

M. Ishibashi has described EDN coatings of dual hardnesses on Japanese Hovercraft propellers⁽³⁾. His correspondence indicates that the propeller blades are coated (entirely) with EDN of about 350 VHN. Parts of the leading edges are then EDN coated with material of VHN in the range of 450 to 500. Overhaul is after 1,500 hours of running time. Replating is required after the second overhaul.

- (1) J. H. Weaver, "Electrodeposited Nickel Coatings for Erosion Protection", Air Force Materials Laboratory, Technical Report AFML-TR-70-111, July 1970, p 18.
- (2) G. F. Schmitt, Jr., "Liquid and Solid Particle Impact Erosion", Wear Control Handbook (Publisher unknown), pp 271-2.
- (3) Private correspondence from Mr. M. Ishibashi, Mitsui Engineering & Shipbuilding Co., Ltd., Tokyo, Japan to Bell Aerospace Textron New Orleans Operations, July 31, 1979

I. C. Snell⁽⁴⁾ studied numerous blade coating systems in the Government owned sand-rain erosion facility located at Bell Aerospace Textron's plant at Wheatfield, New York. Soft EDN of VHN 200 and hard EDN of VHN 570 were employed on separate specimens. His findings indicated that the softer EDN performed slightly better in a sand environment than did the hard EDN. In a rain environment, the reverse performance was found. This led to the conclusion that an intermediate hardness might provide best combined sand-rain erosion protection.

Electrolytes, Facilities, and Procedures Employed to Investigate Hardness Characteristics of EDN Coatings

The most commonly used electrolyte for plating high quality nickel is the nickel sulfamate solution. Selection of this bath was based on the facts that (1) it is chemically simple to formulate and control, (2) it responds to the addition of organic agents to produce deposits with wide ranges of hardness and mechanical properties, and (3) there is an extensive amount of experience with bath operation and control.

Three 159 liter (42 gallon) sulfamate baths were prepared to permit concurrent deposition studies to be conducted. Each plating tank was equipped with a thermostatically controlled heater capable of maintaining temperature within $\pm 1^\circ \text{C}$. Filters powered by in-tank pumps were used to maintain clean plating solutions -- the pumps also providing a forced flow of electrolyte over the surfaces being plated. Nickel anode rounds were housed in titanium baskets covered by knapped polypropylene inner bags and normal weave outer bags to prevent anode sludge from entering the plating baths. Electrolyte acidity was controlled by adding sulfamic acid (SNAC) to lower pH or nickel carbonate to raise pH. Chemical composition and operating parameters of the baths were maintained within the ranges shown in Table 1.

Specimens were produced for testing Vickers hardness and mechanical properties by deposition on stainless steel plates of various sizes. The EDHN does not bond to the stainless steel -- allowing the deposit to be easily separated. Each stainless steel plate (mandrel) was enclosed in a polyvinyl chloride box shield to assure that no nodular edge growth would occur. Such shielding devices promote uniform distribution of primary and secondary currents -- the results of which are more uniform deposit thickness, hardness, and mechanical properties.

All hardness testing was conducted on a Vickers-Armstrong testing machine using a 10 kilogram load. Test coupons were cut from the EDHN samples and hardness impressions made on each face. Four to five readings were made on each surface for averaging. This enabled our evaluating hardness at the start of deposition and at the end of deposition.

(4) 1979 Independent Research & Development Brochure, Bell Aerospace Textron Report No. 0500-927C14, Project 7919.

TABLE 1. ELECTROLYTE COMPOSITION AND OPERATING PARAMETERS

Ingredient or Operating Variable	Units of Measure	Tank No.	Tank No.	Tank No.
		HN-1	HN-2	HN-3
Nickel Metal	g/l	73 - 81	73 - 81	80 - 81
Additive A ^a	g/l	1.9	1.9	2.1
Boric Acid	g/l	30 - 36	30 - 36	31 - 32
SNHAB ^b	ml/l	0 - 3.96	0 - 3.96	0 - 3.96
pH		3.9 - 4.7	3.9 - 4.7	4.1 - 4.6
Temperature	°C	37.8 - 43.8	37.8 - 43.8	36.9 - 37.8
Anodes ^c		S.D. Ni	S.D. Ni	S.D. Ni
Agitation		Sprays	Sprays	Sprays
Current Density Amp/dm ²		1.86 - 3.72	1.86 - 3.72	1.74 - 1.90

^aAdditive A is an anode corrosion agent containing MgCl₂. It is supplied by Allied-Kelite Division, Witco Chemical Corp.

^bSNHA is a hardening agent for the Barrett Sulfamate Nickel electrolyte. It is available in lot controlled liquid form from Allied-Kelite Division, Witco Chemical Corporation.

^cS.D. Ni refers to sulfur depolarized nickel rounds available through International Nickel Company, Inc.

All EDN is subject to internal stresses resulting from crystallographic lattice structure anomalies such as spacial vacancies or atomic crowding. Such stresses are usually tensile in nature; however, they are most often compressive when organic hardening agents are employed in nickel electrolytes. Periodic measurement of such stresses was made with a Brenner-Senderoff Spiral Contractometer(5).

Studies to Determine the Consumption Rate of Hardening Agent

The organic hardening agents used in sulfamate nickel electrolytes are usually aryls containing a functional sulfonate group in the molecular structure⁽⁶⁾. Typical examples of such agents are the sodium salts of naphthalene trisulfonic acid, metabenzene disulfonic acid, and benzoic sulfimide (saccharin). The effectiveness of such agents to harden EDN is dependent on the ability to reduce the sulfur containing group at the surface being plated. Since EDHN deposits contain significantly greater contents of sulfur than conventional soft EDN, one can safely assume that the hardening agent undergoes gradual electrochemical reactions whereby the hardening agent concentration is reduced and the concentration of by-products is increased. Since production of rather narrow hardness ranges in EDHN coatings on propeller blades is essential to optimum combined sand

(5) A. Brenner and S. Senderoff, "A Spiral Contractometer for Measuring Stress in Electrodeposits", Proceedings of the 35th Annual Convention, American Electroplaters' Society, Atlantic City, New Jersey, June 27 - July 1, 1948, pp 53-78.

(6) J. L. Marti and G. P. Lanza, "Hardness of Sulfamate Nickel Deposits", Plating, April 1969.

and rain erosion resistance, the matter of hardening agent life and control is of great importance.

In the initial study, the newly formulated electrolyte in Tank No. HN-1 was peroxide treated and flowed through activated carbon as the standard purification procedure to remove organics prior to use. 0.78 g/l of wetting agent (SNAP) was added to the bath to alleviate hydrogen bubble retention on the deposit surface; such bubbles lead to pit formation. The hardening agent concentration was arbitrarily set at 3.96 ml/l. By the supplier's recommendation, the EDHN bath normally is operated at 7.81 ml/l of hardening agent (SNHA); however, a concentration that high leads to Vickers harnesses which are much greater than those sought for blade coatings. The shielded stainless steel plates used as plating mandrels measured 13.33 cm by 13.33 cm. The backsides were masked to permit plating on one face only.

Ten consecutive EDHN plates were produced to thicknesses in the range of 1.57 mm (0.062 in) to 1.93 mm (0.076 in). After a two week standby period, another nine EDHN plates were plated with greater thicknesses of about 2.40 mm (0.095 in). The total plating time was determined for each panel. Each panel was weighed to the nearest 0.1 gram. From this data, and the knowledge that the sulfamate plating bath efficiency is about ninety-eight percent, it was possible to calculate the average plating current and current density for each EDHN plate. Changes in deposit Vickers hardness could then be evaluated based on accumulated ampere-hours of plating imposed on the electrolyte. It was expected that gradual changes in hardness could be related to accumulated ampere-hours of plating per liter of electrolyte and thus define the life expectancy of the hardening agent. A condensation of the recorded and calculated data for the above specimens appears in Table 2.

From Table 2, it would appear that a significant hardness change occurred after Panel HN-1-110-10 was produced. Since the hardness remained relatively constant from Panel HN-1-110-11 through Panel HN-1-110-19, it was suspected that the increase in VHN was due to the effects of SNHA breakdown products reaching a critical concentration.

It was of immediate concern that the recovery capability of spent EDHN baths be demonstrated. Tank HN-1 was hydrogen peroxide treated by adding 240 ml of 30 percent (by volume) H_2O_2 to the 159 liter bath at room temperature. All anodes were removed to prevent nickel from catalytically decomposing the peroxide. After allowing the peroxide to react with the hardening agent (and by-products), the excess peroxide was boiled out by heating the bath to 61° C (142° F) for one hour. During cool-down, the bath was carbon treated. A test panel was plated to reveal a semi-lustrous surface which indicated that some organic remained in the bath. A second peroxide-carbon treatment satisfactorily removed the remaining organics.

A new series of hardness test panels was produced in Tank HN-1 using a bath temperature of 37.8° C (100° F). The stainless steel mandrel size was changed to 21.59 cm by 11.43 cm. This would permit the fabrication of mechanical property test specimens from the EDHN samples.

TABLE 2. HARDENING AGENT CONSUMPTION RATE STUDY - TEST DATA FOR ELECTROLYTES AT 43° C (110° F),
HARDENING AGENT (SNHA) CONCENTRATION OF 3.96 ML/L, TANK NO. HN-1

Specimen Number	Current Density (Amp/dm ²)	Bath pH	Plating Time (Hours)	Thickness (mm)	Calculated		Accumulated		Vickers Hardness ^a	
					Ampere-Hours	Amperes	Hours	Amperes	Start	End
HN-1-110-01	2.285	4.3	48.00	1.707	225.60		225.60		421	435
HN-1-110-02	2.285	4.3	48.50	1.722	227.95		453.55		415	429
HN-1-110-03	2.230	4.6	48.00	1.669	220.80		674.35		405	422
HN-1-110-04	2.230	4.5	47.67	1.664	219.28		893.63		444	452
HN-1-110-05	2.230	4.3	49.67	1.712	228.48		1122.11		448	454
HN-1-110-06	2.183	4.0	48.00	1.605	216.00		1338.11		442	447
HN-1-110-07	2.090	4.0	47.75	1.560	205.33		1543.44		437	443
HN-1-110-08	2.183	4.1	48.00	1.641	216.00		1759.44		429	441
HN-1-110-09	2.183	4.0	46.50	1.580	209.25		1968.69		437	430
HN-1-110-10	2.230	4.0	55.75	1.941	256.45		2225.14		430	437
Point where two week interruption occurred and bath was in a standby status.										
HN-1-110-11	2.425	4.4	65.58	2.464	327.90		2553.04		490	492
HN-1-110-12	2.285	4.4	72.17		339.05		2892.09		Not Tested	
HN-1-110-13	2.183	4.4	72.00		324.32		3216.41		Not Tested	
HN-1-110-14	2.137	4.5	72.50		314.82		3531.23		Not Tested	
HN-1-110-15	2.183	4.5	71.67	2.426	321.44		3852.67		484	486
HN-1-110-16	2.304	4.5	71.92		341.66		4194.33		Not Tested	
HN-1-110-17	2.183	4.5	71.90		319.38		4513.71		Not Tested	
HN-1-110-18	2.183	4.6	70.00		321.00		4812.87		Not Tested	
HN-1-110-19	2.230	4.7	72.00	2.451	327.96		5140.83		477	494

^aEach Vickers Hardness Number (VHN) represents an average of four(4) indentation readings. VHN readings at "Start" refer to the EDHN sample side adjacent to the stainless steel mandrel while those at "End" represent the final plated surface.

A control specimen was produced prior to adding hardening agent to the bath. Production and test data for the panels electrodeposited in this study is found in Table 3. Between the deposition of Panels HN-1-100-03 and -04, a stress measurement was made using a Brenner-Senderoff Contractometer. The study was terminated after Panel HN-1-100-07 due to an electrolyte contamination problem. The distilled water being supplied from a central water still was found to have lower resistance than specified requirements due to calcium carbonate carry-over to the storage tank.

The study of hardening agent consumption for electrolytes operated at 37.8° C (100° F) was repeated in a new plating bath in Tank HN-3. The bath was carefully purified in the manner previously described for Tank HN-1. The water supply for liquid level control was changed to demineralized water with subsequent carbon treatment. The hardness test specimens were deposited on both front and back sides of the stainless mandrel to achieve a more rapid accumulation of ampere-hours. Prior to adding the hardening agent, a control panel was produced to confirm that the bath was producing acceptable nickel. Since the mandrel provided two duplicate panels for each plating run, only one was tested. Production and test data for this series of panels is shown in Table 4. A contractometer test performed after the final panels were produced revealed that the bath was still furnishing compressively stressed nickel. Panel production was terminated after 3000 ampere-hours due to the fact that the mirror-bright appearance of the EDHN specimens had changed to a semi-bright, hazy look.

Studies to Determine Controls Necessary to Produce Discrete Vickers Hardness Ranges

The initial study of the effects of hardening agent (SNHA) concentration and electrolyte temperature on Vickers hardness was performed in a 159 liter bath in Tank HN-2. Plating current density was not varied in this study. The plating solution was purified by the standard single hydrogen peroxide-carbon treatment procedure. Stainless steel mandrels measuring 13.33 cm by 13.33 cm were used as cathodes. A control panel was produced prior to introducing hardening agent into the bath. The starting concentration of SNHA was 1.85 ml/l. Since higher than desired Vickers hardnesses had been previously encountered when 3.96 ml/l of SNHA was used, it was thought that 1.85 ml/l would be a more appropriate concentration to start the study.

Current density was maintained close to 2.0 amp/dm² (21.5 amp/ft²). Only one side of the stainless steel cathode was plated. For each level of SNHA concentration, two specimens were deposited -- one at a bath temperature of about 37.8° C (100° F) and the other at about 43° C (110° F). Periodic stress measurements were made with a Brenner-Senderoff Spiral Contractometer to determine what changes in compressive stresses would result from different SNHA concentrations. Sample production was halted prematurely when the previously discussed problem of calcium contamination from the distilled water supply was encountered in Tank HN-1. Production data and test results for this series of EDHN specimens are found in Table 5. The plating bath was

TABLE 3. HARDENING AGENT CONSUMPTION RATE STUDY - TEST DATA FOR ELECTROLYTES AT 37.8° C (100° F),
HARDENING AGENT (SNHA) CONCENTRATION OF 3.96 ML/L, TANK NO. HN-1

Specimen Number	Current Density (Amp/dm ²)	Bath ^a pH	Plating Time (Hours)	Plated Thickness (mm)	Calculated Ampere-Hours	Accumulated Ampere-Hours	Vickers ^b Hardness ^b Start	Vickers ^b Hardness ^b End
Control ^c	1.784	4.3-4.4	50.17	1.232-1.316	250.61	225.60	268	237
HN-1-100-01	1.812	4.1-4.4	49.92	1.209-1.275	252.75	252.75	507	512
HN-1-100-02	1.747	3.9-4.3	48.08	1.171-1.227	235.88	488.63	Not Tested	
HN-1-100-03	1.765	3.9	50.22	1.242-1.295	248.65	737.28	500	542
Contractometer indicated a compressive stress of 148.2 MPa (21.49 kpsi) at 1.681 Amp/dm ² .								
HN-1-100-04	1.784	4.0	49.50	1.222-1.288	247.44	984.72	Not Tested	
HN-1-100-05	1.784	4.0	49.00	1.209-1.278	243.99	1228.71	512	529
HN-1-100-06	1.765	4.1-4.2	49.75	1.222-1.280	246.41	1475.12	Not Tested	
HN-1-100-07	1.784	4.0-4.4	48.75	1.196-1.260	243.15	1718.27	510	524

^aSignificant changes in pH (greater than 0.1 pH unit) during a specimen plating run were indicative of a bath feed-water pH problem. This was confirmed by the discovery of calcium salts in the feed-water storage tank.

^bEach Vickers Hardness Number (VHN) represents an average of four(4) indentation readings. VHN readings at "Start" refer to the EDHN sample side adjacent to the stainless steel mandrel while those at "End" represent the final plated surface.

^cNo hardening agent (SNHA) was present when the control specimen was produced.

TABLE 4. HARDENING AGENT CONSUMPTION RATE STUDY - TEST DATA FOR ELECTROLYTES AT 37.8° C (100° F),
HARDENING AGENT (SNHA) CONCENTRATION OF 3.96 ML/L, TANK NO. FN-3

Specimen Number	Current Density (Amp/dm ²)	Bath ^a pH	Plating Time (Hours)	Plated Thickness (mm)	Calculated Ampere-Hours	Accumulated Ampere-Hours	Vickers ^a Hardness	
							Start	End
Control-00A ^b	1.802	4.1	54.75	1.245-1.316	498.13	498.13	289	281
HN-3-100-01A	1.839	4.5	48.10	1.247-1.308	490.69	490.69	514	531
HN-3-100-02A	1.858	4.5	51.87	1.321-1.379	511.08	1001.77	505	534
HN-3-100-03A	1.904	4.6	49.12	1.316-1.394	503.07	1504.84	518	528
HN-3-100-04A	1.886	4.6	47.88	1.293-1.356	491.71	1996.55	507	525
HN-3-100-05A	1.886	4.6	48.98	1.306-1.387	501.40	2497.95	514	530
HN-3-100-06A	1.904	4.6	48.87	1.300-1.369	502.70	3000.65	512	531

Contractometer indicated a compressive stress of 159.0 MPa (23.06 ksi)

Mechanical Properties Test Results

Specimen Number	Ultimate Strength MPa	Yield Strength MPa	Yield Strength ksi	Elongation, % in	
				2.54 cm (1 in)	Gauge Length
Control-00A	824.0	624.0	90.5	8.5	
HN-3-100-03A	1812.7	1276.3	185.1	13.0	
HN-3-100-04A	1818.2	1190.8	172.7	12.5	
HN-3-100-05A	1811.1	1236.3	179.3	13.0	

^aEach Vickers Hardness Number (VHN) represents an average of five (5) indentation readings. VHN readings at "Start" refer to the EDHN sample side adjacent to the stainless steel mandrel while those at "End" represent a final plated surface.

^bNo hardening agent (SNHA) was present when the control specimen was produced. For each specimen designated by a suffix letter "A", there was a corresponding specimen "B" which was not tested.

TABLE 5. HARDENING AGENT CONCENTRATION STUDY - TEST DATA FOR ELECTROLYTES AT 37.8° C (100° F) AND 43° C (110° F); HARDENING AGENT (SNHA) CONCENTRATIONS OF 1.85 TO 3.43 ML/L; TANK NO. HN-2

Specimen Number	SNHA Conc. (ml/l)	Current Density (Amp/dm ²)	Temp. (°C)	Bath pH	Plating Time (Hours)	Plated Thickness (mm)	Accumulated Ampere-Hours	Vickers Hardness ^a Start	Vickers Hardness ^a End
Control ^b	0.00	2.174	37.2	4.3-4.6	48.67	1.455-1.552	298.51	295	308
HN-2-100-01	1.85	1.979	38.3	3.9-4.1	50.17	1.374-1.450	278.56	511	521
Contractometer	1.85	1.951	38.3	Compressive stress was 132.8 MPa (19.26 ksi).					
HN-2-100-03	2.38	1.960	37.2	4.0-4.2	49.00	1.331-1.405	549.02	517	517
HN-2-100-05	2.91	2.007	37.8	4.1-4.3	49.67	1.339-1.448	829.91	508	527
Contractometer	2.91	2.062	37.8	Compressive stress was 94.2 MPa (13.66 ksi).					
HN-2-100-07	3.43	1.997	37.2	4.1-4.2	48.50	1.372-1.410	1102.51	Not Tested	
HN-2-110-02	1.85	2.100	43.0	4.0-4.1	49.97	1.448-1.527	1397.29	492	492
Contractometer	1.85	5.295	43.0	Compressive stress was 76.7 MPa (11.13 ksi).					
Contractometer	1.85	3.920	43.0	Compressive stress was 115.6 MPa (16.76 ksi).					
Contractometer	1.85	1.654	43.0	Compressive stress was 146.4 MPa (21.23 ksi).					
HN-2-110-04	2.38	2.062	43.1	4.0-4.1	51.50	1.476-1.549	1696.64	485	493
HN-2-110-06	2.91	2.044	42.7	4.0-4.2	49.92	1.443-1.488	1983.69	479	492
Contractometer	2.91	1.440	42.7	Compressive stress was 118.7 MPa (17.21 ksi).					

^aEach Vickers Hardness Number (VHN) represents an average of five(5) indentation readings. VHN readings at "Start" refer to the EDHN sample side adjacent to the stainless steel mandrel while those at "End" represent the final plated surface.

^bNo hardening agent (SNHA) had been added when the control specimen was produced. The VHN data for the control panel is high for conventional "soft" nickel -- indicating that some hardening agent remained after the single peroxide-carbon treatment purification.

scrapped since it is economically impractical to remove calcium as a nickel plating bath impurity.

It appeared to be impractical to conduct simultaneous temperature, current density, and hardening agent concentration studies in one electrolyte due to the long-term chemical decomposition effects on the hardening agent. Completely new electrolytes were prepared in Tanks HN-1 and HN-2. Starting compositions of both baths were the same. Standard purification treatments were used on each bath, including low current density electrolyzation to remove trace metal contaminants. Tank HN-1 was operated at 37.8° C (100° F) and Tank HN-2 at 43° C (110° F). Plating current densities of 1.858 and 3.716 amp/dm² (20 and 40 amp/ft²) were selected for producing panels at each fixed condition of bath temperature and hardening agent concentration.

Control specimens were produced from each bath, and at each of the two current densities, prior to adding hardening agent to the electrolytes. Hardening agent was increased in controlled increments in each tank with samples being produced at both current densities between SNHA additions. Periodic stress measurements were made. Panel sizes were sufficient to permit testing of mechanical properties. Plating was confined to one side of the shielded mandrel. Hardening agent concentration was varied from 1.85 to 3.96 ml/l. Production data and test results for Tank HN-1 samples (37.8° C electrolyte) are shown in Table 6. Similar tabulations for Tank HN-2 samples (43° C electrolyte) are in Table 7. It was noted that the hardnesses exhibited by the control panels were higher than expected for conventional "soft" nickel. Since no SNHA had been added to either bath, it was suspected that the abnormal hardness was due to leaching of SNHA and SNHA by-products from the anodes and polypropylene anode bags which had been only rinsed prior to re-insertion in the electrolyte. The amount of organics thus introduced was believed to be very small since hardness continually decreased to normal values as the plating progressed on the two consecutive control panels for each bath.

A final hardness study was conducted using very low concentrations of SNHA. Based on the better ductility shown by EDHN plated from 43° C (110° F) electrolytes, this was the bath temperature used in the study. Tank HN-1 electrolyte was conditioned by removing hardening agent with two hydrogen peroxide treatments -- each followed by twenty-four hour carbon treatments. The anodes were well rinsed and the anode basket bags were leached in a sulfamic acid solution before reuse. Table 8 lists production data and test results on the EDHN panels in this study. Much lower VHN's were found for the control panels, confirming the effectiveness of the purification method.

Discussion of Hardness Studies

Data from Tables 2 through 4 indicates that hardening agent breakdown is a relatively slow electrochemical process in the electrolyte temperature range of 37.8° to 43° C (100° to 110° F) and when current densities of 1.75 to 2.42 amp/dm² (18.8 to 26.0 amp/ft²) are employed.

TABLE 6. EFFECTS OF CURRENT DENSITY AND INTERMEDIATE RANGE HARDENING AGENT CONCENTRATIONS
ON VICKERS HARDNESS OF NICKEL FROM ELECTROLYTES AT 37.8° C (100° F) - TANK NO. HN-1

Specimen Number	SNHA Conc. (ml/l)	Current Density (Amp/dm ²)	Bath pH	Plated Thickness (mm)	Vickers Hardness ^a Start End	Mechanical Properties			
						Ult. Strength	Yield Str.	Elong. in	
						MPa	ksi	MPa	ksi
Control ^b	0.00	1.793	4.2	1.262-1.367	319 311	768.1	111.4	595.7	86.4
Control ^b	0.00	3.716	4.2	1.196-1.316	264 240	600.5	87.1	416.5	60.4
Contractometer	1.85	1.793	4.4	Compressive stress was 130.6 MPa (18.94 ksi).					
Contractometer	1.85	3.642	4.4	Compressive stress was 117.4 MPa (17.03 ksi).					
HN-1-100-2001	1.85	1.886	4.37	1.273-1.349	503 522	1746.5	253.3	1039.1	150.7
HN-1-100-4001	1.85	3.911	4.58	1.298-1.372	527 533	Not Tested			
HN-1-100-2002	2.38	1.932	4.4	1.364-1.402	513 524	Not Tested			
HN-1-100-4002	2.38	3.762	4.4	1.359-1.420	520 550	Not Tested			
HN-1-100-2003	2.91	1.849	4.68	1.255-1.313	505 516	1760.3	255.3	1183.2	171.6
HN-1-100-4003	2.91	3.697	4.7	1.237-1.290	518 534	Not Tested			
HN-1-100-2004	3.43	1.923	4.6	1.344-1.405	508 517	1526.6	221.4	1125.3	163.2
HN-1-100-4004	3.43	3.809	4.49	1.313-1.367	521 527	Not Tested			
HN-1-100-2005	3.96	1.877	4.4	1.250-1.339	509 517	Not Tested			
HN-1-100-4005	3.96	3.707	4.4	1.247-1.311	521 529	Not Tested			
Contractometer	3.96	1.849	4.4	Compressive stress was 135.6 MPa (19.67 ksi).					
Contractometer	3.96	3.549	4.4	Compressive stress was 121.8 MPa (17.67 ksi).					

^a Each Vickers Hardness Number (VHN) represents an average of five(5) indentation readings. VHN readings at "Start" refer to the EDHN sample side adjacent to the stainless steel mandrel while those at "End" represent the final plated surface.

^b No hardening agent (SNHA) had been added when the two control specimens were produced.

TABLE 7. EFFECTS OF CURRENT DENSITY AND INTERMEDIATE RANGE HARDENING AGENT CONCENTRATIONS ON VICKERS HARDNESS OF NICKEL FROM ELECTROLYTES AT 43° C (110° F) - TANK NO. HN-2

Specimen Number	SNHA Conc. (ml/l)	Current Density (Amp/dm ²)	Bath pH	Plated Thickness (mm)	Vickers Hardness ^a	Mechanical Properties			
						Start	End	Ult. Strength	Elong. in
						MPa	ksi	MPa	1 in. (%)
Control ^b	0.00	1.979	4.27	1.372-1.458	335	309	812.2	117.8	88.6
Control ^b	0.00	4.078	4.35	1.450-1.542	283	266	764.7	110.9	79.7
Contractometer	1.85	1.644	4.35	Compressive	stress was 127.7 MPa (18.52 ksi).				
Contractometer	1.85	3.242	4.40	Compressive	stress was 126.1 MPa (18.29 ksi).				
HN-2-110-2001	1.85	2.267	4.45	1.562-1.656	492	497	1633.4	236.9	154.4
HN-2-110-4001	1.85	3.762	4.39	1.374-1.471	518	518	Not Tested		11.0
HN-2-110-2002	2.38	1.923	4.35	1.298-1.379	494	508	1693.4	245.6	1123.2
HN-2-110-4002	2.38	3.948	4.53	1.341-1.410	519	546	Not Tested		11.0
HN-2-110-2003	2.91	1.839	4.61	1.372-1.453	503	507	1699.6	246.5	1254.9
HN-2-110-4003	2.91	3.874	4.56	1.293-1.359	516	533	1815.5	263.3	1448.6
HN-2-110-2004	3.43	2.230	4.48	1.481-1.557	500	513	1688.6	244.9	1050.8
HN-2-110-4004	3.43	4.041	4.32	1.351-1.425	518	534	1778.2	257.9	1057.0
HN-2-110-2005	3.96	2.137	4.38	1.425-1.494	490	501	1670.0	242.2	1325.9
HN-2-110-4005	3.96	3.837	4.38	1.316-1.382	495	524	1742.4	252.7	1234.9
Contractometer	3.96	1.802	4.38	Compressive	stress was 114.9 MPa (16.66 ksi).				
Contractometer	3.96	3.623	4.38	Compressive	stress was 108.5 MPa (15.74 ksi).				

^a Each Vickers Hardness Number (VHN) represents an average of five(5) indentation readings. VHN readings at "Start" refer to the EDHN sample side adjacent to the stainless steel mandrel while those at "End" represent the final plated surface.

^b No hardening agent (SNHA) had been added when the two control specimens were produced.

^c B.O.G. refers to the sample having failed by fracture outside of the gauge marks used to determine elongation.

TABLE 8. EFFECTS OF CURRENT DENSITY AND LOW RANGE HARDENING AGENT CONCENTRATIONS ON VICKERS HARDNESS OF NICKEL FROM ELECTROLYTES AT 43° C (110° F) - TANK NO. HN-1

Specimen Number	SNHA Conc. (ml/l)	Current Density (Amp/dm ²)	Bath pH	Plated Thickness (mm)	Vickers Hardness ^a	Mechanical Properties			
						Ult. Strength	Yield Str.	Elong. in	
						MPa	ksi	MPa	1 in. (%)
Control ^b	0.00	3.930	4.40	1.328-1.402	270	583.3	84.6	385.4	55.9
Control ^b	0.00	2.016	4.60	1.344-1.422	270	704.7	102.2	477.8	69.3
HN-1-110-4006	0.13	3.809	4.70	1.252-1.323	327	852.9	123.7	557.8	80.9
HN-1-110-2006	0.13	2.044	4.65	1.372-1.422	348	878.4	127.4	609.5	88.4
HN-1-110-4007	0.26	3.818	4.50	1.252-1.328	357	991.5	143.8	671.6	97.4
HN-1-110-2007	0.26	2.081	4.50	1.547-1.613	375	1105.3	160.3	701.9	101.8
HN-1-110-4008	0.40	3.865	4.40	1.288-1.364	372	1088.7	157.9	748.1	108.5
HN-1-110-2008	0.40	2.007	4.50	1.354-1.430	390	1203.9	174.6	750.9	108.9
HN-1-110-4009	0.53	3.855	4.58	1.280-1.367	403	1021.1	148.1	687.4	99.7
HN-1-110-2009	0.53	1.988	4.58	1.334-1.417	411	1307.3	189.6	854.3	123.9
Contractometer	0.53	3.441	4.60	Compressive stress was 42.7 MPa (6.20 ksi)					
Contractometer	0.53	1.718	4.60	Compressive stress was 79.0 MPa (11.46 ksi)					

^aEach Vickers Hardness Number (VHN) represents an average of five (5) indentation readings. VHN readings at "Start" refer to the EDHN sample side adjacent to the stainless steel mandrel while those at "End" represent the final plated surface.

^bNo hardening agent (SNHA) had been added when the two control specimens were produced.

^cB.O.G. refers to the sample having failed by fracture outside of the gauge marks used to determine elongation.

These current densities represent the range of average densities used on actual blades. Because of the critical, and restrictive, shielding necessary for full sized blades, the use of higher current densities would impose an excessive tank voltage which increases bath temperature in an uncontrolled manner.

The sudden change in hardness for specimens in Table 2 after 2,225 ampere-hours was erroneously thought to be due to a change in bath chemistry caused by hardening agent breakdown. However, results later obtained for another bath with similar chemistry and operating conditions show VHN's in the range of 490 to 500 to be normal for this level of hardening agent, Table 7, Specimen HN-2-110-2005. This hardness level shift in Table 2 is believed to be the result of an aging (breaking-in) phenomenon normal for new electrolytes when new anode rounds are also used -- later electrolytes employed used anodes. Discussions of this behavior may be found in the literature⁽⁷⁾ (8). Hardness values were in a consistently narrow range between 2,225 and 5,140 accumulated ampere-hours of plating. Had this been an aged bath, it is believed that VHN's would have shown little change over the entire plating study. Based on bath volume of 159 liters, temperature of 43° C (110° F), and SNHA concentration of 3.96 ml/l, it can be stated that hardening agent is stable for the plating period of 32.3 ampere-hours per liter.

Tables 3 and 4 show that VHN's are slightly higher for deposits from EDHN baths operated at 37.8° C (100° F) and 3.96 ml/l of SNHA. Data from both tables are in excellent agreement regarding hardness levels obtained under these operating conditions. The only significant difference in the electrolytes studied to derive these tables was the calcium contamination in Tank HN-1. This appeared to have little effect on hardness and tends to confirm similar findings by Marti and Lanza⁽⁹⁾ where VHN increased less than ten points with calcium ion concentrations of up to 10 grams per liter.

Dropping the EDHN bath temperature from 43° C (Table 2) to 37.8° C (Table 4) appears to accelerate SNHA breakdown since deposits from the lower temperature bath started to appear frosty after only 3000 ampere hours of plating -- although VHN's did not exhibit significant changes. This amounts to 18.9 ampere-hours of plating per liter.

(7) O. J. Klingenmaier, "The Effect of Anode Efficiency on the Stability of Nickel Sulfamate Solutions", Plating, November 1965, pp 1138-41.

(8) B. B. Knapp, "Notes on Nickel Plating from Sulfamate Solutions", Plating, December 1971, pp 1187-93.

(9) J. L. Marti and G. P. Lanza, "Hardness of Sulfamate Nickel Deposits", Plating, April 1969.

Tables 2 through 4 show that hardness is not significantly affected by deposit thickness. VHN results were generally slightly lower on the side of the specimen where plating was started than on the final deposited surface. The occasional exception occurred when electrolyte spray was too severe and slight roughness resulted on the final surface. Table 4 shows mechanical property test results which indicate material strength remains acceptably uniform through long plating periods. The high mechanical strength is typical of extremely fine-grained EDHN. Ductility was much better than expected.

All VHN's from the hardening agent consumption study were higher than the 400 to 450 range considered desirable for propeller blade coatings. In the first studies to evaluate methods for obtaining specific hardness values, SNHA concentrations ranging from 1.85 to 3.96 ml/l were examined. As shown in Tables 5 through 7, this range still produced hardnesses higher than desired at current densities appropriate for blade coating. From these tables it was found that --

- (1) Increasing current density for any concentration of SNHA also increased hardness.
- (2) Increasing bath temperature slightly decreased hardness.
- (3) Changing SNHA concentration from 1.85 to 3.96 ml/l had almost no effect on hardness.

Tables 5 through 7 list deposit compressive stress values ranging from 94 to 146 MPa (13.7 to 21.2 ksi). At this range of SNHA concentration, it is difficult to define effects on stress due to current density or bath temperature. All stress values were compressive, as desired for good coating fatigue life. However, the magnitude of the stresses was of concern due to their potentially deleterious effects on bond strengths of such coatings on propeller blade substrates. Based on the work of Marti⁽¹⁰⁾, it would appear that such compressive stresses are typical when sodium benzoic sulfimide (sodium saccharin) is used as the hardening agent and current densities lower than 6.5 amp/dm² (60 amp/ft²) are employed.

Results of mechanical property tests shown in Tables 6 and 7 indicate expected mechanical strength levels for EDHN product. From these tables, the ductility appears to be consistently better for EDHN produced from an electrolyte at 43° C (110° F). On this basis, continued investigation was confined to solutions at this temperature.

(10)

J. L. Marti, "The Effect of Some Variables Upon Internal Stress of Nickel as Deposited from Sulfamate Electrolytes", Plating, January 1966.

Working with electrolytes containing 0.13 to 0.53 ml/l of SNHA, the entire range of VHN's sought for the program could be produced as shown in Table 8. These results have been plotted, Figure 2, to show the effects of current density and SNHA concentration on VHN. The most suitable SNHA concentration appears to be 0.50 to 0.75 ml/l for producing VHN's in the range of 400 to 450. Since actual propeller blades have been observed to undergo as much as five percent creep during their service life, it is essential that the EDHN coatings have adequate ductility. Suitable ductility has been confirmed by the elongation results reported in Table 8.

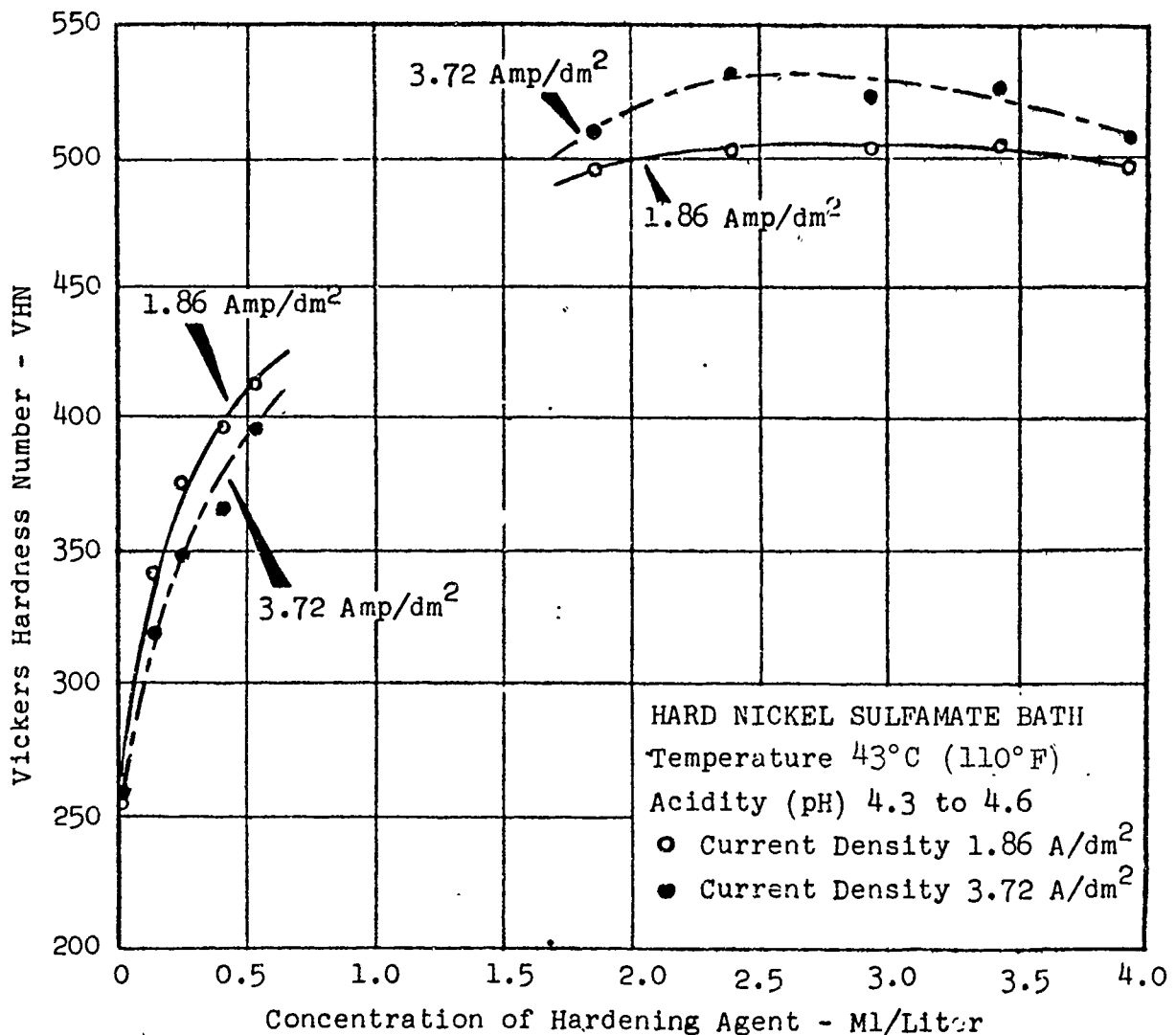


Figure 2. Effects of Current Density and Hardening Agent (SNHA) Concentration on Vickers Hardness of EDHN.

Equally important is the evidence that compressive stresses are reduced to a range which is acceptable to bonding requirements for the coating of blades. Coating stresses, whether tensile or compressive, would tend to produce a counter reaction to the adhesive forces between the coating and the blade substrate. Table 8 discloses that a hardening agent concentration of 0.53 ml/l in the electrolyte produces EDHN with only 42.7 MPa (6.2 ksi) compressive stress at a current density of 3.44 amp/dm² (37 amp/ft²) -- a plating parameter typical of that to be expected in the regions of propeller blade tips and edges.

Compressive stress measurement appears to be a valuable tool for controlling hardening agent in the electrolyte. The amount of compressive stress in EDHN appears to be closely related to SNHA concentration -- at least in the range required to produce VHN's lower than 450. Measurements can be made in a very short time frame. Combining this measurement with data from less frequently produced VHN test specimens, it should be possible to adequately control SNHA concentration in a full sized production bath.

Figure 2 provides further evidence that the hardening agent is sodium benzoic sulfimide (sodium saccharin). The hardness increase is quite rapid with very small additions of SNHA. Marti and Lanza⁽¹¹⁾ point out that less of this agent is required to reach maximum hardness than is required for most other hardening agents. It was previously established that a bath containing 3.96 ml/l of SNHA and operated at 43° C (110° F) would have a hardening agent stability life of at least 32.3 ampere-hours per liter. This leads to two questions not considered at the start of these studies --

- (1) Does decreasing the SNHA concentration from 3.96 ml/l to 0.50 ml/l shorten the stability life of the hardening agent?
- (2) Once the ampere-hour per liter limit has been met by plating, should additional SNHA be added, or should the electrolyte be peroxide-carbon treated for a new make-up of hardening agent?

In answer to the first question, Bocker and Bolch⁽¹²⁾ found that mechanical properties (and hardness) are related very closely to the ratio of the consumption of hardening agent per ampere-hour; the actual content of organic agents (breakdown products) is not important. They

(11)

J. L. Marti and G. P. Lanza, "Hardness of Sulfamate Nickel Deposits", Plating, April 1969.

(12)

J. Bocker and Th. Bolch, "Nickel Electroforming - Some Aspects for Process Control", AES International Symposium on Electroforming/Deposition Forming", Los Angeles, California, March 23-24, 1983.

studied benzoic sulfimide (saccharin) as a hardening agent in Watts type nickel baths. The predominant breakdown products were o-toluene sulfonamide and benzamide. High Performance Liquid Chromatography (HPLC) was employed to analyze for saccharin and the major by-products. Figure 3 illustrates concentrations of organic products as a function of electrolysis (age) of the bath. Various test results from EDHN specimens from this bath are plotted as functions of the bath age in Figure 4.

It is apparent that significant changes in properties of the deposits begin once the concentrations of benzoic sulfimide and the by-product o-toluene sulfonamide reach equivalent concentrations. Hardness increases -- followed by a long period in which it returns to an intermediate range. Most significant is the fact that residual stress in the deposits changes uni-directionally, going from compressive to tensile. This substantiates our earlier observation that compressive stress measurements would afford a logical and rapid method for controlling bath hardening agent performance.

Figure 4 implies that the EDHN bath is only stable until about sixteen ampere-hours per liter of plating has been performed. Since Bocker and Bolch worked with a Watts type bath under greatly different operating parameters, this observation does not necessarily apply to the sulfamate bath described for the present studies. The slope for saccharin consumption (steady rate region) may be much different than that shown in Figure 3.

In answering the second question, Bocker and Bolch claimed successful reconstitution of the EDHN bath by saccharin additions. Since Figure 3 shows a sixty percent depletion of saccharin before properties change, we surmise that the addition should be sixty percent of that used in the original electrolyte formulation. Eventually the bath will require peroxide-carbon treatment because of benzamide accumulation -- with the possibility of adverse effects on stress. Determination of how many additions can be made before purification is necessary will depend on the size of the production bath and the work schedule. Experience shows that coating of single full sized propeller blades requires about 2,800 ampere-hours per blade. If we conservatively set the SNHA stability limit at 15 ampere-hours per liter and used a 2,000 liter production bath, about eleven blades could be plated before SNHA correction measures would be necessary. A single SNHA addition would extend the bath stability life to perhaps twenty blades, whereafter a peroxide-carbon treatment would be recommended. It must be recognized that larger baths require more time for purification and this would enter into the decision as to when treatment would be most expeditious.

Metallographic examination of EDHN specimens produced from bath SNHA concentrations in the 0.0 to 0.5 ml/l range was performed. Results are shown in Figure 5. Addition of SNHA to a sulfamate nickel plating bath causes a change in the microstructure -- the columnar grains become smaller and more equiaxed, with a formation of bands at intervals regulated by the amount of hardening agent present.

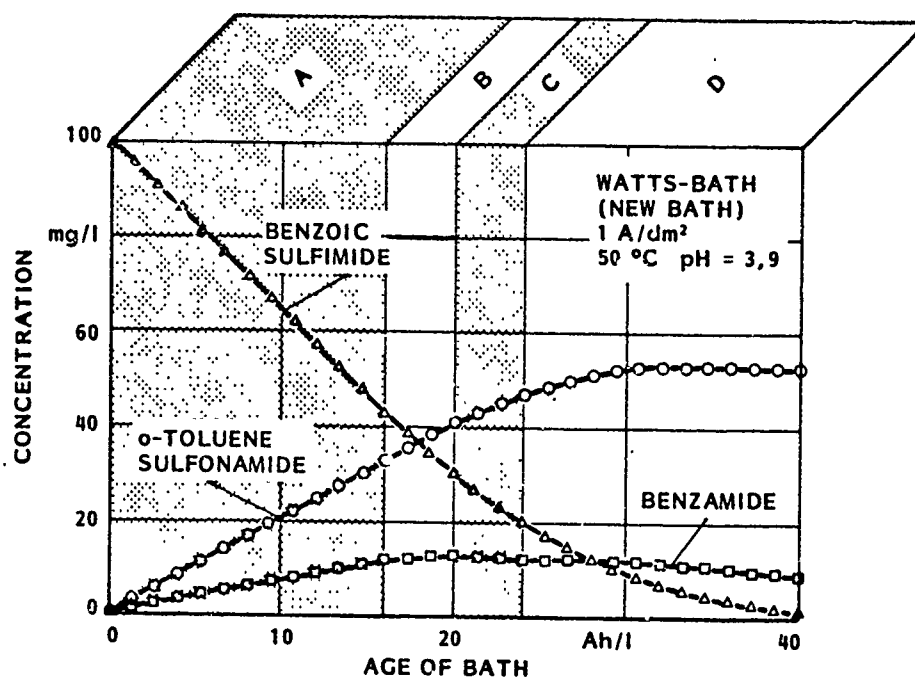


Figure 3. Decomposition of Benzoic Sulfimide during Electrolysis.

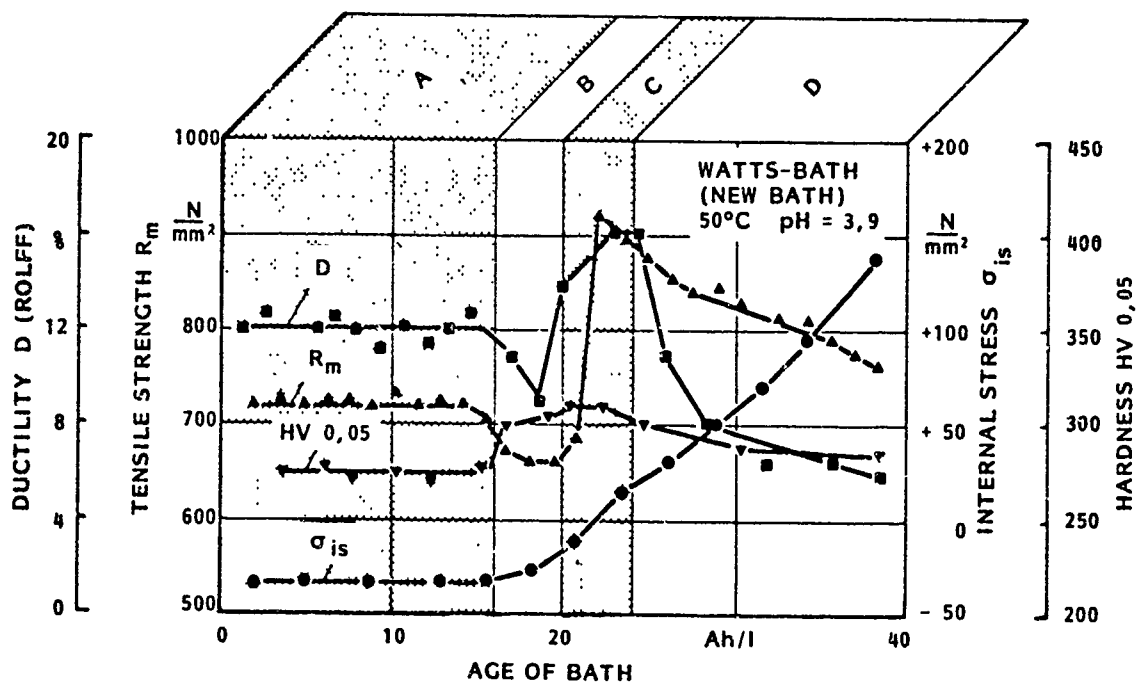
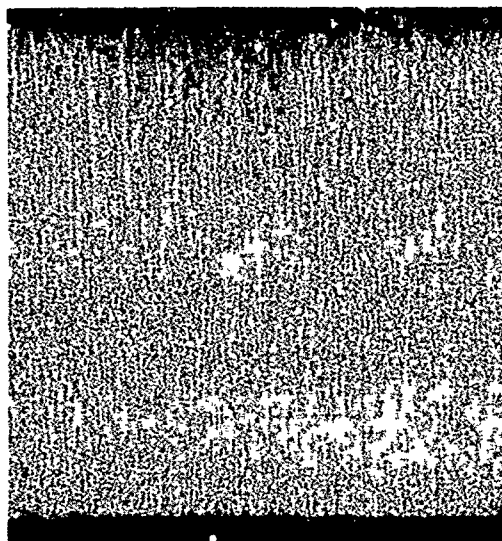
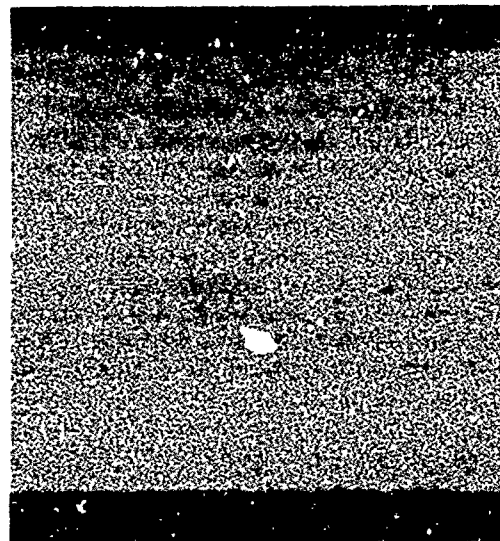


Figure 4. Changing of the Mechanical Properties during Electrolysis.

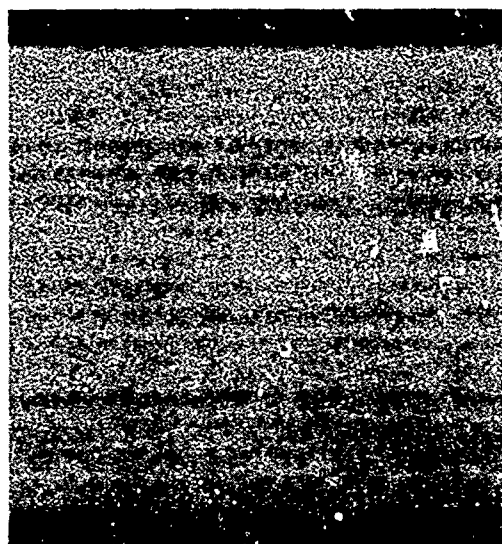
(Reprinted by permission of AES Press - Copyright 1983; March 1983 Proceedings of the AES International Symposium on Electroforming/Deposition Forming)



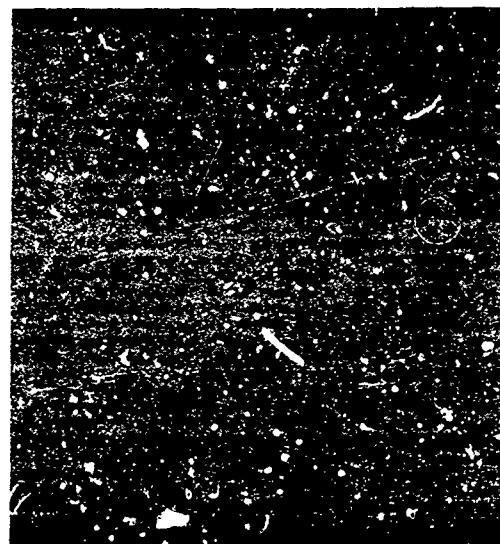
Control Specimen
 Current Density: 3.93 Amp/dm²
 SNHA Concentration: 0.0 ml/l
 Magnification: 50X



Specimen HN-1-110-4007
 Current Density: 3.82 Amp/dm²
 SNHA Concentration: 0.26 ml/l
 Magnification: 50X



Specimen HN-1-110-4009
 Current Density: 3.86 Amp/dm²
 SNHA Concentration: 0.53 ml/l
 Magnification: 50X



Specimen HN-1-110-2009
 Current Density: 1.99 Amp/dm²
 SNHA Concentration: 0.53 ml/l
 Magnification: 50X

Figure 5. Effects of SNHA Concentration and Current Density on Microstructure of Hard Nickel Coatings

Hardness Study Conclusions

Controlled additions of a proprietary hardening agent (SNHA) to conventional sulfamate nickel plating baths can be employed to produce electrodeposited hard nickel (EDHN) of various Vickers Hardness Numbers (VHN's) for application as rain/sand erosion protection coatings on LACV-30 propeller blades. VHN's in the range of 255 through 530 are obtainable by simply adding SNHA in concentrations of 0.0 to 2.5 ml/l. Additions of greater SNHA concentrations do not appear to increase hardness in electrolytes operated at temperatures and current densities appropriate for propeller blade coating. From previous studies, optimum VHN for best combination sand/rain erosion resistance has been estimated as 400 to 450. This VHN range can be achieved with SNHA concentrations of 0.5 to 0.7 ml/l, electrolyte temperature at 43° C (110° F), and current densities in the range of 1.86 to 3.72 amp/dm² (20 to 40 amp/ft²).

The hardening agent is believed to be sodium benzoic sulfimide (sodium saccharin) which electrochemically reacts during plating to co-deposit sulfur in the nickel, leaving two significant by-products in the bath. As long as the reaction rate is constant, no degradation of hardness or mechanical properties occurs. Once the chief by-product, o-toluene sulfonamide, reaches the equivalent concentration as SNHA, undesirable changes in material properties are initiated. Decomposition of the SNHA is sufficiently slow that corrective action can be taken in a relatively short time span to permit controlled use of the process in production plating of full sized propeller blades. Sophisticated control of the bath hardening agent can be accomplished with High Performance Liquid Chromatography (HPLC); however, measurements of compressive stresses appears to offer the more simple production control.

Once the hardening agent degrades to a point where hardness and mechanical properties cannot be controlled, the bath can be restored by (1) adding about sixty percent of the original SNHA concentration, or (2) by combination hydrogen peroxide/carbon treatment. It was found that VHN of deposits were not affected to any significant degree by thickness. All deposits tested in the desired VHN range were found to be compressively stressed -- these stresses having magnitudes acceptable for improving coating fatigue performance without seriously impairing expected bond strength between the EDHN and the blade substrate.

Mechanical properties of coatings produced in the desired VHN range exhibited ductilities suitable for propeller blades subject to slight creep during their service lives. EDHN deposits were found to be extremely smooth, a factor which should enhance wear resistance and aerodynamic stability.

SECTION III

PREPARING 7075 ALUMINUM PROPELLER BLADES FOR OPTIMUM BONDING OF NICKEL COATINGS

Background

Aluminum alloys are not ideal substrates for bonding electrodeposited coatings due to the rapidly formed oxide films characteristic of these materials. Since aluminum propeller blades operate at very high tip speeds, the centrifugal forces generated by an attached coating are very significant. The need for good bond strength of such coatings cannot be over-emphasized.

Preparatory treatment of aluminum for bonding is based largely on one of two techniques; either the oxide film is completely removed before deposition or, alternatively, it may be artificially thickened by methods of anodic oxidation which produce a coating of well defined porosity onto which a metallic layer can be anchored. Wernick and Pinner⁽¹³⁾ further classify these processes as:

- (1) Direct plating methods.
- (2) Processes based on mechanical preparation.
- (3) Chemical etching procedures.
- (4) Processes based on preparation by anodic oxidation.
- (5) The Vogt process.
- (6) Processes based on the zincate technique.

From the above list, methods (4) and (6) were selected for this study. Most of the other methods have shortcomings, such as inferior bond strength or poor reproducibility features. The zincate bond preparation process is widely used in the United States and materials and procedures are readily available. The anodic oxidation process, using thirty percent phosphoric acid, was originally developed in Germany. It was not extensively used due to costs in comparison with the zincate process. More recently, development of anodized coatings for bonding from three percent phosphoric acid solutions has demonstrated this to be a viable process.

(13)

S. Wernick and R. Pinner, Surface Treatment of Aluminum, 3d Ed., Robert Draper Ltd., Teddington, England (1964), pp. 582-4.

Solutions, Facilities, and Processes Used to Characterize Zincate Bonding of EDN to Aluminum 7075 Substrates

A series of 16.51 cm by 10.16 cm by 0.635 cm thick panels were made from a sheet of Aluminum 7075 T-7351 for use as substrate material for bond evaluations. Following a procedure recommended by NASA⁽¹⁴⁾, each panel was chemically milled to remove surface scale, oxides, and other surface imperfections. Approximately 0.025 mm of metal was removed from each surface. The milling solution formulation and operating conditions were as shown in Table 9.

TABLE 9. CHEMICAL MILLING SOLUTION FOR ALUMINUM 7075

<u>Ingredient/Operating Parameter</u>	<u>Concentration/Range</u>
Distilled Water	3.8 liters
Sodium Hydroxide	270 grams per liter
Sodium Meta-aluminate	120 grams per liter
Sodium Sulfide	120 grams per liter
Sulfur	7.5 grams per liter
Sodium Gluconate	0.5 grams per liter
Temperature	65.6 to 71.1° C (150 to 160° F)

A series of processing tanks was established to perform the zincate treatment. Tank volumes ranged from ten to fifteen liters. Since Aluminum 7075 contains copper, silicon, and magnesium, a mixed acid dip composed of Actane⁽¹⁵⁾, nitric acid, and sulfuric acid was used to remove these unwanted surface residuals which adversely affect bond performance. The zincate salts were a commercial formulation available under the trade name "Alumon"⁽¹⁶⁾. A second zincating solution, inhibited to better control zincate film thickness,

(14)

NASA Tech Brief No. 66-10312, "Chemical Milling Solution Produces Smooth Surface Finish on Aluminum", July 1966.

(15)

Actane 70 is a proprietary aluminum acid conditioning additive available from Enthone Incorporated, West Haven, Connecticut 06508.

(16)

Alumon is a proprietary salt for zincate solutions available from Enthone Incorporated, West Haven, Connecticut 06508.

was investigated for comparative purposes; this material was "Bondal"⁽¹⁷⁾. The bond strengths reportedly achieved by zincating are dependent on aluminum surface cleanliness, acid conditioning, the number of zincate immersions, and the ability to achieve a uniformly thin zinc film from the zincate immersion. Actual propeller blades are of sufficient length that the zincate immersion time -- and consequently, film thickness -- is difficult to control. The "Bondal" process was expected to promote better bond strengths.

The full zincating process is shown in Table 10. Double zincating was used, with acid stripping of the initial zincate film, since experience has shown this procedure to promote higher bond integrities. The hot sulfuric acid dip, shown as Step 4 in Table 10, was suggested by the zincate supplier for use on aluminum alloys containing appreciable amounts of magnesium. Specimens were processed with, and without, this treatment for comparative purposes. Although Table 10 shows the detailed process when "Alumon" was used for zincating, the "Bondal" process was similar -- the only change being that the "Bondal" is a ready-to-use liquid formulation.

The electrodeposit bonded to the zincated surfaces was conventional nickel, rather than hard nickel. The selection of the softer nickel was made to accommodate machining of the conical head bond test bars to be described later.

Solutions, Facilities, and Processes Used to Characterize Bonding of EDN to Phosphoric Acid Anodized Aluminum 7075

Panels of the same configuration and material employed in the zincate bonding study were used in this work. These panels were chemically milled in the same manner as the previous ones used in the zincate characterization. The solutions and process details are presented in Table 11. Although Steps 2 and 4 are not essential to successful bonding with the phosphoric anodizing process, some form of surface conditioning is advised. Steps 2 and 4 were employed to provide identically conditioned surfaces to those used in the zincate studies. This was for the primary purpose of comparing anodic film and zincate bond strengths from processes made as similar as practical. The dilute phosphoric anodizing facility is illustrated in Figure 6.

Method of Bond Evaluation

Most bond strength data in the literature is based on peel tests performed on various electrodeposited coatings applied to anodized or zincated aluminum surfaces. Such data is very difficult to correlate with mechanical properties of the materials being bonded. For this

(17)

Bondal is a ready-to-use, inhibited zincating solution marketed under license by Frederick Gumm Chemical Company, Incorporated, Lyndhurst, New Jersey 07071.

TABLE 10. PROCESS SEQUENCE FOR DOUBLE ZINCATE BONDING

<u>Operation</u>	<u>Composition</u>	<u>Control</u>
1. Preliminary Clean	Alconox Detergent in distilled water	Good water break after rinsing.
2. Actane-Acid Dip Actane 70 Sulfuric Acid Nitric Acid Distilled Water Temperature Time	110 g/l 25% by volume 50% by volume 25% by volume	Ambient 5 seconds
3. Rinse	Tap water	Ambient temperature
4. Hot Sulfuric Acid Sulfuric Acid Distilled Water Temperature Time	15% by volume 85% by volume	140° to 150°F 4 minutes
5. Rinse	Tap water	Ambient temperature
6. Zincate Dip No. 1 Alumon Salts Distilled Water Specific Gravity Temperature Time	540 g/l Balance	1.407 minimum 60° to 75°F 2 minutes
7. Rinse	Tap water	Ambient temperature
8. Rinse	Tap water	Ambient temperature
9. Nitric Strip Nitric Acid Distilled Water Temperature Time	50-67% by volume Balance	Ambient Until zinc removed
10. Rinse	Tap water	Ambient temperature
11. Rinse	Tap water	Ambient temperature
12. Zincate Dip No. 2 Same as Step 6. Temperature Time		60° to 75°F Varies with alloy
13. Rinse* *Vigorous agitation required to arrest excess zincate filming.	Tap water	Ambient
14. Acidified Rinse Sulfuric Acid Distilled Water Temperature Time	0.5% by volume Balance	Ambient As quickly as poss.
15. Rinse and Wipe* *Gently remove loose zinc salts with soft brush and running water.	Tap water	Ambient temperature
16. Nickel Plate - Enter plating bath with 4 to 6 volts applied from power supply to minimize attack of plating solution on zinc film.		

NOTE: The Bondal process is identical to the above with the exception that the Bondal Dip is substituted for the Alumon Zincate Dips in Steps 6 and 12.

TABLE 11. PROCESS SEQUENCE FOR PHOSPHORIC ANODIC FILM BONDING

<u>Operation</u>	<u>Composition</u>	<u>Control</u>
1. Preliminary Clean	Alconox detergent in distilled water	Good water break after rinsing
2. Actane-Acid Dip Actane 70 Sulfuric Acid Nitric Acid Distilled Water ^a Temperature Time	110 g/l 25% by volume 50% by volume 25% by volume	Ambient 5 seconds
3. Rinse	Tap water	Ambient temperature
4. Hot Sulfuric Acid Sulfuric Acid Distilled Water ^a Temperature Time	15% by volume 85% by volume	140° to 150°F 4 minutes
5. Rinse	Tap water	Ambient temperature
6. Phosphoric Acid Anodizing Phosphoric Acid (85%) Distilled Water ^a Cathodes Agitation Temperature Voltage Time	3% by volume 97% by volume Chemical lead Air (filtered)	Area at least twice that of anode Valved air pump 60° to 75°F 60 volts 12 minutes
7. Acidified Rinse Sulfamic Acid Distilled Water ^a Temperature Time	2 g/l Balance	Ambient temperature 30 seconds maximum
8. Low pH Nickel Plate Nickel Sulfamate Nickel Metal Boric Acid Distilled Water ^a pH Temperature Anodes Current Density Time Agitation	72 to 80 g/l 30 g/l minimum Balance Soak anodized part for 30 to 50 seconds prior to applying voltage. The process is then voltage controlled. Raise voltage in 0.5 volt steps every 20 seconds until 1.5 volts is obtained. Hold at 1.5 volts for 5 minutes and gradually increase voltage to 3 to 4 in next two minutes. 90 to 120 minutes after 3 to 4 volt plating level is achieved. Pumped electrolyte (sprays)	2.4 to 2.6 128° to 132°F S.D. nickel rounds
9. Nickel Plate	Transfer with no rinse, voltage applied, to conventional nickel (or hard nickel) tank, and plate to required thickness at 20 to 40 amp/ft ²	

^a Demineralized water may be substituted for distilled water.



Figure 6. Dilute Phosphoric Anodizing Facility



Figure 7. Components and Hardware for Producing Bond Test Bars

study, the conical head test specimen was selected since results provide absolute strength over a known bond area. The test is performed on a standard tensile testing machine.

The aluminum panels previously described were subjected to the zincate or phosphoric anodizing treatments. The nickel coat deposited was of sufficient thickness to provide the necessary material for machining conical head test specimens. Due to the thick nickel coating requirements, it was necessary to use box type shields to assure uniform deposit thickness and prevent the formation of edge nodules. Once the required thickness of nickel plating on both sides of an aluminum panel was achieved, it was electric discharge machined to provide cylinders -- each containing two nickel-to-aluminum bonds. These cylinders were lathe turned to the conical head test specimen configuration. Figure 7 shows the aluminum substrate plate, the plate affixed in the plating box shield fixture, and the thick nickel coated plate with electric discharge machined cylinders.

In attaching the box shield to the aluminum plate being processed, certain precautions had to be exercised. Generally, the top wall of the box shield was attached to the aluminum plate through either the zincate or anodizing treatment. This would permit better rinsing to prevent carry-over of processing solutions into the nickel plating tank. Attachment of the box shield sidewalls and bottom were made once the panel was in the nickel plating tank.

Figure 8 depicts the configuration of the conical head test specimens after machining.

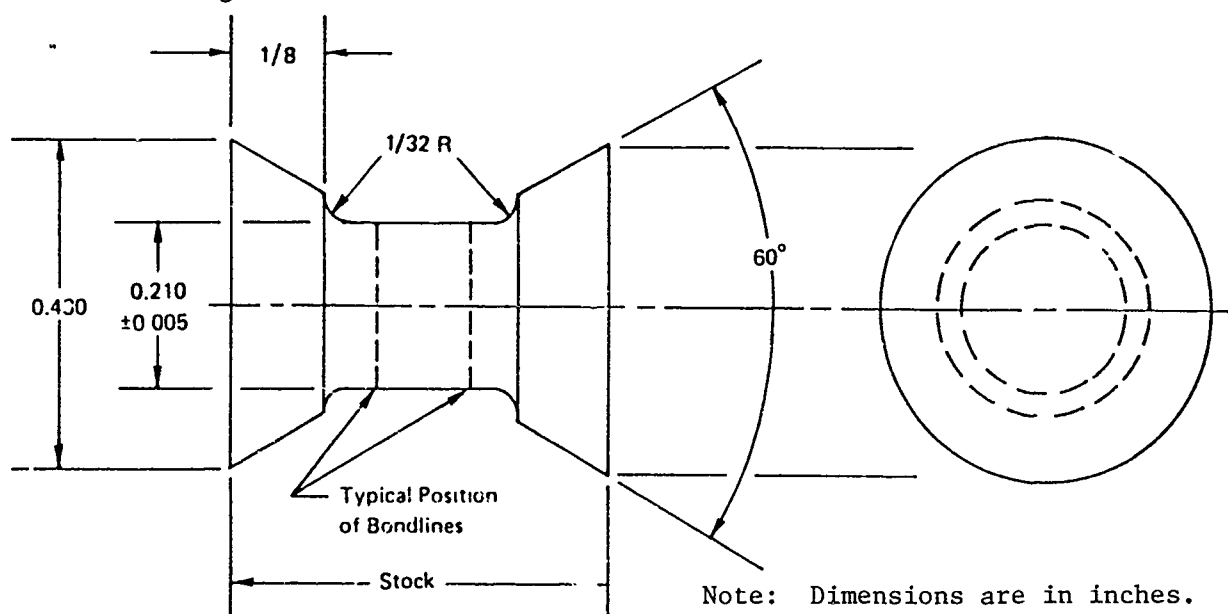


Figure 8. Conical Head Bond Strength Test Specimen

Bond Evaluation Studies

Two Aluminum 7075 plates were processed in accordance with the process shown in Table 10 -- one was double zincated in Alumon and the other in Bondal. The suppliers' literature⁽¹⁸⁾ ⁽¹⁹⁾ was carefully followed with regards to temperature control and agitation of the zincating solutions. The hot sulfuric acid dip was not used on these two "control" panels to determine if magnesium surface residuals were actually influential on bond strengths obtained by the zincating process on Aluminum 7075. This alloy is not classified as a high magnesium alloy. The final zincate immersion time for the control panels was 40 seconds.

Three aluminum panels were processed through the double Alumon zincate bonding process using the fifteen percent sulfuric acid dip prior to the zincate immersions. These panels differed only in the time of the final Alumon immersion -- one was for 20 seconds, the second for 40 seconds, and the third for 60 seconds. Another series of three panels was similarly processed through the Bondal process using the sulfuric acid dip prior to zincating. Final Bondal immersion times were identical to those used for the Alumon panels. All panels were coated with conventional electrodeposited nickel to sufficient thicknesses for producing conical head specimens. Generally, six cylinders were electric discharge machined from each panel to accommodate spoilage which might be expected in the lathe turning operation. The objective was to produce at least three machined specimens from each panel to obtain a range for expected bond strengths.

It should be noted that the Alumon zincate solution used in this study was several months aged. It had been used in contractual work for Transport Canada wherein several full sized propeller blades had been prepared for bonding⁽²⁰⁾. At the time this solution was new, bond strength data was obtained using procedures and test methods similar to those employed in the present study. This data has been included in the current program as an aid in evaluating aging effects of zincate solutions on resulting bond performance.

(18)

Enthronics Data Sheet, "Alumon, Process for Electroplating Upon Aluminum", Enthone Incorporated, West Haven, Conn., December, 1963.

(19)

Technical Bulletin, "The Clepo Bondal Process for Plating Aluminum and Its Alloys", Frederick Gumm Chemical Company, Inc., Lyndhurst, New Jersey.

(20)

G. A. Malone, "Nickel Plating of Voyageur ACV Propeller Blades to Improve Their Erosion Resistance", Transport Canada Report No. TP 3147, April 1981.

In using the dilute phosphoric acid anodizing system for bonding electroplated nickel to Aluminum 7075, the procedures developed and reported by Wittrock⁽²¹⁾ were initially planned for study in this program. This process differed from that described in Table 11 in that Wittrock suggested anodizing solution temperatures of 60° C (140° F) or higher. A subsequent paper presented by Thomas⁽²²⁾ recommended use of an ambient phosphoric anodizing bath temperature for best adhesive strength. The latter recommendation was followed in this study. Table 12 presents bond test data results for the various bonding processes. Each average bond strength reported represents at least three tests from the specific master panel.

It was planned to incorporate specific corrosion protection layers between the zincated, or anodized, Aluminum 7075 and the final nickel coating for evaluation of bond strength performance. These protective intermediate layers are discussed in a subsequent section of this report. The layers selected consisted of electroplated zinc and zinc-nickel alloy. Only zinc deposited from an alkaline bath could be deposited on zincated Aluminum 7075 with sufficient adhesion to survive the conical head fabrication operations. Test data for samples with the zinc layer are found in Table 13.

Discussion of Bonding Studies

Data from Table 12 reveals that Alumin zincating can produce excellent bonding surfaces for the deposition of nickel onto Aluminum 7075. Bond strengths do not appear to deteriorate with age of the Alumin solution as long as the solution temperature and specific gravity are maintained within the range specified by the supplier. From the work performed for Transport Canada, it appeared that use of a fifteen percent sulfuric acid dip at 82.2° C (180° F) prior to zincating for 15 seconds did not significantly enhance bond strengths. Dropping the sulfuric acid temperature to 60° C (140° F) resulted in a substantial improvement for a 15 second final zincate immersion, with bond strengths to 400 MPa (about 61 ksi) being noted. This may be due to the fact that aluminum provides a good heat sink which maintains surface temperature sufficiently high to accelerate zincate film formation -- even though the first film is stripped before the second film initiation in the double zincate process. Thus, lowering the sulfuric acid solution temperature results in less

(21)

H. J. Wittrock, "Adhesion of Sulfamate Nickel Electrodeposits on Aluminum-Zinc-Magnesium Alloys Anodized in Phosphoric Acid", Plating and Surface Finishing, January 1980, pp. 44-7.

(22)

D. E. Thomas, "Adhesion Failure of Electrodeposited Coatings on Anodized Aluminum Coatings, The Second AES Plating on Difficult-to-Plate Materials Symposium, March 25, 1982, St. Louis, Missouri

heat input to the aluminum. The Transport Canada work also showed that increasing the final zincate immersion time from 15 seconds to 40 seconds resulted in decreased bond strength. Although the current program tests showed excellent bond values with immersion times up to 40 seconds, longer exposures led to poor bonds.

TABLE 12. BOND STRENGTH TEST RESULTS FOR ZINCATED AND ANODIZED ALUMINUM 7075 ONTO WHICH NICKEL HAS BEEN ELECTRODEPOSITED

Bonding Process	Zincating Time (Seconds)	Bond Strength Test Data			
		Minimum		Average	
		MPa	Ksi	MPa	Ksi
<u>Transport Canada Program</u>					
Alumon Zincate (New) - Processed per Table 10, but without 15% sulfuric acid dip and mild post-zincate rinse.	15	275.1	39.9	282.7	41.0
Alumon Zincate (New) - Processed per Table 10, but with sulfuric acid dip at 180°F and mild post-zincate rinse.	15	285.5	41.4	295.8	42.9
Alumon Zincate (New) - Processed per Table 10, but with sulfuric acid dip at 180°F and good post-zincate rinse.	15	257.2	37.3	339.2	49.2
Alumon Zincate (New) - Processed per Table 10.	15	399.9	58.0	419.2	60.8
Alumon Zincate (New) - Processed per Table 10.	40	161.3	23.4	195.8	28.4
Alumon Zincate (Aged) - Processed per Table 10.	30	231.0	33.5	290.3	42.1
<u>U.S. Army - MERADCOM Program</u>					
Alumon Zincate (Aged) - Processed per Table 10, but without 15% sulfuric acid dip (Control).	40	264.1	38.3	276.5	40.1
Bondal Zincate (New) - Processed per Table 10, but without 15% sulfuric acid dip (Control).	40	265.5	38.5	284.3	41.3
Alumon Zincate (Aged) - Processed per Table 10.	20	430.2	62.4	445.4	64.6
Bondal Zincate (New) - Processed per Table 10.	20	508.9	73.8	523.3	75.9
Alumon Zincate (Aged) - Processed per Table 10.	40	288.9	41.9	350.3	50.8
Bondal Zincate (New) - Processed per Table 10.	40	180.6	26.2	195.1	28.3
Alumon Zincate (Aged) - Processed per Table 10.	60	Failed during fabrication			
Bondal Zincate (New) - Processed per Table 10.	60	187.5	27.2	197.2	28.6
Phosphoric Anodize - Processed per Table 11.		327.5	47.5	355.8	51.6

TABLE 13. BOND STRENGTH TEST RESULTS FOR ZINCATED ALUMINUM 7075 ONTO WHICH ZINC, COPPER, AND NICKEL HAVE BEEN ELECTROPLATED

Bonding Process	Condition	Bond Strength Test Data			
		Minimum		Average	
		MPa	Ksi	MPa	Ksi
Bondal Zincate - Processed per Table 10, plated in sodium zincate bath at 85°F for 2 hours at 10 amp/ft ² , bright dipped in dilute nitric acid, rinsed, copper struck in Rochelle bath at 130°F for 5 minutes, rinsed, activated in dilute sulfuric acid, rinsed, nickel plated.	As deposited.	200.0	29.0	219.3	31.8
	Heat treated @ 300°F for 2 hours.	182.7	26.5	205.5	29.8

The anticipated improvements in bond strengths with the use of Bondal were not realized, except for short immersion times in the neighborhood of 20 seconds, where the highest bond strength of any of the processes was achieved. Unlike the Alumon process, Bondal afforded bonds of some integrity when zincating times of 60 seconds were used. From the data it appears that only zincating times below 40 seconds can be used to produce good bonds on Aluminum 7075, regardless of the zincate process selected. This introduces a problem with actual propeller blades due to their dimensions and the resulting time required to immerse and withdraw them from a zincating bath. Since the zincating solutions are quite viscous, there is considerable drag-out on the blade surfaces which remains active during the transfer to the rinse tank. It thus becomes most difficult to keep the final zincate exposure time below 40 seconds.

Shortly after this study was conducted, several full sized blades were hard nickel coated for field testing at Panama City, Florida. Procedures were modified for performing the zincating in the shortest immersion time that was practical. Some of the blades exhibited blistering and delamination of the hard nickel after only a few hours of use in water and sand exposure. The problem areas were confined to the leading edge very near the blade tip and the edge of the tip itself. Since this condition was not prevalent on all blades, the zincate exposure time at the tips was not believed to be the primary cause, although it may have been contributory.

The above problem was discussed with the Bondal supplier⁽²³⁾ and it was advised that they had encountered similar difficulty with Aluminum 7075-T6.

(23)

Private correspondence from Mr. J. C. Cahill, Product Manager, Frederick Gumm Chemical Company, Inc., to Mr. G. A. Malone, Electroforming Operations, Bell Aerospace Textron, October 7, 1982.

They have attributed the poor, or erratic, bond performance to zinc segregation. Aluminum 7075 is a zinc rich alloy and prone to segregation. Since the blades are forged, it is likely that the tips and corners of the tips would be most susceptible to segregation. They suggested a modification of the Bondal process in which the Aluminum 7075 receives a glass bead blast treatment followed by the normal zincating treatment up to the point where the first zincate film is stripped in nitric acid and the part is rinsed. The second zincate filming is performed electrolytically with the part cathodic at 1.5 volts (approximately 8 amp/ft²) for 1.5 to 3 minutes. This is followed by a Watts nickel strike for 3 to 5 minutes at 10 to 20 amp/ft². Cyanide copper is then applied before plating the bright or hard nickel.

The electrolytic zincate process was not evaluated in this study since it appeared too complex for ready application to propeller blades. It is mentioned as an alternate process which would require a thorough evaluation should other techniques prove unsuitable for blade coating. Fortunately, dilute phosphoric acid anodizing of Aluminum 7075 produced most acceptable bonding surfaces for electrodeposited nickel as the results in Table 12 indicate. The use of anodized bonding films also provides an added benefit in improved corrosion resistance as will be discussed later.

Since few of the corrosion protective zinc or zinc-nickel alloy deposits could be satisfactorily bonded to either anodized or zincated Aluminum 7075, the results of this portion of the study were disappointing. For the corrosion protection system incorporating electrodeposited zinc between zincated Aluminum 7075 and electroplated nickel, Table 13 shows a much lower bond strength than when the zinc plate is not present. Heating the specimens to 148.9° C (300° F) for two hours did not improve the bond strength -- in fact, it was degraded. The lowered bond strength due to zinc probably results from the low mechanical strength of this metal. The same performance would be expected with zinc-nickel alloy which is predominantly zinc.

Bond Study Conclusions

Of the Alumin (conventional) double zincate, Bondal (inhibited) double zincate, and dilute phosphoric acid anodizing methods of producing surfaces on Aluminum 7075 for bonding nickel coatings, only the anodizing method appears to satisfy the requirements for coating of ACV propeller blades. The bond strengths obtained by the two zincate processes are best when the zincate solution immersion time is short -- less than 40 seconds and preferably around 20 seconds. Such times are difficult to achieve with full sized blades. Zinc segregation in Aluminum 7075 may lead to erratic bond performance in critical blade areas where erosion is greatest and where thicker coatings are necessary.

Anodized bond films, produced from dilute phosphoric acid baths at ambient temperature and sixty volts, show bond strengths around 345 MPa (50 ksi) -- a

value well in excess of the 137.9 MPa (20 ksi) goal set at the start of the program. The anodized bond surfaces have the added advantage of providing corrosion protection by impeding the flow of galvanic current between the anodic aluminum blade and the cathodic nickel erosion protection coating.

Introduction of intermediate corrosion protection plates of zinc or zinc-nickel alloy appear to degrade the overall bond strength of the system based on limited data from this study.

SECTION IV

DEVELOPMENT OF A CORROSION DETERRENT FOR HARD NICKEL COATINGS ON ALUMINUM 7075 ALLOY

Background

Aluminum alloys behave very anodically when coupled in direct contact with nickel. In other words, aluminum exposed to a water environment will oxidize at a lower rate than that experienced by the same aluminum exposed to water and in contact with nickel. This is not a problem as long as the aluminum, or aluminum alloy, is encapsulated with nickel and the liquid media cannot make contact with the aluminum to form corrosion compounds. However, nickel coated propeller blades will erode to a point where the coating is locally removed. A similar condition can arise when hard objects contact the rapidly revolving blade to cause fracture or penetration of the hard nickel coating. Corrosion is then easily initiated, particularly in a marine environment.

Corrosion of the aluminum substrate of coated blades can theoretically be arrested, or at least deterred, (1) by introducing a high impedance barrier layer which disconnects the galvanic battery formed by the hard nickel in contact with the aluminum blade, or (2) by insertion of a different metal between the cathodic nickel coating and the highly anodic aluminum substrate. In the latter case, the metal inserted must be a slow corroder, since it is sacrificial and must be anodic (or very slightly cathodic) with respect to the aluminum.

In selecting a high impedance system, it was natural to consider the dilute phosphoric anodizing process which was found to provide excellent bond strengths between nickel coatings and Aluminum 7075 substrates. Although porous, to accommodate the mechanical locking of electroplated coatings, the dilute phosphoric anodic film would be expected to inhibit lateral growth of corrosion at the nickel-aluminum interface. Galvanic current flow, an essential factor in corrosion rate would be restricted.

Very few electrodepositable metals and alloys possess the mechanical properties and anodic characteristics, with respect to Aluminum 7075, to provide suitable corrosion protection as intermediate layers. Mansfield, Hengstenberg, and Kenkel⁽²⁴⁾ studied the galvanic corrosion of aluminum alloys when contacted with dissimilar metals in air saturated 3.5 percent sodium chloride solutions. Table 14 shows the results of their study to determine the galvanic series for Aluminum 7075-T6 when coupled to the listed materials. The term i_g represents the galvanic current and r_A is

(24)

F. Mansfield, D. H. Hengstenberg, and J. V. Kenkel, "Galvanic Corrosion of Aluminum Alloys: Effect of Dissimilar Metal", Corrosion, 30:10, pp. 343-53.

TABLE 14. GALVANIC SERIES FOR AL 7075-T6 IN 3.5% SODIUM CHLORIDE

No.	Coupled To	i_g ($\mu\text{A}/\text{cm}^2$)	r_A (mdd)	$\Delta\phi$ (mV)	Overall No.
1	Ag	63.8	68.8	-696	1
2	Cu	45.0	58.8	-566	6
3	4130	25.0	26.0	-282	12
4	Ni	22.0	22.6	-677	15
5	A286	17.0	18.1	-728	20
6	SS304L	17.0	16.1	-781	21
7	SS347	16.8	16.2	-761	22
8	PH13-8Mo	16.5	16.2	-767	24
9	SS301	15.3	17.1	-718	26
10	Inco 718	12.2	11.6	-681	39
11	Haynes 188	8.9	6.9	-454	49
12	Ti-6-4	8.3	8.5	-406	51
13	Cd	5.9	5.9	-8	55
14	Sn	5.8	7.3	-346	57
15	Al 2219	3.8	4.2	-77	64
16	Al 2024	2.6	-1.3 ⁽¹⁾	-74	69
17	Al 6061	0.66	-1.8	-36	76
18	Al 1100	-0.26	-2.3	+1	79
19	Zn	-0.35	4.0	+234	92

⁽¹⁾ Negative values of r_A correspond to weight gain.

the dissolution rate of the Aluminum 7075-T6 expressed in $\text{mg}/\text{dm}^2/\text{day}$. Based on this data, cadmium, tin, and zinc appeared to be the electroplateable metals with the least corrosive effect on Aluminum 7075-T6 (when compared to nickel at $22.6 \text{ mg}/\text{dm}^2/\text{day}$). Use of cadmium or tin did not appear attractive as candidates due to the poor mechanical strength each exhibits. Zinc was the logical choice because of the higher mechanical strength of around 138 MPa (20 ksi). The fine grain structure expected in electro-deposited zinc might contribute to even higher tensile strength.

Electrodeposited zinc-nickel alloy was selected as an alternate corrosion protection layer based on work by Dini and Johnson⁽²⁵⁾ which showed an 8 percent nickel alloy to be superior to zinc for corrosion resistance.

(25)

J. W. Dini and H. R. Johnson, "Electrodeposition of Zinc-Nickel Alloy Coatings", Sandia Laboratories Report No. 77-8511, Sandia Laboratories, Livermore, California

Materials and Processes Used to Prepare Aluminum 7075 for Corrosion Protection Coatings

Material chemistry and microstructure are believed to play a significant role in corrosion performance. On this basis, Aluminum 7075-T651 was procured to the requirements of Federal Specification QQ-A-250/12. Material thickness was 0.635 cm (0.25 in). A certified test report was furnished to verify that the material complied with specification chemical and mechanical property requirements. Specimens, measuring 7.62 cm by 25.30 cm (3 in by 10 in), were prepared for the coating and corrosion performance study. Edges and corners were sanded to produce radii to minimize nodular effects and corner defects during the subsequent plating operations. Each panel was chemically milled using the solution described in Table 9. Milling was brief and only to remove a very thin "skin" from the surfaces. Each panel was numbered on one edge.

All panels subjected to plating of a corrosion protection layer on anodized surfaces were processed in accordance with Table 11, except for the plating of low pH nickel (unless low pH nickel was required). All panels subject to plating the corrosion protection layer on zincated aluminum were processed according to Table 10 using the Bondal double zincate method; the nickel plate not being applied unless specified. These bonding processes were applied immediately prior to plating the corrosion protection layer.

Although use of double zincated surfaces for bonding received unfavorable rating at the conclusion of the bonding study, the process was employed in this section of the program since these studies were performed in over-lapping time spans.

Corrosion Study Control Specimens

For every condition of coating for corrosion evaluation, three identical panels were processed. After all processing, one panel was struck with a center-punch, at a central position on each face, to simulate effects expected when a hard fragment impinges with sufficient force to fracture, or penetrate, the erosion-corrosion control coating. This panel and one undisturbed coated panel, were submitted to salt fog testing per Specification ASTM B117. The third panel was retained in the original coated state as a reference.

A total of nine control panels were made. Panel Numbers 1, 2, and 3 were not coated in order to assess salt fog corrosion of the Aluminum 7075-T651 providing the substrate material representative of a propeller blade. Panel Numbers 4, 5, and 6 were double Bondal zincated per Table 10 and hard nickel plated for one hour at 1.86 amp/dm^2 (20 amp/ft^2) to produce a coating about 0.0254 mm (0.001 in) thick. The thin hard nickel coating was expected to be somewhat porous. This was intentional to allow the salt fog atmosphere to produce readily discernable chemical reactions with the aluminum and coating system during the 336 hour standard exposure.

Panel Numbers 7, 8, and 9 were dilute phosphoric acid anodized per Table 11 and given a thin hard nickel coat such as applied to the previous panels. Figure 9 illustrates some corrosion study panels at various stages of processing. The use of shielding for most plating operations was not necessary due to the thinness of the coatings applied. It will be noted that masking has been applied to the coated panel edges. This is a standard procedure for corrosion study panels, since edge and corner defects promote rapid corrosion paths which produce oxidation products that may affect the performance of the primary surface being evaluated. The center-punch mark is visible on the bottom left panel in Figure 9.

Corrosion Study Specimens Coated With Zinc Electroplate

The composition and operating conditions for the zinc plating bath were carefully considered before coating the soluble zincated and phosphoric anodized panels. It was recognized that any zinc bath suitable for anodized surfaces would require excellent throwing power -- that is, ability to plate into pores in the anodic film. Based on previously discussed work by Wittrock, a bath of low pH (highly acid) would be required. Such a bath would be unsuitable for zinc plating on zincated films because of acid attack on the zincate layer; this would lead to blistering and delamination. It was also recognized that nickel cannot be adhesively plated on zinc surfaces without first applying a strike (thin cover plate) with a metal such as copper(26).

Zincated specimens were plated in an alkaline sodium zincate bath containing a brightening and leveling additive. This bath was commercially available under the name Ecolozinc 2001R and operated at about 29.4° C (85° F)(27). The alkalinity was due to sodium hydroxide and the pH was in the 11 to 12 range. Although deposits were smooth and bright, minute pits were noted, particularly in areas of higher current density. The use of various current densities and high electrolyte agitation were of no avail in preventing all of the pitting. A Vogt (low zinc cyanide) strike(28) was used to protect the

(26)

W. H. Safranek, "Plating on Zinc Alloy Die Castings", Modern Electroplating 3d Ed., Edited by F. A. Lowenheim, Wiley-Interscience, John Wiley & Sons, Inc., New York City, N.Y. (1973) pp. 605-17.

(27)

Ecolozinc 2001R additives and processing instructions are available from R. O. Hull & Company, Inc., Cleveland, Ohio 44102.

(28)

S. Wernick and R. Pinner, Surface Treatment of Aluminum, 3d Ed., Robert Draper Ltd., Teddington, England (1964), p. 636

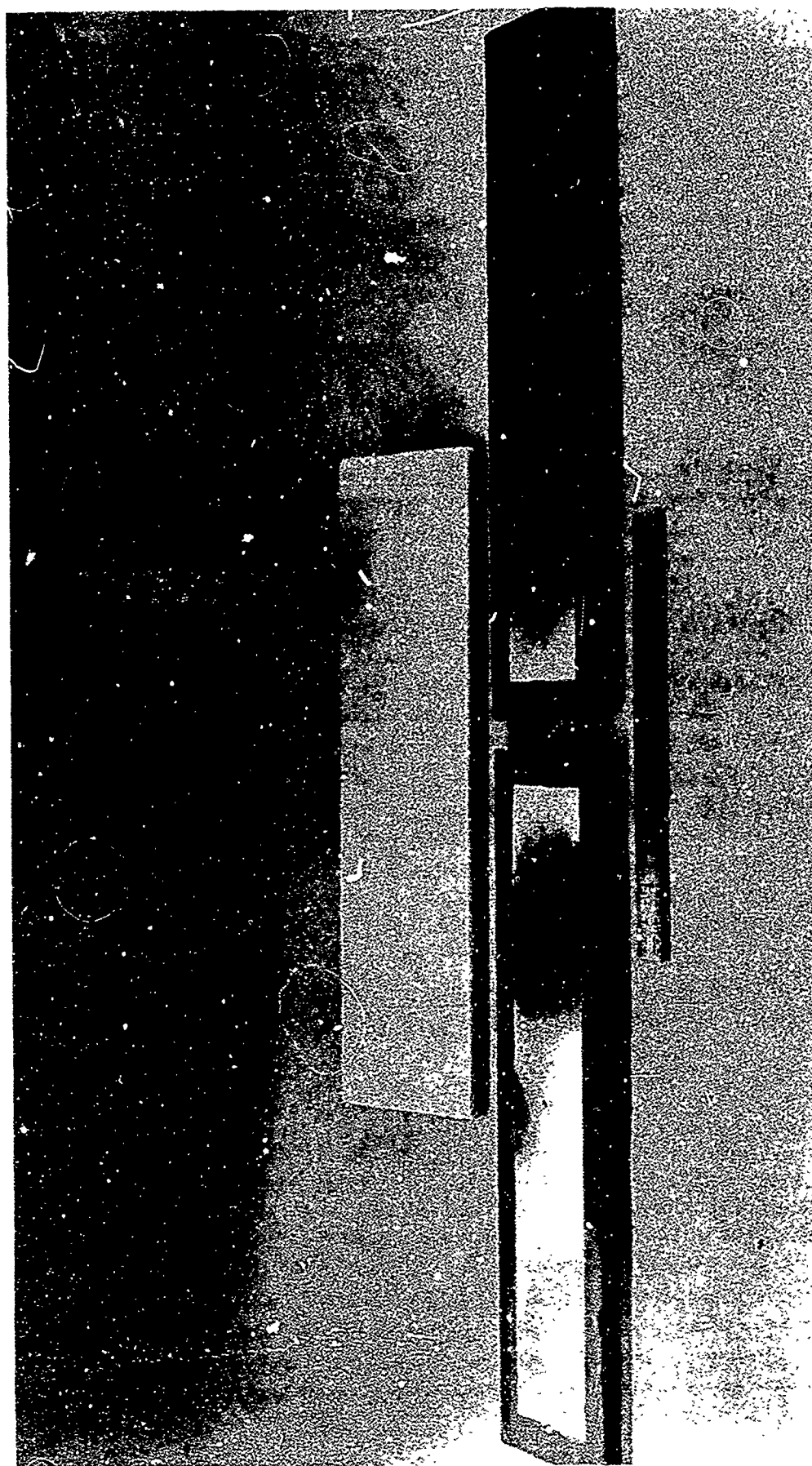


Figure 9. Corrosion Study Panels

Bondal zincate film. After alkaline zinc plating, Rochelle copper striking, and hard nickel coating, little pitting was evident. However, minute blisters appeared after 24 hours. Using the best known operating conditions for the alkaline zinc bath, and no Vogt strike, a panel was Bondal zincated, zinc plated, copper struck, and nickel plated for bond evaluation. Results were shown in Table 13.

Subsequent zinc plating was conducted in moderately acid, or near neutral, plating baths, since it was suspected that the alkaline bath was attacking the zincate film and pitting the aluminum in localized areas before zinc plating could seal the surfaces. For application on Bondal zincated panels, an acid zinc chloride bath was prepared based on a formulation suggested by Frederick Gumm Chemical Company⁽²⁹⁾:

Zinc Chloride	8 g/l	(10.6 oz/gal)
Potassium Chloride	240 g/l	(32.0 oz/gal)
Potassium Acetate	10 g/l	(1.2 oz/gal)
pH	4.6	
Temperature	15.6° to 43.3° C	(60° to 110° F)

Bagged slab zinc anodes were used. The electrolyte was circulated with a filter pump. Sodium lauryl sulfate was used as a wetting agent to prevent pitting. The brightening and leveling agents normally employed in most proprietary acid zinc baths were not used. Preliminary plating trials disclosed that best deposits were obtained at a bath temperature of about 31.1° C (88° F) and very little solution movement.

Panel Numbers 16 and 17 were Bondal zincated and acid zinc plated for two hours at 2.32 amp/dm² (25 amp/ft²). Some surface sanding was necessary to alleviate zinc roughness. A Rochelle copper strike was applied over the zinc, followed by the thin hard nickel coating. Based on weight measurements before, and after zinc plating, the zinc plating thickness was calculated as 0.083 mm (0.0033 in) -- a value slightly greater than the 0.051 mm originally planned.

Panel Numbers 18, 19, and 20 were Bondal zincated and acid zinc plated in the same electrolyte as the previous panels, with the exception that periodic reverse current deposition was used to improve deposit smoothness. Plating times were varied so that Panel Number 20 had a zinc thickness of 0.033 mm (0.0013 in) while Panel Numbers 18 and 19 had zinc thicknesses of 0.066 mm (0.0026 in). All three panels were struck with Rochelle copper, followed by a thin hard nickel coating. After a six week storage period, prior to salt fog testing, Panels 18 and 20 were observed to have a few minute high spots

(29)

Clepo Acid Zinc Process SR-420, Frederick Gumm Chemical Company, Inc.,
Lyndhurst, New Jersey 07071.

indicative of blister formation. Panel Number 19, which showed no indication of blisters, was inadvertently hard nickel plated for ninety minutes, rather than the usual 60 minutes.

A low pH acid zinc bath was required for the phosphoric anodized panels. A slight modification of a bath suggested by Safranek and Faust(30) was used in this work. A nineteen liter (five gallon) bath was prepared and operated as follows:

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	250 g/l
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	30 g/l
NH_4Cl	15 g/l
H_3BO_3	14 g/l
Glycerine	6.84 g/l
Sodium Citrate	13.2 g/l
Citric Acid	13.2 g/l
Sodium Saccharin	7.74 g/l
p-Toluene Sulfonimide	2.53 g/l
pH	2.5 to 2.7
Temperature	26.7° to 29.4° C (80° to 85° F)
Anodes	Bagged slab zinc

Preliminary studies indicated that best zinc deposits were obtained with the use of periodic reverse current (PR). The PR current was applied with 15 seconds "forward" plating and 5 seconds "reverse" plating. Initial plating was performed in the direct "forward" mode for eight minutes so as to deposit sufficient zinc to accommodate the brief deplating periods occurring in the PR mode. Plating was started at very low voltage which was gradually raised in the manner recommended for nickel by Wittrock. PR plating current density was 4.65 amp/dm² (50 amp/ft²). Plating times for full current density were 45 minutes to deposit a zinc thickness of 0.046 mm (0.0018 in) on each panel. Thin Rochelle copper strike and hard nickel plate was then applied after appropriate activation dips in dilute acid. Panel Numbers 10, 11, and 12 were thus processed.

Corrosion Study Specimens Coated With Zinc-Nickel Alloy

Zinc-nickel alloy plating is an anomalous codeposition process -- i.e., the less noble metal, zinc, tends to plate in preference to the more

(30)

W. H. Safranek and C. L. Faust, "Improved Electroplated Finishes for Zinc Die Castings", Plating, October 1958, p. 1029.

noble metal, nickel. All references in the literature dealt with depositing this alloy on low carbon steels for rust inhibition. The application in this program, plating on anodized or zincated Aluminum 7075-T651, should be considered unique -- hence, some development work was required.

Shibuya, Kurimoto, and Noji⁽³¹⁾ show best salt spray corrosion resistance to occur with zinc-nickel alloys having a nickel content of 10 to 15 percent by weight. Unfortunately, their electrolyte operated at very low pH and extremely high current densities of 20 amp/dm² (215 amp/ft²) -- conditions totally unacceptable for coating propeller blades with zincated surfaces. The bath first evaluated was an all sulfamate zinc-nickel formulation similar to that used by Dini and Johnson⁽³²⁾. Metal contents in this bath were about 35 g/l nickel and 57 g/l zinc. Bath pH was 4.7 and the temperature was 60° C (140° F). High electrolyte agitation resulted in rough and unacceptable deposits. Increasing bath pH to 5.0 led to precipitation of salts believed to be zinc oxide hydrates. Zinc anode corrosion was difficult to control and this may have been a primary reason for the precipitates. Operating the bath at 3.72 amp/dm² (40 amp/ft²) provided the soundest deposits containing about eight percent by weight nickel. Lower current densities increased nickel content in the alloy; however, deposits were rough and smutted after plating on zincated aluminum.

Tsuji and Kamitani⁽³³⁾ recommended near-neutral amino-chloride complexed zinc-nickel electrolytes for depositing alloys containing 5 to 20 percent by weight nickel. An all sulfamate zinc-nickel electrolyte was modified by adding ammonium sulfamate and ammonium chloride. pH was adjusted to the recommended 5.5 to 6.0 range. Zinc to nickel metal ratio in the bath was 3:2. At electrolyte temperatures of 32.2° to 40° C (90° to 104° F) this bath produced deposits of excellent appearance with little solution agitation. Anodes were S.D. nickel chips mixed with sliced sections from slab zinc and housed in titanium baskets with polypropylene cloth outer bags. At current densities of 1.86 amp/dm² (20 amp/ft²), alloy nickel contents were

(31)

A. Shibuya, F. Kurimoto, and K. Noji, "Corrosion Resistance of Ni-Zn Alloy Plated Steel Sheet", Proceedings of Interfinish '80, pp. 128-32.

(32)

J. W. Dini and H. R. Johnson, "Electrodeposition of Zinc-Nickel Alloy Coatings", Sandia Laboratories Report No. SAND 77-8511, Sandia Laboratories, Livermore, California, p. 16.

(33)

H. Tsuji and M. Kamitani, "Electrodeposition and Passivation of Bright Zinc-Nickel Alloys", 69th AES Annual Technical Conference, June 24, 1982, San Francisco, California.

about 15 percent; at 3.72 amp/dm^2 (40 amp/ft^2), the nickel contents decreased to about 12 percent. Panel Numbers 22, 23, and 24 were Bondal zincated and zinc-nickel alloy plated with this bath at 1.86 amp/dm^2 (20 amp/ft^2) for two hours. Zinc-nickel alloy thickness for each panel was about 0.066 mm (0.0026 in). This was followed by a thin strike with Rochelle copper and one hour of hard nickel plating. The alloy bath composition and operating parameters, together with panel processing steps, are shown in Table 15.

TABLE 15. PROCESSING OF CORROSION STUDY PANELS WITH ZINC-NICKEL ALLOY LAYERS ON BONDAL ZINCATED ALUMINUM 7075-T651

Zinc-Nickel Bath and Operating Conditions

Zinc Metal	45 g/l
(Zinc Sulfamate) (22.4% Zn)	(200.9 g/l)
Nickel Metal	30 g/l
(Nickel Sulfamate) (21.4% Ni)	(140.2 g/l)
Ammonium Ion	90 g/l
(Ammonium Sulfamate and Ammonium Chloride as Required for NH_4^+ Concentration)	
Sodium Lauryl Sulfate (Wetting Agent)	.1-.2 g/l
Temperature	$32.2^\circ - 40.0^\circ \text{ C}$
Agitation	Mild
Anodes	Zinc Slab + S.D. Ni Chips
pH	5.5 to 6.0

Panel Processing

1. Process the panel through the Bondal double zincating procedure per Table 10, except for hard nickel plating.
2. Attach electrical connection from power supply with voltage applied. Immerse panel in amino-chloride complexed zinc-nickel alloy bath and plate at 20 amp/ft^2 for two hours.
3. Rinse and scrub panel surfaces. Lightly sand with 180 to 400 grit metallurgical paper if required to remove light surface and edge roughness. Scrub clean and rinse.
4. Activate for Rochelle copper strike by dipping panel in 1% by volume fluoboric acid for 5 seconds. Double rinse.
5. Immerse (with voltage applied) into Rochelle copper bath and strike for 2 minutes at 24 amp/ft^2 followed by plating for 35 to 40 minutes at 16 amp/ft^2 . Bath is air agitated and at a temperature of 48.9° to 54.4° C .
6. Rinse vigorously to remove Rochelle bath drag-out. Activate for nickel plating by dipping panel in 1% by volume sulfuric acid. Double rinse.
7. With voltage applied, immerse panel in hard nickel plating bath at 43.3° C and plate for one hour at 20 amp/ft^2 .

Panel Numbers 25, 26, and 27 were Bondal zincated with zinc-nickel alloy plated according to the steps shown in Table 15, with the exception that current density for alloy plating was 3.72 amp/dm^2 (40 amp/ft^2). Alloy thicknesses were about the same as those obtained on the previous zincated panels. An additional set of panels was processed through the alloy plating bath modified by adding 9 g/l of ammonium acetate for better pH buffering. Air agitation was used in the alloy bath and current density was increased to 4.18 amp/dm^2 (45 amp/ft^2). Panel Numbers 21, 28, and 29 were processed with this bath. Alloy thicknesses on these panels were about 0.051 mm (0.002 in). Panel Number 29 differed from the other two specimens in this series due to the fact that hard nickel plating was erroneously performed for two hours, making the thickness double that planned.

In attempts to deposit zinc-nickel alloys onto phosphoric anodized Aluminum 7075 surfaces, it was found that low pH baths of chemistries similar to those of previous alloy baths would not produce the nickel contents desired -- at least for the current density ranges being examined. Studies indicated that lowering the pH resulted in crossing a transition condition in which decreasing the current density led to decreased nickel contents in the alloy, rather than the reverse -- as found for near neutral alloy baths. The use of bidentrate ligands (such as citric acid) to strongly complex the metal ions did not shift the deposition potentials of zinc and nickel in a favorable direction to promote higher nickel contents. A final resolution to the problem was achieved when the bath chemistry was changed to reverse the ratio of zinc to nickel. By making the total electrolyte metal ion concentration as sixty percent nickel, alloy deposits could be obtained with 12.5 percent nickel. Bath efficiency was initially poor. This was corrected by adding sodium acetate for better buffering and ammonium chloride for better conductivity. The bath chemistry and operating parameters were as follows:

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	175 g/l	Zn Metal = 40 g/l
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	269 g/l	Ni Metal = 60 g/l
Wetting Agent	1 g/l	
Sodium Acetate	10 g/l	
NH_4Cl	10 g/l	
pH	2.4 to 2.9	
Temperature	48.9° to 51.7° C	
Anodes	Slab zinc (bagged)	
Agitation	Slight to none.	

Periodic reverse plating can be used at such low electrolyte pH values without adverse effects. This appeared to improve nickel content in the alloy. The most effective plating procedure was found as starting the deposition at about 1.5 volts after a 30 second soak with no voltage applied. The voltage was gradually increased until a current density of 3.25 amp/dm^2 (35 amp/ft^2) was achieved. After 30 minutes, the current density was

increased to 3.72 amp/dm^2 (40 amp/ft^2) and periodic reverse (PR) plating was conducted for another 50 minutes. This procedure was performed on anodized Panel Numbers 13, 14, and 15. The average alloy layer thickness for these panels was 0.056 mm (0.0022 in). Panels were completed by applying a Rochelle copper strike and a thin hard nickel coat.

Results of Salt Fog Testing Per ASTM B117

All panel edges and corners were carefully coated with an air cured masking compound as previously discussed and shown in Figure 9. Weights were obtained to the nearest 0.01 gram for each specimen. All panels entered the salt fog environmental cabinet at the same time and were exposed for 336 hours. After exposure, the panels were removed and gently rinsed to remove loose salts. After drying, the panels were individually weighed again. Photographs were taken of each pair of panels representing a planned control or coating sequence. Areas of selected panels were sectioned for metallographic examination and photographic documentation.

Figure 10 illustrates the appearance of the uncoated Aluminum 7075-T651 control specimens, Panel Numbers 1 and 2, after salt fog testing. Photomicrographs show the progress of corrosion at the center-punch indentation on Panel Number 1. Figures 11 through 19 provide documentary evidence of the corrosion performance of the various series of panels subjected to the salt fog environment. Table 16 summarizes panel weight changes, surface appearance, and metallographic examination results for the corrosion study. Judgmental ratings were assigned based on relative performances.

Discussion of Corrosion Study Results

Only one series of coated panels exhibited outstanding corrosion performance in the 336 hour salt fog test. This series was the dilute phosphoric anodized Aluminum 7075-T651 subjected to low pH sulfamate nickel plate followed by electrodeposited hard nickel. From Figure 12 it is evident that the low pH nickel layer is very adherant to the anodized layer and quite ductile. This would encourage use of this coating system on full sized blades, since the processing sequence is easily performed. This excellent performance is attributed to the fact that hard or bright nickel deposited on "pure" electroplated nickel forms what is normally called "duplex nickel plate". The hard nickel contains appreciable amounts of sulfur which makes the metal less noble (more anodic) than "pure" nickel. The hard nickel will thus corrode in preference to the low pH nickel coating which seals the phosphoric anodized film.

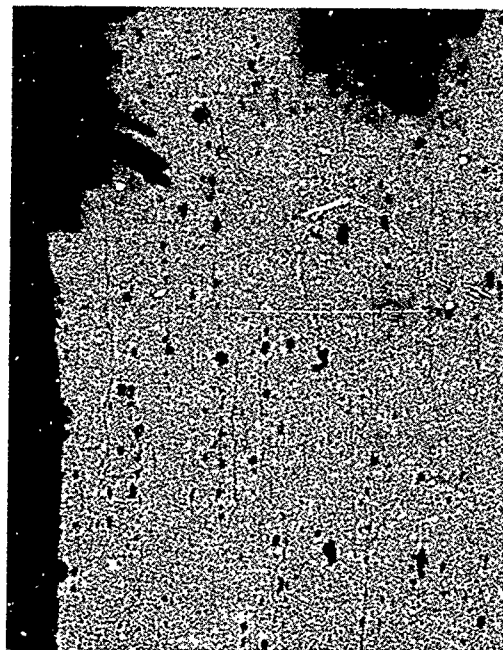
The anodic film, although thin and porous, inhibits the flow of galvanic current between the noble (cathodic) low pH nickel and the anodic Aluminum 7075-T651. As long as the anodized film remains unbroken, and the low pH nickel deposit is continuous, the hard nickel coating will be the only material subject to erosion and corrosion. The aluminum blade will thus be fully protected.



Panel No. 1

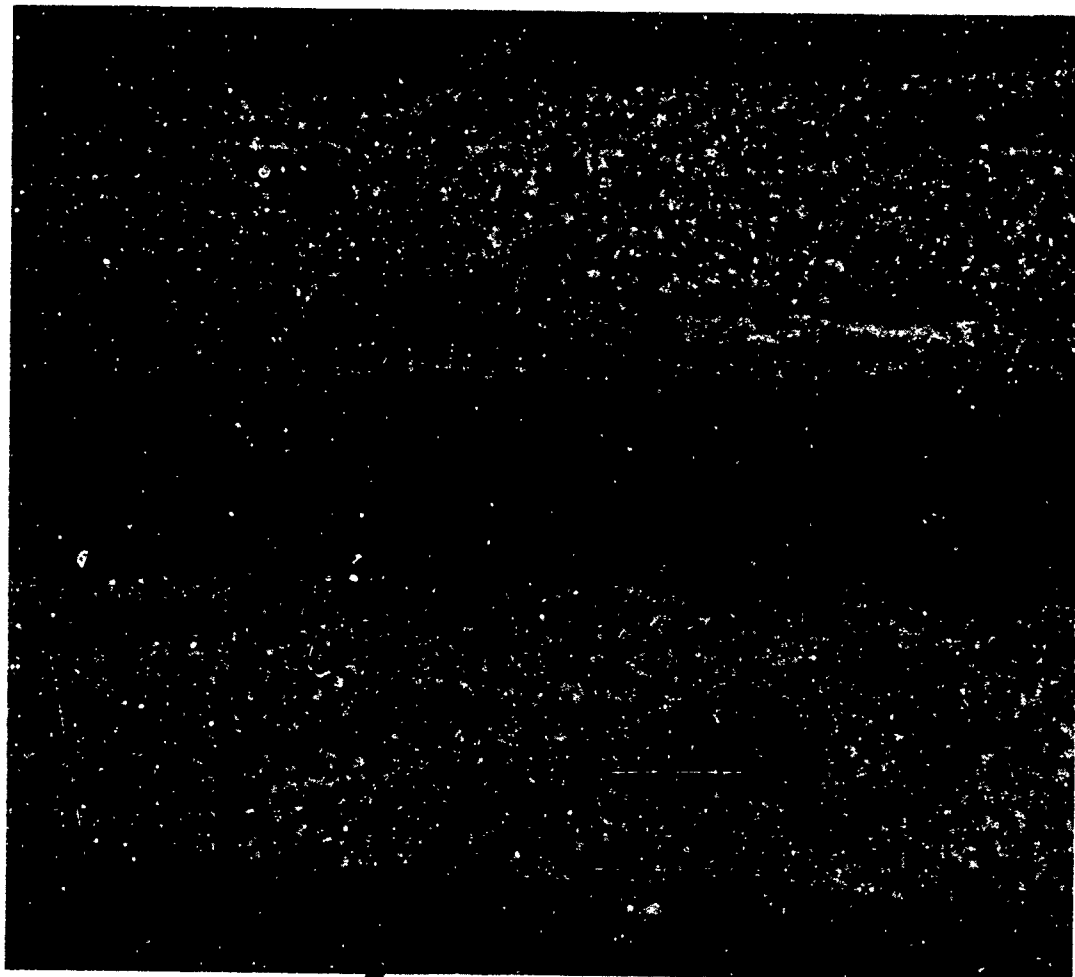
32X

View of center-punch area (above).
Enlarged view of upper left edge
of the same region (below).



Panel No. 1

200X



Panel No. 1

Panel No. 2

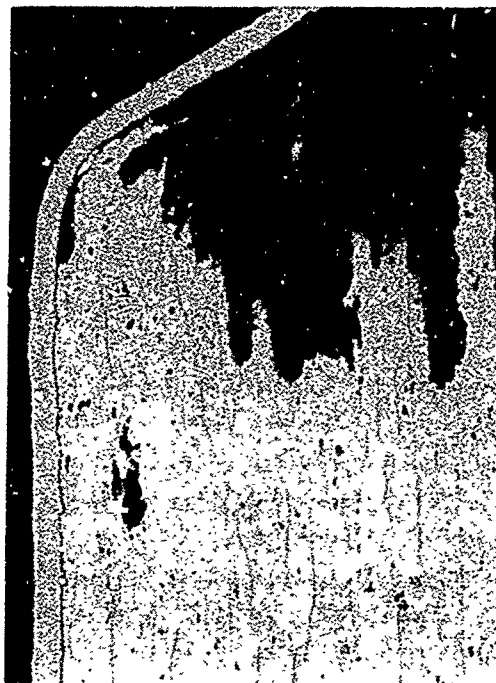
Figure 10. Illustrations of Salt Fog Corrosion Performance of Uncoated



Panel No. 4

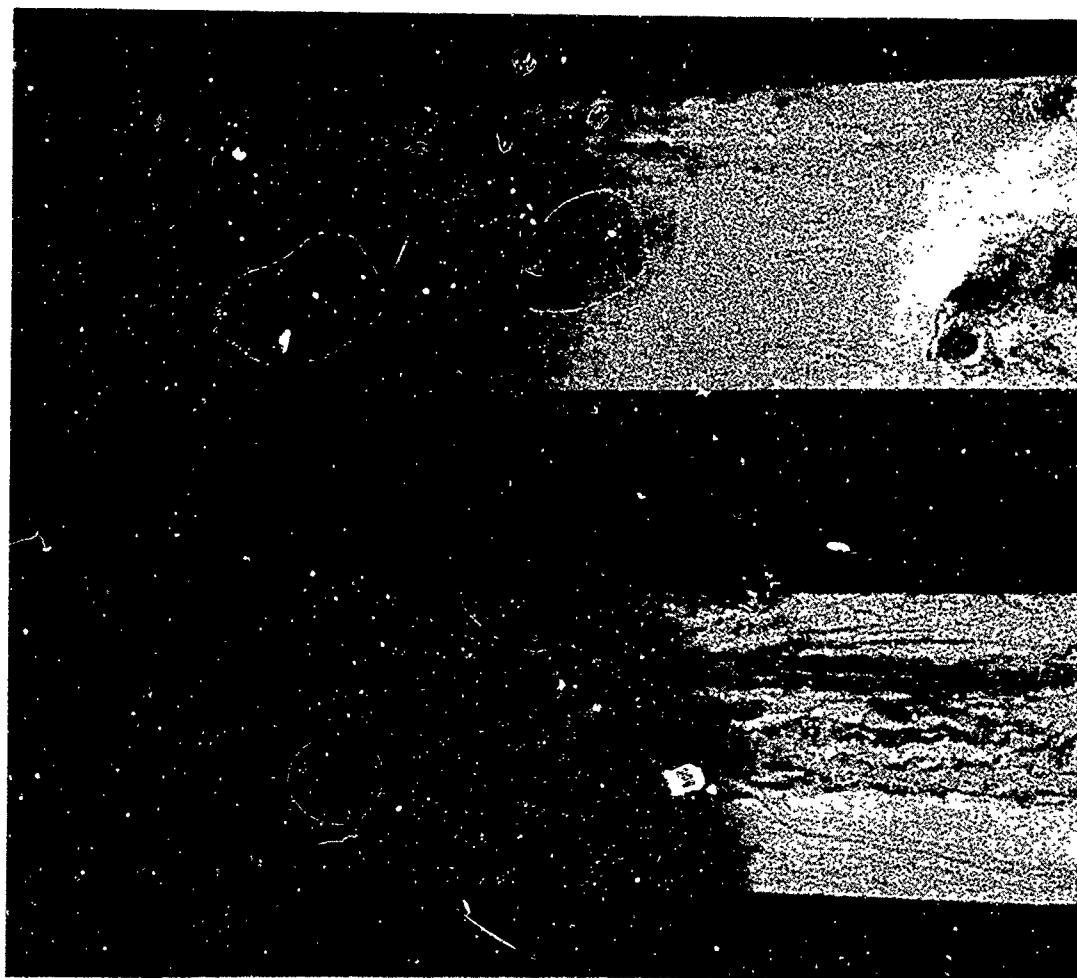
32X

Corrosion pit in Aluminum 7075-T651
(above). Enlarged view showing the
undermining of the hard nickel coat
(below).



Panel No. 4

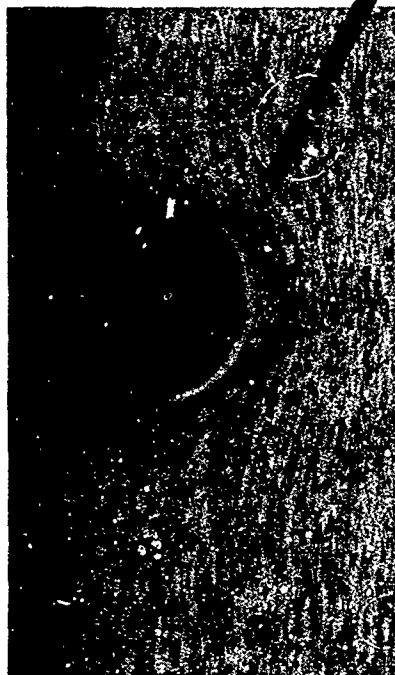
200X



Panel No. 4

Panel No. 5

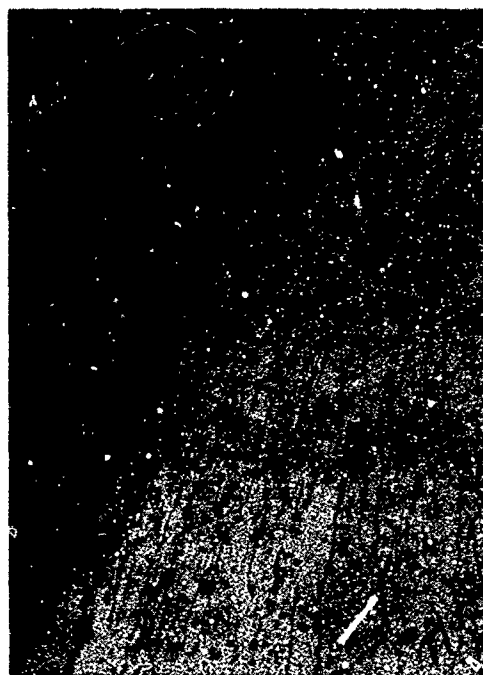
Figure 11. Illustrations of Salt Fog Corrosion Performance of Bondal Zincated and
Hard Nickel Plated Aluminum 7075-T651 Test Specimens



Panel No. 7

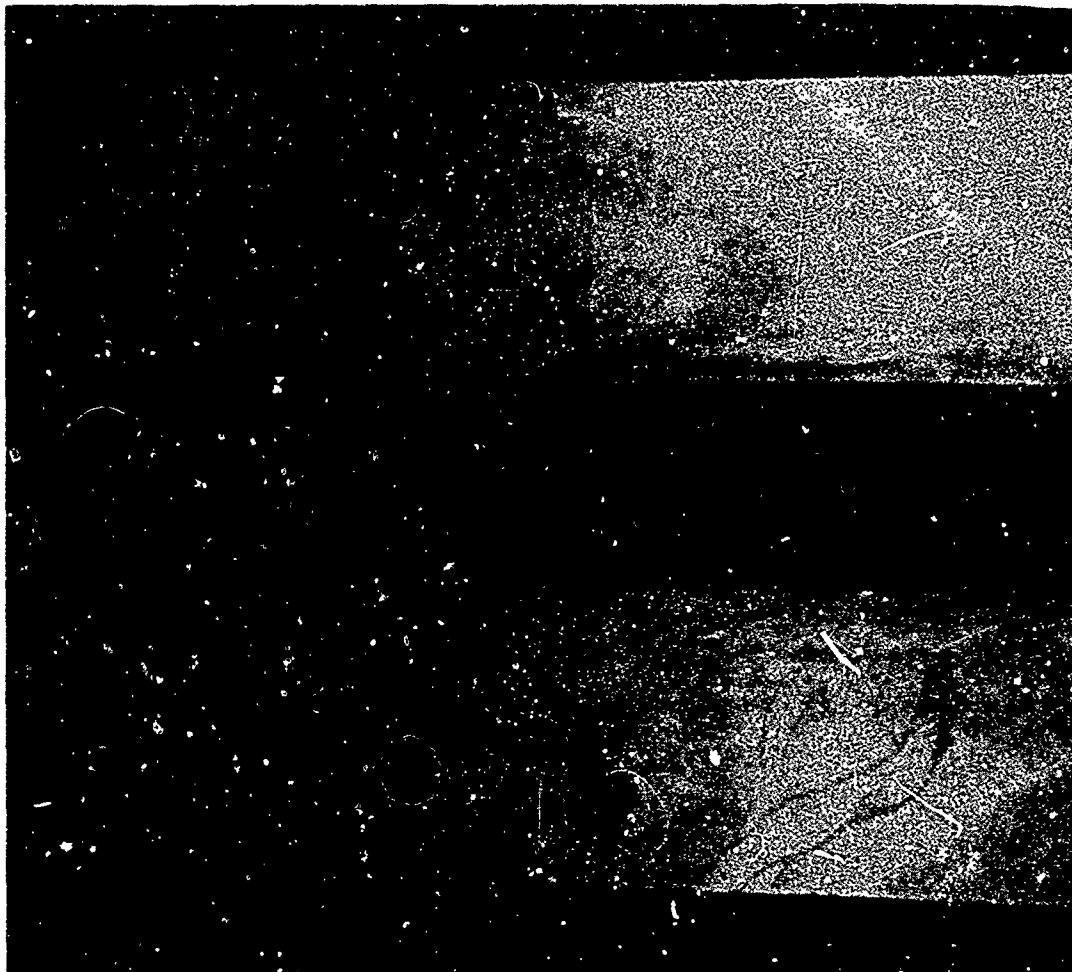
32X

Center-punch region showing no signs or corrosion (above). View of hard nickel plate on phosphoric anodized aluminum in deformed area (below).



Panel No. 7

200X



Panel No. 7

Panel No. 8

Figure 12. Illustrations of Salt Fog Corrosion Performance of Phosphoric Anodized, Low pH Nickel Plated, and Hard Nickel Plated Aluminum 7075-T651 Specimens

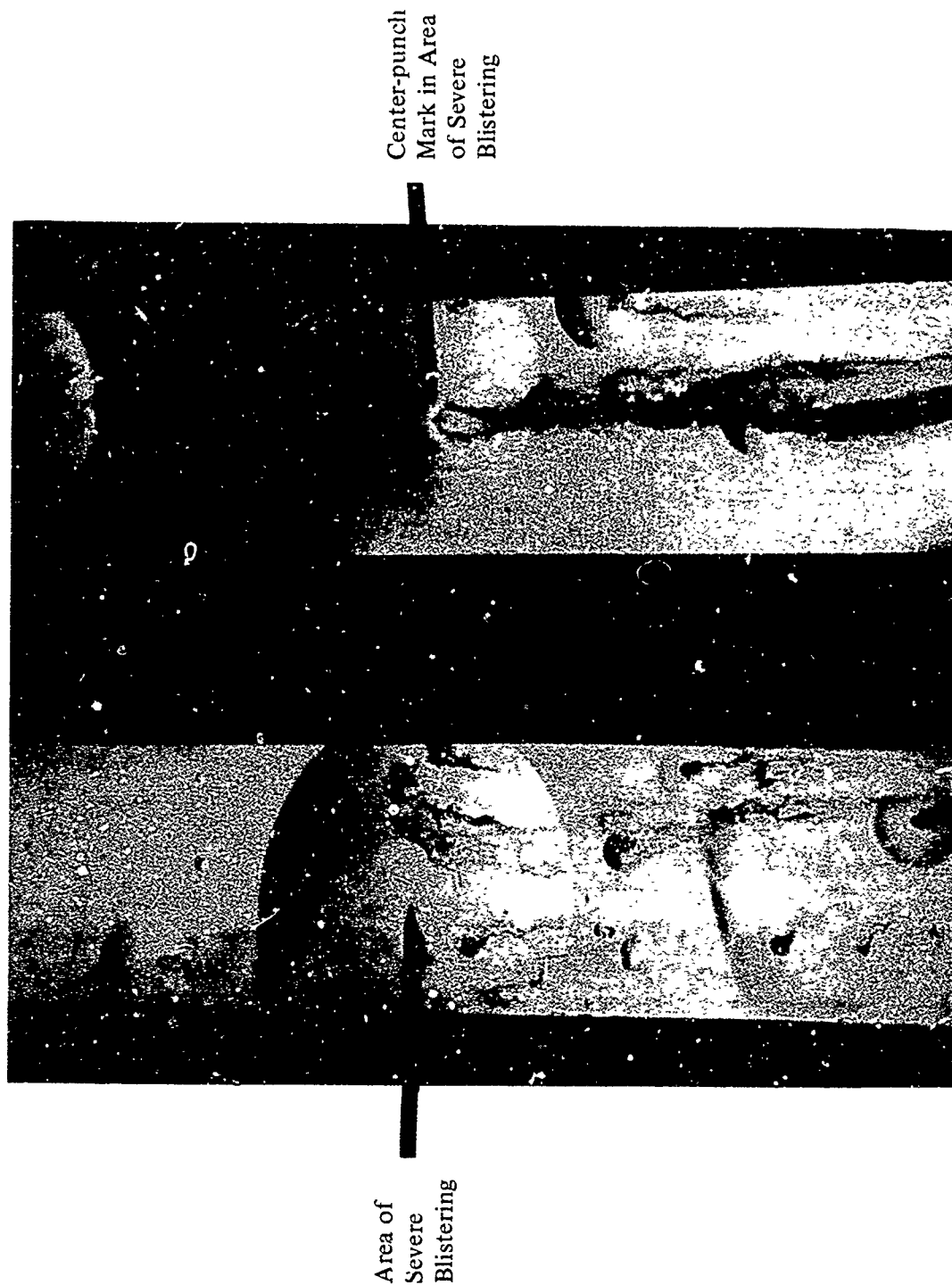
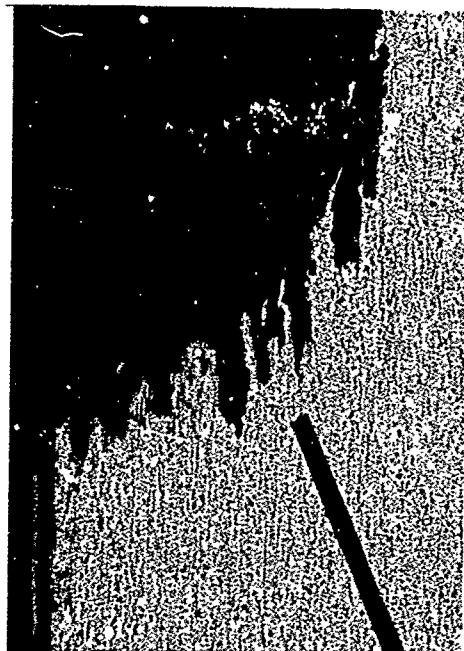


Figure 13. Illustrations of Salt Fog Corrosion Performance of Phosphoric Anodized Aluminum 7075-T651 Test Specimens PR Plated with Zinc (50 amp/ft²), Rochelle Copper Struck, and Hard Nickel Plated



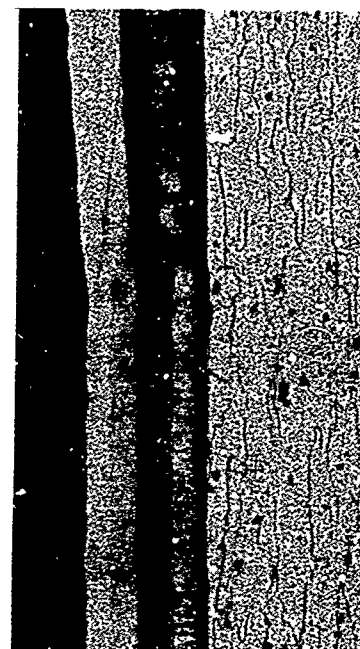
Panel No. 13



Panel No. 15

32X

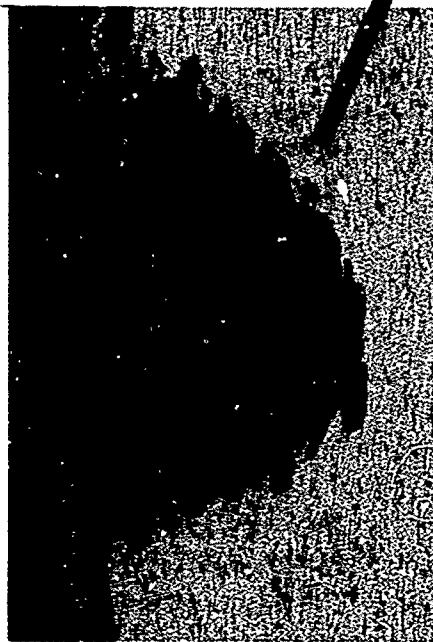
Center-punch area showing corrosion of aluminum substrate (above). The adjacent coating system shows separation from the Aluminum 7075-T651 (below).



Panel No. 15

200X

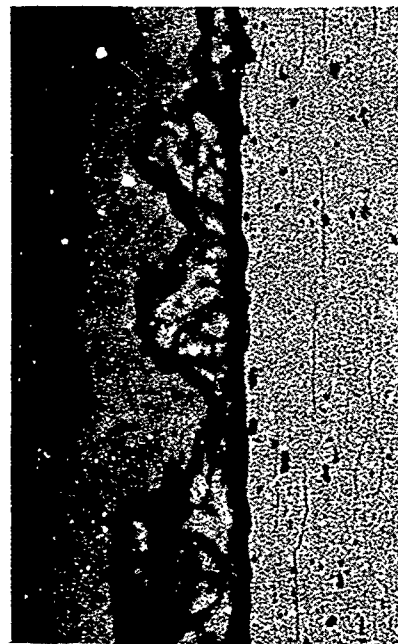
Figure 14. Illustrations of Salt Fog Corrosion Performance of Phosphoric Anodized Aluminum 7075-T651 Test Specimens PR Plated with Zn-Ni Alloy (40 amp/ft²), Rochelle Copper Struck, and Hard Nickel Plated



Panel No. 16

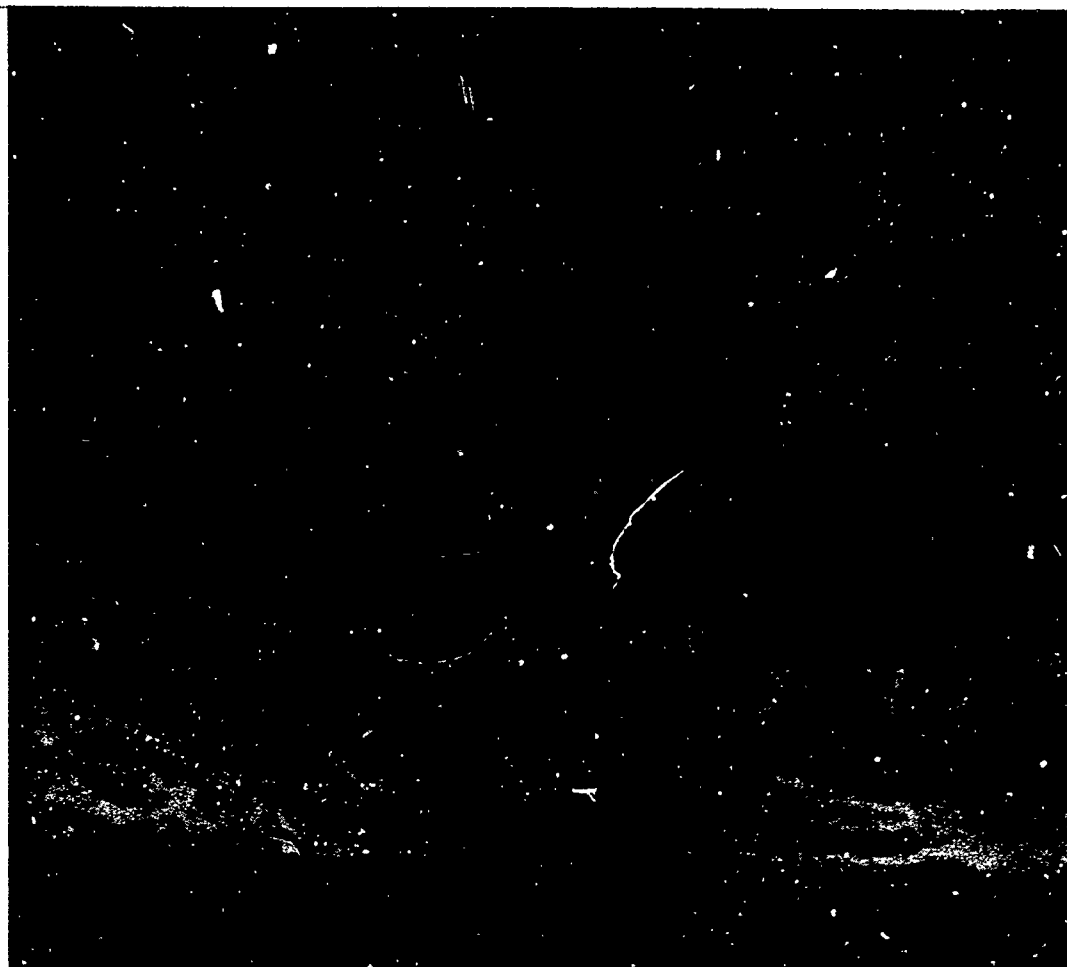
32X

Center-punch area showing corrosion of aluminum substrate (above). The adjacent surface exhibits corrosion salts where zinc plate had existed (below).



Panel No. 16

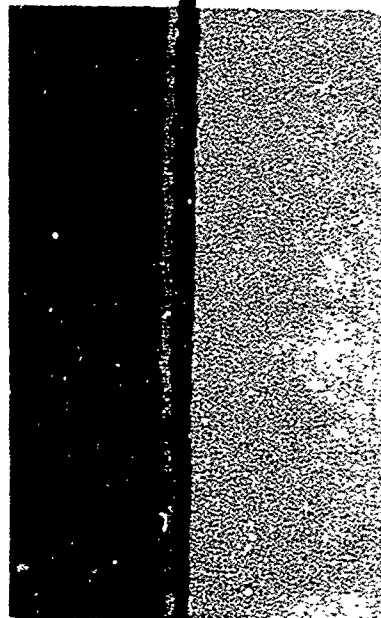
200X



Panel No. 16

Panel No. 17

Figure 15. Illustration of Salt Fog Corrosion Performance of Bondal Zincated Aluminum 7075-T651 Test Specimens Plated with Zinc (25 amp/ft², No PR), Rochelle Copper Struck, and Hard Nickel Plated



Panel No. 19

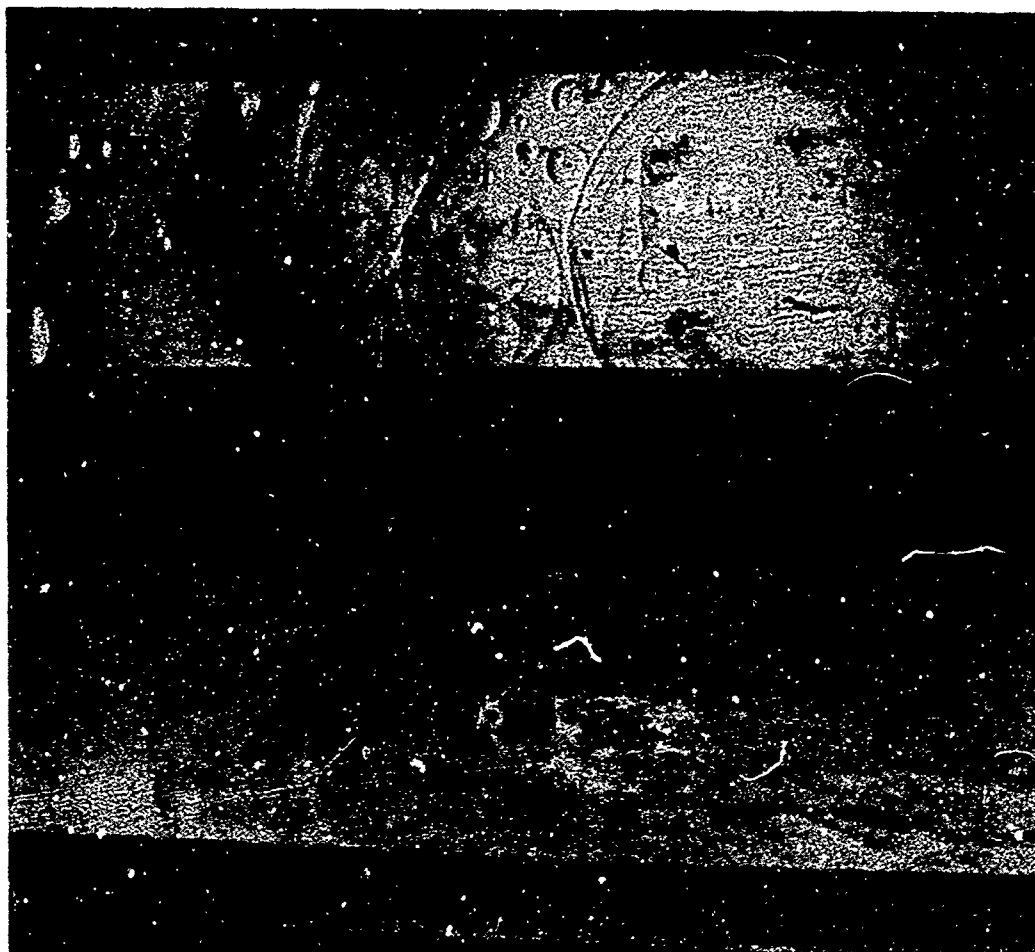
32X

Region of plated coating system
separation at edge of blister (above).
Separation has occurred at the
Bondal zincated surface (below).



Panel No. 19

200X



Panel No. 19

Panel No. 20

Figure 16. Illustrations of Salt Fog Corrosion Performance of Bondal Zincated Aluminum
7075-T651 Test Specimens PR Plated with Zinc (20 amp/ft²),
Rochelle Copper Struck, and Hard Nickel Plated



Panel No. 22

32X

Center-punch area shows severe corrosion of the aluminum (above). Area adjacent to center-punch region depicts fracture and lifting of Zn-Ni alloy at zincate surface (below).



Panel No. 22

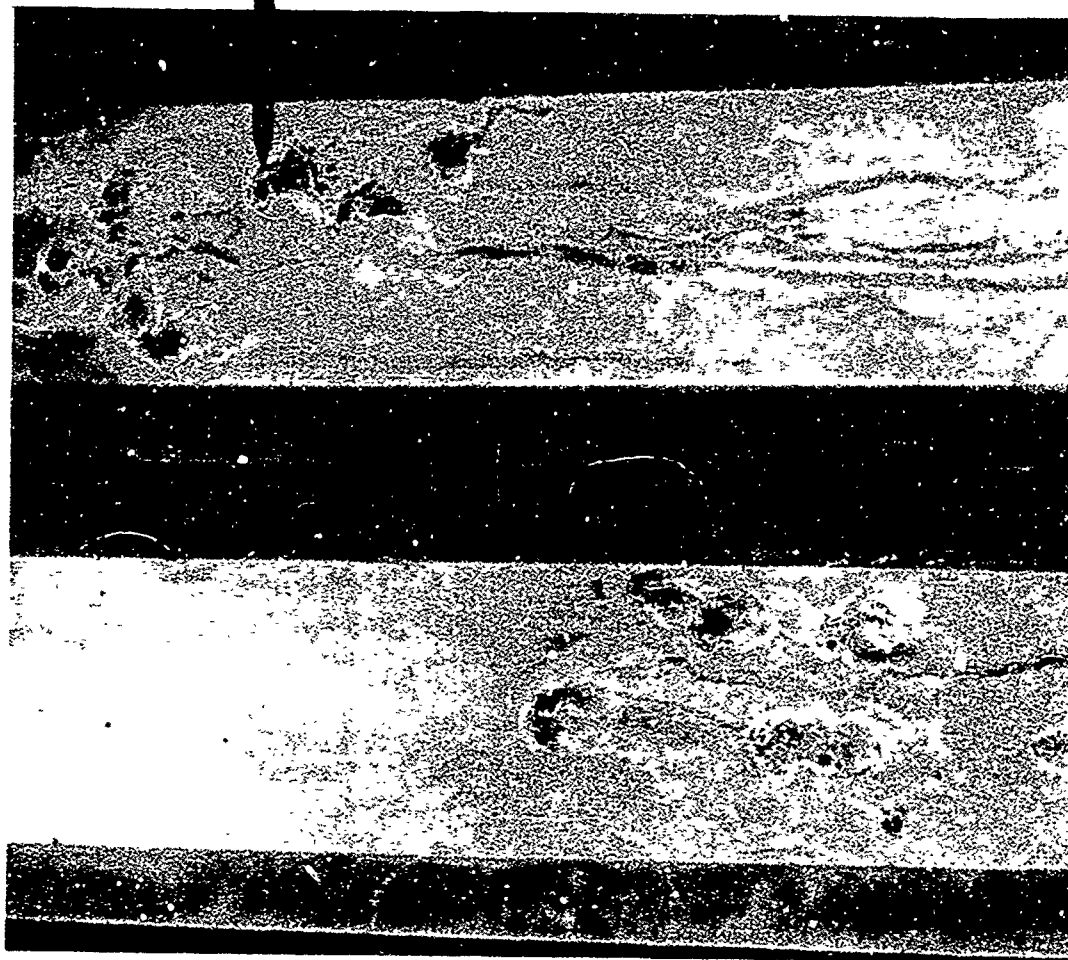
200X



Panel No. 22

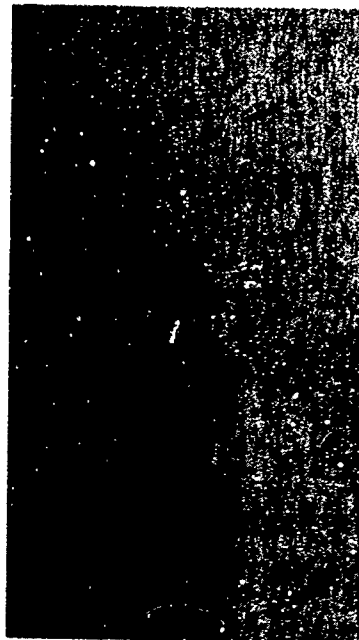
Panel No. 23

Figure 17. Illustrations of Salt Fog Corrosion Performance of Bondal Zincated Aluminum 7075-T651 Test Specimens Plated with Zn-Ni Alloy (20 amp/ft²), Rochelle Copper Struck, and Hard Nickel Plated



Panel No. 25

Panel No. 26



Panel No. 26

32X

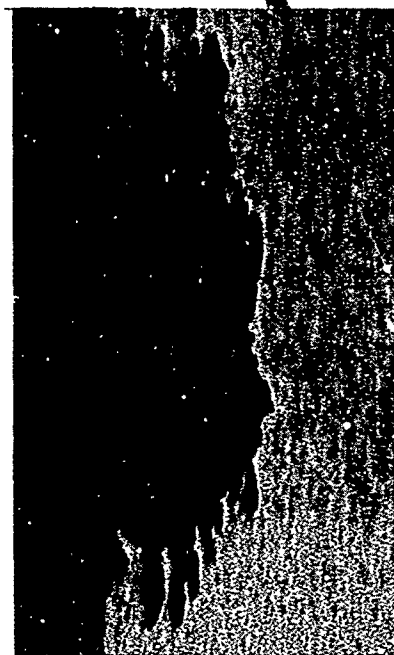
View of corrosion pitting of the aluminum substrate (above). The Zn-Ni alloy in this region was very fragmented which likely provided a path for attack on the aluminum (below).



Panel No. 26

200X

Figure 18. Illustrations of Salt Fog Corrosion Performance of Bondal Zincated Aluminum 7075-T651 Test Specimens Plated with Zn-Ni Alloy (40 amp/ft²), Rochelle Copper Struck, and Hard Nickel Plated.



Panel No. 21

32X

View of corrosion pit in aluminum substrate (above). The coating on the edge of the pit showed fragmentation of the Zn-Ni alloy with some separation between the copper strike and the Zn-Ni alloy (below).



Panel No. 21

200X



Panel No. 21

Panel No. 29

Figure 19. Illustrations of Salt Fog Corrosion Performance of Bondal Zincated Aluminum 7075-T651 Test Specimens Plated with Zn-Ni Alloy (45 amp/ft², Acetate Buffered), Rochelle Copper Struck, and Hard Nickel Plated.

TABLE 16. SUMMARY OF SALT FOG CORROSION TEST DATA AND RATINGS

Panel Number	Processing Description	Masked Panel Weight (Grams)		After Salt Fog & Light Scrub
		Before Salt Fog	After Salt Fog	
1 ^a	Aluminum 7075-T651 Controls containing no added coatings.	350.24	350.57	350.36
2		350.42	350.59	350.39
4 ^a	Aluminum 7075-T651, double Bondal zincated, hard nickel plated at 20 ASF for 1 hour.	362.38	362.36	362.30
5		362.43	362.42	362.34
7 ^a	Aluminum 7075-T651, dilute phosphoric anodized, low pH nickel plated 2 hours, hard nickel plated at 20 ASF for 1 hour.	392.99	393.02	393.03
8		391.24	391.26	391.26
10 ^a	Aluminum 7075-T651, dilute phosphoric anodized, low pH acid zinc plated at 50 ASF for 50 minutes (45 min. with PR at 15 sec. "forward" and 5 sec. "reverse"), Rochelle copper strike and plate for 40 minutes, hard nickel plated at 20 ASF for 1 hour.	389.02	389.03	389.01
11		387.86	387.91	387.90
13 ^a	Aluminum 7075-T651, dilute phosphoric anodized, low pH acid zinc-nickel alloy plated at 35 ASF for 30 minutes and PR plated at 40 ASF for 50 minutes, Rochelle copper strike and plate for 40 minutes, hard nickel plated at 20 ASF for 1 hour.	387.81	387.69	387.65
15 ^a		389.73	389.59	389.51
16 ^a	Aluminum 7075-T651, double Bondal zincated, acid zinc chloride plated at 25 ASF for 2 hours, Rochelle copper strike and plate for 45 minutes, hard nickel plated at 20 ASF for 1 hour.	382.17	382.60	382.40
17		385.49	386.10	386.03
19 ^a	Aluminum 7075-T651, double Bondal zincated, acid zinc chloride plated at 20 ASF for 2.5 hours with PR current, Rochelle copper strike and plate for 45 minutes, hard nickel plated for 1 hour at 20 ASF,	396.57	396.65	396.99
20		395.63	395.70	395.85
22 ^a	Aluminum 7075-T651, double Bondal zincated, zinc-nickel alloy plated from a neutral amino complexed sulfamate bath at 20 ASF for 2 hours, Rochelle copper strike and plate for 50 minutes, hard nickel at 20 ASF for 1 hour.	386.80	386.81	386.75
23		389.40	389.41	389.35

^a Indicates panels with center-punch mark after plating.

<u>Panel Appearance After Salt Fog, Rinse, and Drying</u>	<u>Metallographic Examination Results</u>	<u>Rating</u>
Both panels were severely corroded and had an etched appearance. Refer to Figure 10.	Moderate corrosion on all surfaces.	Poor
Both panels exhibited localized corrosion at spots where the nickel coating was punctured or contained pinhole porosity. Deep pitting of the Al 7075 was noted - with displacement copper plating from the dissolved Al alloy. Refer to Figure 11.	Corroded only where coating was porous or discontinuous; pitted badly in these areas.	Fair
Both panels showed few traces of corrosion. The minute salts present appeared to be from pinholes present in the thin hard nickel layer. No penetration to Al 7075 was evident. Refer to Figure 12.	Excellent performance in all respects. Noted traces of nickel salts where hard nickel was possibly porous.	Excellent
Each panel exhibited significant blistering believed to have originated at the zinc-anodized interface. The corrosion salts were white (indicative of zinc) with some light green salts also present (probably nickel). Refer to Figure 13.	Blistered very severely due to lack of adhesion of zinc to anodic film.	Poor to Bad
Both panels had small blisters from which corrosion products were evolved. Deep corrosion pitting occurred on Panel 15 at the area of the punch mark. Visible signs of copper displacement plating on the hard nickel were noted (probably from the Rochelle copper layer. See Fig. 14.	Provided acceptable protection, except where alloy was fractured (possibly due to questionable adhesion strength to anodic film).	Fair
Both panels were so severely blistered that the hard nickel coating was lifted from the aluminum. The corrosion salts were pale bluish-white (indicative of zinc). Refer to Figure 15.	Any salt fog access to zinc plate resulted in severe lateral corrosion with loss of adhesion between the hard nickel and Aluminum 7075.	Bad
These panels performed in much the same manner as Panels 16 and 17. Blistering was severe and some light displacement copper plating was noted on the hard nickel around pores, Figure 16.	Poor adhesion of zinc plate to zincate resulted in very severe blistering.	Bad
Blistering was very moderate on both panels. Isolated pores in the hard nickel showed areas of copper displacement plating. In one pore, some nickel salts were evident. Attack on the zinc-nickel alloy layer appeared to be moderate compared with most other panels in this study, Fig. 17.	Provided good protection, except for small isolated areas where adhesion to zincate was poor and alloy layer fragmented.	Fair

TABLE 16. SUMMARY OF SALT FOG CORROSION TEST DATA AND RATINGS
(Continued)

Panel Number	Processing Description	Masked Panel Weight (Grams)		
		Before Salt Fog	After Salt Fog	After Salt Fog & Light Scrub
25 ^a	Aluminum 7075-T651, double Bondal zincated, zinc-nickel alloy plated from a neutral amino complexed sulfamate bath at 40 ASF for 2.25 hours (Panel 25) and 1.25 hours (Panel 26), Rochelle copper strike and plate for 40 minutes, hard nickel plated at 20 ASF for 1 hour.	398.39	398.41	398.20
26		396.69	396.70	396.54
21 ^a	Aluminum 7075-T651, double Bondal zincated, zinc-nickel alloy plated from a neutral amino complexed sulfamate bath (buffered with sodium acetate) at 45 ASF for 50 minutes, Rochelle copper strike and plate for 40 minutes, hard nickel plated at 20 ASF for 1 hour (Panel 21) and 2 hours (Panel 29).	369.35	369.39	369.31
29		389.86	389.95	389.87

^a Indicates panels with center-punch mark after plating.

<u>Panel Appearance After Salt Fog, Rinse, and Drying</u>	<u>Metallographic Examination Results</u>	<u>Rating</u>
Both panels exhibited displacement copper plating on the hard nickel. The copper likely came from the Rochelle layer. Some zinc-nickel alloy salts were in evidence at pores in the hard nickel coat. Blistering was very nominal. Refer to Figure 18.	Fractures in brittle Zn-Ni alloy created corrosion paths, otherwise fair protection was provided.	Fair
Numerous small blisters were noted over much of the surface of each panel. Pale green and white salts (probably from corroded zinc-nickel alloy) were observed. Copper displacement plating was seen in localized areas near pores in the hard nickel coating. Refer to Figure 19.	Zn-Ni alloy layer was badly fractured (brittle) and copper strike did not adhere well to alloy, resulting in numerous small blisters.	Poor

The uncoated aluminum control panel appeared badly corroded, but metallographic examination indicated only moderate attack. This was as expected, since the Aluminum 7075-T651 was not in contact with a dissimilar, and more noble, metal. It would explain why marine atmospheric corrosion of bare ACV blades has not received significant attention -- metal loss by erosion is simply much faster than by corrosion. The panels directly hard nickel plated over zincated surfaces were rated as fair from an appearance standpoint. They could have been correctly rated "poor" due to the corrosion pitting of the aluminum where porosity or pinholes existed in the thin hard nickel. The pitting thus noted was a classic example of galvanic corrosion cell formation due to dissimilar metals in contact and of greatly different electrode potentials.

Specimens plated with zinc performed poorly due to rapid corrosion of the zinc layer once the protection layer was exposed. Formation of corrosion products of zinc was so rapid and extensive that massive blisters occurred. Part of the problem may have been due to poor adhesion between the zinc and the anodized or zincated aluminum substrate. Specimens plated with the zinc-nickel alloy exhibited much less corrosion than the zinc plated samples. Lateral attack through this sacrificial protection layer was very slow. Unfortunately, the alloy was rather brittle and fissures developed which permitted galvanic coupling to copper and nickel in the outer coating system. Most corrosion with the zinc-nickel alloy system was localized pitting type. In some instances, poor adhesion between the alloy layer and the substrate led to extensive fracturing of the zinc-nickel which further aggravated corrosion pitting. A heat treatment would likely make the alloy layer more ductile; however, the temperatures required would not be acceptable due to the temper state of the Aluminum 7075-T651.

Corrosion Study Conclusions

Uncoated Aluminum 7075-T651, an alloy similar to that used for ACV propeller blades, undergoes significant corrosion in marine environments. This behavior is probably obscured by the more rapid and severe erosion experienced by these blades while in operation. Coating such blades with an erosion resistant electrodeposit, such as hard nickel, introduces an unfavorable galvanic couple which induces corrosion pitting wherever the aluminum substrate is exposed.

By dilute phosphoric anodizing the Aluminum 7075 alloy, applying a ductile layer of "pure" nickel from a low pH sulfamate nickel electrolyte, and hard nickel plating a final erosion coating, excellent corrosion protection can be obtained. The phosphoric anodic film appears to impede the flow of galvanic current between the cathodic coating and the anodic aluminum -- hence, corrosion is retarded. The ductile nickel layer adheres well to the anodic film and readily deforms on hard object impact to prevent environmental exposure of the aluminum substrate.

The use of intermediate coatings of zinc or zinc-nickel alloy to provide sacrificial protection for the aluminum blades does not appear to be

practical at this time. Zinc corrodes too rapidly under the galvanic conditions governed by the highly cathodic nickel outer electroplate. Zinc-nickel alloy corrodes quite slowly, making this material attractive as a sacrificial coating. However, this alloy is brittle and difficult to bond to either zincated or anodized aluminum surfaces. Zinc is also difficult to bond to similar surfaces. This may be due to zinc displacement reactions, plus attack from the acid plating electrolytes on displacement zinc films. More extensive investigations and development work would be required to make zinc-nickel alloy plating useful as an intermediate coating for propeller blade applications.

SECTION V

EVALUATION OF SPECIAL HARD ANODIC FILM SYSTEMS AS RAIN AND SAND EROSION RESISTANT CANDIDATES

Background

At the request of U.S. Army-MERADCOM, this program was expanded to include the evaluation of rain and sand erosion performance of Aluminum 7075 specimens coated by two different proprietary hard anodizing processes. Although previous Bell Aerospace experience with anodized aluminum surfaces had not indicated any significant improvements in erosion performance, this new effort incorporated certain modifications in processing which were worthy of evaluation.

Under the guidance of MERADCOM, this study required that Aluminum 7075 specimens be shot peened and divided into two separate groups for the specific anodizing processes requested. One group was to be integral color anodized by the hardcoating process commercially known as "Duranodic", and the other group required low voltage anodizing in accordance with the Sanford Process. Two different anodize thicknesses were required for each process. It was originally directed that various quantities of panels from each anodic process be in various states of surface seal, including unsealed, duplex sealed, and Teflon impregnation sealed (coated). Sealing instructions were later changed, at MERADCOM request, to require duplex sealing of all specimens, followed by coating with Sandstrom LC-300, a heat cured corrosion inhibiting dry film lubricant in a thermosetting resin base.

The shot peening work and hard anodizing efforts were subcontracted to commercial vendors suggested by MERADCOM:

Duranodic Process - Hytek Finishes Company, 8202 South 290th Street,
Kent, Washington 98032

Sanford Process - Duralectra, Inc., 61 North Avenue,
Natick, Massachusetts 01760

Specimen Fabrication

All Aluminum 7075-T651 used in this segment of the program was procured to conform to requirements of Federal Specification QQ-A-250/12. Certified test reports were received to confirm this requirement. 0.635 cm (0.25 in) thick stock was cut into twelve plates, measuring 21 cm (8.26 in) by 10.2 cm (4 in), for shot peening, anodizing, sealing, and (in some cases) coating with Sandstrom LC-300. These pieces were cut in half after anodizing and sealing to provide twenty-four 10.2 cm (4 in) by 10.2 cm (4 in) plates. They were later used for anodic coating thickness measurements, Taber abrasion testing, and simulated creep evaluations.

Eight airfoil shaped "wedge" specimens were machined from 0.953 cm (0.375 in) Aluminum 7075-T651 stock. They were made to a length of 16.5 cm (6.5 in), a length sufficient to provide two wedge specimens for separate sand and rain erosion tests. Figure 20 illustrates a machined erosion test



Figure 20. Rain/Sand Erosion Test Specimen

wedge. Cutting the long wedges in half -- after hard anodizing, sealing, and Sandstrom coating -- would provide twice as many test specimens as actually required. The extra pieces were to provide spares in case of spoilage during coating or in event retesting became necessary. An additional ten long wedges were machined at this time to provide specimens for evaluation of erosion performance of uncoated Aluminum 7075-T651 and for studies on hard nickel coated material.

Wedges and flat plates were processed through the shot peening, hard anodizing and sealing operations in identical manners. Therefore, no attempt will be made to distinguish configurational differences in the following discussion.

Shot Peening

Shot peening, a controlled abrasive blasting process, induces plastic flow from 0.005 to 0.010 inch below the metal surface and improves the distribution of stress, particularly on ground or machined surfaces. Surface tensile stresses are thereby changed to the more beneficial compressive mode which improves fatigue life. Since the induced compressive stress is affected by the type and size of the abrasive, the driving force of the

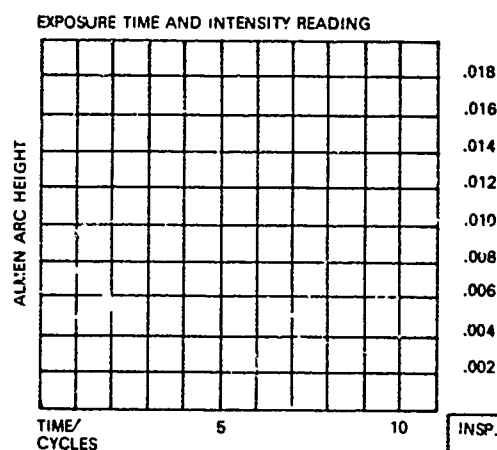
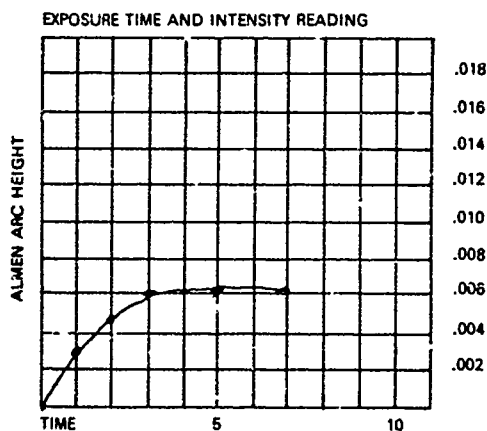
peening, and the time, it is necessary to impose controls to assure that all parts obtain similar levels of compressive stress. The requirements of Specification MIL-S-13165 were imposed to meet this requirement. Almen strips are required by this specification to demonstrate the effects of the shot peening media and parameters on steel strips of a specified thickness, composition, and hardness. Peening these strips on one side results in an arc which is measured.

Hytek Finishes Company performed the shot peening of all Aluminum 7075-T651 wedges and flat plates in accordance with Specification MIL-S-13165. Shot peening parameters and Almen arc height results are shown in Figure 21.

Special Hardcoat Anodizing

The Sanford Plus Process (SP), was applied to one group of aluminum plates and wedges in this portion of the program. The Sanford Plus Process, introduced in 1979, is a low voltage electrochemical process for hardcoating any aluminum alloy. The special properties afforded aluminum alloys by this process are harder, thicker, more uniform, high dielectric coatings. The process reportedly imparts wear qualities in parts which are superior to case hardened steel, exceeding the requirements of Specification MIL-A-8625. So called "file hard" coatings have been measured as high as Rockwell 70C.

DATE <u>11/22/82</u>		HEATH PLATING		P/N <u>Test Specimens</u>	
CUSTOMER <u>Bell Aerospace</u>	INVOICE NO. <u>30306</u>	DESCRIPTION <u>Wedge/Plate 10</u>	QUANTITY <u>60</u>	MACHINE NO. <u>60</u>	OPERATOR <u>KACTE</u>
MAT'L TYPE <u>ALUM.</u>	PROCESS SPEC. <u>MIL-S-13165</u>	ALMEN TEST	ACTUAL <u>006A2-006A2</u>	REQ'D	
SHOT SIZE <u>240</u>	DISTANCE TO PART <u>54</u>	TABLE R.P.M. <u>8</u>	SHOT SIZE	DISTANCE TO PART	NOZZLE SIZE
DOWN WHEEL R.P.M. <u>700</u>	ACROSS WHEEL R.P.M. <u>700</u>		No. OF NOZZLES	ID MACHINE F.P.M.	AIR PRESSURE
DOWN WHEEL AMPS <u>19</u>	ACROSS WHEEL AMPS <u>19</u>		LANCE R.P.M. <u>86</u>		



Form PL-3

PHOTO OR SKETCH OF SET UP OR REMARKS ON REVERSE SIDE

INSP.



Figure 21. Data Sheet for Shot Peening Parameters and Almen Arc Height Results.

The Sanford Plus Process is based on the patents of Sanford⁽³⁴⁾ and Franklin⁽³⁵⁾ and is conducted in sulfuric acid with a weak acid additive. The process is performed at 4.4° to 10° C (40° to 50° F) by raising the voltage in a stepped time pattern until 20 volts is applied to the parts. This protects the parts from burning. A special power supply superimposes a.c. over d.c. voltage to produce a high quality hard coat on the aluminum.

The Duranodic Process (DP) is widely used for exterior aluminum architectural applications. The coating is integral with the aluminum and can be clear or colored. The final appearance of the anodic finish is dependent on the alloy and its temper. The finish is a dense, abrasion resistant coating. Duranodic hard coatings are achieved by anodizing in a specially mixed acid electrolyte and are reportedly harder than most anodic finishes. Such coatings are available through licensed processors.

The two processors of the proprietary hard anodizing systems were requested to produce coating thicknesses of 0.051 mm (0.002 in) and 0.102 mm (0.004 in) on the individual substrate configurations supplied by Bell Aerospace Textron.

Each vendor was requested to apply a duplex seal to all anodized specimens. Part of the rationale for sealing all pieces, rather than leaving some unsealed, was the fact that unsealed anodic coatings will partially seal themselves through absorption of moisture from the atmosphere. It was further concluded that unsealed anodized aluminum was not a proper baseline from which to judge abrasion or wear resistance of the coated metal. The duplex seal was a two step operation. The first seal consisted of immersion of the anodized specimens in a nickel acetate solution at a temperature of 70° to 90° C (158° to 194° F). The second seal was in water at 95.6° to 100° C (204° to 212° F).

Final Coating With Dry Film Lubricant

The decision to change the final coating from Teflon to Sandstrom LC-300 was based on comparative sizes of the anodize pores and the Teflon particles. The latter has sufficient diameter to leave pores unsealed and accessible to corrosion. The particle sizes for the inhibited molybdenum disulfide filler were in the range of one to five nm. Since the hard anodic film pores are approximately ten nm, any partially sealed pores

(34)

P. L. Sanford, U.S. Patent No. 2,743,221 (April 1956).

(35)

J. B. Franklin, U.S. Patent Nos. 2,897,125 (July 1959), 2,905,600 (September 1959), 2,977,294 (March 1961), and 3,020,213.

TABLE 17. IDENTIFICATION OF SPECIAL HARD ANODIZED SPECIMENS

Flat Plates (10.2 cm x 10.2 cm x 0.635 cm Thick)

<u>Specimen No.</u>	<u>Qty.</u>	<u>Anodic Hard Coat</u>	<u>Final Coat</u>	<u>Test Use</u>
SP-1	1	0.05 mm Sanford Plus	Sandstrom LC-300	Taber
SP-2	1	0.10 mm Sanford Plus	Sandstrom LC-300	Taber
SP-3	1	0.05 mm Sanford Plus	None	Taber
SP-4	1	0.10 mm Sanford Plus	None	Taber
SP-5	1	0.05 mm Sanford Plus	None	Creep
SP-6	1	0.10 mm Sanford Plus	None	Creep
SP-7	1	0.05 mm Sanford Plus	None	Thickness
SP-8	1	0.10 mm Sanford Plus	None	Thickness
SP-9	2	0.05 mm Sanford Plus	None	Spares
SP-10	2	0.10 mm Sanford Plus	None	Spares
DP-1	1	0.05 mm Duranodic	Sandstrom LC-300	Taber
DP-2	1	0.10 mm Duranodic	Sandstrom LC-300	Taber
DP-3	1	0.05 mm Duranodic	None	Taber
DP-4	1	0.10 mm Duranodic	None	Taber
DP-5	1	0.05 mm Duranodic	None	Creep
DP-6	1	0.10 mm Duranodic	None	Creep
DP-7	1	0.05 mm Duranodic	None	Thickness
DP-8	1	0.10 mm Duranodic	None	Thickness
DP-9	2	0.05 mm Duranodic	None	Spares
DP-10	2	0.10 mm Duranodic	None	Spares

Wedge Configuration (7.62 cm Long)

SP-2A	1	0.05 mm Sanford Plus	Sandstrom LC-300	Rain
SP-4A	1	0.10 mm Sanford Plus	Sandstrom LC-300	Rain
SP-2B	1	0.05 mm Sanford Plus	Sandstrom LC-300	Sand
SP-4B	1	0.10 mm Sanford Plus	Sandstrom LC-300	Sand
-	2	0.05 mm Sanford Plus	Sandstrom LC-300	Spares
-	2	0.10 mm Sanford Plus	Sandstrom LC-300	Spares
DP-3A	1	0.05 mm Duranodic	Sandstrom LC-300	Rain
DP-1A	1	0.10 mm Duranodic	Sandstrom LC-300	Rain
DP-3B	1	0.05 mm Duranodic	Sandstrom LC-300	Sand
DP-1B	1	0.10 mm Duranodic	Sandstrom LC-300	Sand
-	2	0.05 mm Duranodic	Sandstrom LC-300	Spares
-	2	0.10 mm Duranodic	Sandstrom LC-300	Spares

could be impregnated with the molybdenum disulfide filler. The Sandstrom LC-300 also contains corrosion inhibiting pigments in its epoxy-phenolic resin system. The resin system was expected to provide good adhesion to the hard coat.

Application of the Sandstrom LC-300⁽³⁶⁾ to the hard anodized and sealed aluminum specimens was made according to the supplier's recommendations by dip coating, air drying for one hour, and baking at 148.9° C (300° F) for one hour.

Using the designations SP for Sanford Plus Process and DP for Duranodic Process, Table 17 identifies all flat plates and wedge specimens subjected to special anodizing treatments and designates the test use.

Test Results

Results of rain and sand erosion testing of the wedge specimens are reported in the section of this report dealing with erosion studies.

Hard anodized coating thicknesses are best determined by instrumental means since, like all anodized coatings, roughly one half of the coating is due to penetration into the original aluminum metal and the other half is a result of build-up from oxidation of aluminum accompanied by crystalline growth. Therefore, a Dermatron instrument was used to check anodic film thickness. Table 18 shows aim and actual thicknesses achieved for the Sanford Plus and Duranodic coatings.

TABLE 18. HARD ANODIZE THICKNESS TEST RESULTS

<u>Process</u>	<u>Configuration</u>	<u>Thickness</u>	
		<u>Aim (mm)</u>	<u>Actual (mm)</u>
Sanford Plus	Flat Plate	0.05	0.06
Sanford Plus	Flat Plate	0.10	0.09
Sanford Plus	Wedge	0.05	0.08
Sanford Plus	Wedge	0.10	0.11
Duranodic	Flat Plate	0.05	0.06
Duranodic	Flat Plate	0.10	0.09
Duranodic	Wedge	0.05	0.06
Duranodic	Wedge	0.10	0.09

Measurements made by micrometer before and after application of the Sandstrom LC-300 indicated that the dry film lubricant varied between 0.010 mm and 0.046 mm in thickness.

(36)

Sandstrom LC-300 is commercially available from Sandstrom Products Company, Port Byron, Illinois 61275.

Taber abrasion testing was performed on a Taber Abraser Model 503 with CS-17 wheels. Samples were tested for 10,000 cycles using a 1,000 gram weight. Each specimen was weighed to the nearest 0.1 milligram before and after test. Taber abraser test results are shown in Table 19.

TABLE 19. TABER ABRASER TEST RESULTS

Specimen ^a	Coating	Wt. Loss (grams)	Thickness Loss (mm)
SP-1	Sanford Plus with Sandstrom LC-300	0.1069	0.025
SP-2	Sanford Plus with Sandstrom LC-300	0.1129	0.025
SP-3	Sanford Plus	0.0389	0.018
SP-4	Sanford Plus	0.0312	0.018
DP-1	Duranodic with Sandstrom LC-300	0.2465	0.050
DP-2	Duranodic with Sandstrom LC-300	0.1408	0.044
DP-3	Duranodic	0.0201	0.013
DP-4	Duranodic	0.0181	0.013

^aSpecimens SP-2, SP-4, DP-2, and DP-4 were thick hardcoat.

Many propeller blades appear to elongate during their service lives, possibly due to creep developed by the high centrifugal forces during rotation at high speeds. Overall stretch of the blade may be as great as five percent of original length. This creep effect was simulated by applying plastic deformation to machined tensile strips from representative plates coated with the proprietary hard anodic coatings. The effects of such elongation on the hardcoat integrity were examined under magnification. These specimens were not coated with Sandstrom LC-300. Figure 22 illustrates the hardcoat appearance after simulated creep.

Discussion of Special Anodic Film Studies

In general, the proprietary hard anodic coatings were produced within reasonable tolerance of the aim values requested. The 0.05 mm (0.002 in) thickness coatings were actually thicker than requested, particularly on the Sanford Plus (SP) wedge specimens. Dip coating of the flat plates in Sandstrom LC-300 was performed without difficulty. Coating of the wedges required pre-masking of the holes used to mount and fasten the specimens in the erosion facility rotating blade. Although the dry film coating formulation is quite viscous, dip coating resulted in some sag which was difficult to control. The Duranodic (DP) flat plates coated with about the same weight increases, regardless of hardcoat thickness. Application of the Sandstrom LC-300 to Sanford Plus (SP) flat plates resulted in weight increases three to four times that noted for DP samples.

Taber abrasion test results for specimens not coated with Sandstrom LC-300 indicated slightly better wear performance for the DP coating. The thicker hard coatings displayed slightly better resistance to wear than the thinner hard anodize. The Sandstrom LC-300 coated specimens displayed Taber test results which were not expected. The thinner dry film coating



Specimen SP-6

100X



Specimen SP-6

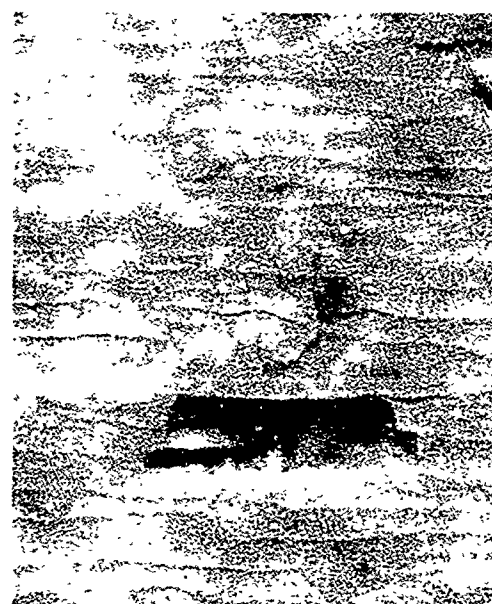
100X

Above photographs show 0.09 mm thick Sanford Plus hard anodized film after 5.0 percent plastic elongation of Aluminum 7075-T651 substrate. All views are normal to anodized surface. Left view employed vertical lighting while view of same surface with oblique lighting is at the right.



Specimen DP-6

100X



Specimen DP-6

100X

Photographs above illustrate 0.09 mm thick Duranodic hard anodized film after elongations of 4.0 percent (left) and 5.5 percent (right). All views are normal to anodized surface and illuminated by oblique lighting. Fracture of anodic coat has resulted in loss of hard anodize fragments in localized areas.

Figure 22. Appearance of Special Hard Anodized Coatings after Moderate Elongation of Aluminum 7075

on the DP hard coatings broke down more rapidly, and to a greater extent, than the much thicker coatings on the SP hardcoats. It would appear that the SP hardcoat accepted and retained the dry film compound much better than did the DP hard anodized coating. This is possibly due to a difference in actual sealing performance between the two types of hardcoat.

The simulated creep tests indicated that elongating the Aluminum 7075-T651 substrate by as little as five percent resulted in damage to the hard anodize coating. Damage was more severe to the DP coating, where tiny fragments of coating were actually removed.

Hard Anodic Film Study Conclusions

Dimensionally acceptable hard anodic coatings can be applied to Aluminum 7075-T651 by either the Sanford Plus (SP) Process or the Duranodic (DP) Process. Both exhibit good adherence to the aluminum substrate and perform well in Taber abrasion tests. Acceptance and retention of dry film lubricant, such as Sandstrom LC-300, appeared to be better with the SP hard anodized coatings than with the DP hardcoats. Flexibility of both hard coatings was poor, based on the simulated creep test. The judgement as to acceptability of such coatings for erosion resistant applications on propeller blades will be reserved for comment in the next section.

SECTION VI

SAND AND RAIN EROSION TESTING AND EVALUATION

Background

Erosion of materials by impact with water drops can become a serious problem as the velocity of the impacted object rises above 222.5 m/sec (730 ft/sec). The reasons for the damage are now fairly well understood. The impact of a drop on a target material induces a stress whose magnitude depends on the physical and mechanical properties of the target, the size of the drop, and the velocity of impact. Relatively simple analytical models of drop impact show that these stresses will exceed the fracture strength of any material if the impact velocity is raised sufficiently high. The microstructure and defect level of a material can also affect its response to the stresses. Although rain, or water droplet, erosion resistance generally increases with hardness, it is not usually possible to accurately predict the behavior of a material -- erosion testing under carefully controlled conditions, is necessary.

Analytical models and experimental data show erosion from water drop impact to be proportional to the impact velocity raised to a high power, typically 5 to 7. Such a high value for the exponent leads to an apparent damage threshold velocity for a given material. No significant erosion occurs, even after long exposures, just below this threshold. Erosion rate has also been shown to decrease continuously with a decrease in the angle of impact at a constant velocity. This decrease has been explained by the assumption that only the velocity component normal to the impacted surface induces the stress.

Erosion by solid particle impact is quite different from that of water droplet impact. The most notable differences are in the effects of impact velocity and impact angle. The rate of erosion from solid particle impact for most materials is found to increase with the velocity raised to a power ranging from 2.0 to 2.5. Thus a small reduction in velocity does not give such a dramatic decrease in erosion rate in a sand environment as it does in a water drop environment.

For solid particle impact, the erosion rate for ductile materials (essentially all metals) is greatest at an angle of about 20 degrees and decreases as the angle increases to 90 degrees (impact perpendicular to the target surface). Brittle materials, on the other hand, have a maximum erosion rate at 90 degrees. The solid particle erosion of ductile materials is considered to be a result of two simultaneous processes. Abrasive cutting dominates at angles below 45 degrees, and deformation wear dominates at high angles. Cutting is not found to be a significant erosion mechanism for hard, brittle materials.

Water droplet impact erosion of almost all material shows a relationship with impact angle analogous to that for solid particle erosion for brittle

materials. Therefore, it is not surprising that metals can exhibit different behaviors in the two erosion environments.

Erosion Test Specimens

The fabrication and configuration of the special hard anodized erosion test wedges was described in the prior section. Similar erosion test wedges were produced with hard nickel coatings. Four of the long wedges were plated to represent all processing variables of interest for this material. All Aluminum 7075-T651 wedge substrates were dilute phosphoric anodized by the procedure detailed in Table 11. A thin, low pH sulfamate nickel deposit was applied to the anodic film to provide a strongly adherent layer for subsequent hard nickel deposition. At this point, the variations of interest were introduced. Hard nickel thickness was varied on two specimens plated at 1.86 amp/dm^2 (20 amp/ft^2). One wedge was plated at this current density for sixteen hours, while the other was plated for twenty-four hours. A third wedge was plated at a higher current density of 3.72 amp/dm^2 (40 amp/ft^2) for twelve hours to simulate, more closely, the actual current density expected on leading edges and tips of full sized blades, where erosion is greatest. A fourth wedge was zinc-nickel alloy plated over the low pH nickel layer prior to copper striking and hard nickel plating at 1.86 amp/dm^2 (20 amp/ft^2) for sixteen hours. At these hard nickel plating current densities (and the use of an electrolyte at 43° C (110° F) with 0.5 ml/l of hardening agent), the deposit Vickers hardnesses were about 400 to 420.

To simplify identification of the various hard anodized and hard nickel plated test wedges, code numbers have been given the specimens as shown in Table 20.

Test Facility

All water droplet erosion and sand erosion evaluation of the test wedges was conducted in the Bell Aerospace Erosion Test Facility. This facility, shown in the water droplet erosion mode in Figure 23, consists of the following major components: A rotating arm (test blade) of 2.74 meters (9 ft.) radius, a drive system and power station, a vacuum chamber and vacuum pump, environmental generators (rain and sand), and video monitor and controls. The test facility is located in a concrete pit, 6.1 meters (20 ft.) deep. A control room is located in a separate building approximately 30 meters (100 ft.) from the test facility.

Water droplet test environments are generated by an array of spray nozzles located at the center of the test chamber above the plane of rotation of the blade for the standard rainfield (2.54 cm/hr; 1.8 - 2.0 mm drop size). For a fine rainfield (1 cm/hr; 0.7 mm drop size) a second array is located around the periphery of the chamber. In order to achieve a suitable rate of erosion, parameters were adopted which were identical to those used in 1977-1978 IR&D studies of LACV-30 propeller erosion -- i.e., extra nozzles were installed in the rain generation system to achieve a 3.81 cm/hr rain fall with a nominal 1.8 - 2.0 mm drop size. All tests were conducted at a speed of 274.3 m/sec (900 ft/sec) to simulate propeller tip velocity.

TABLE 20. IDENTIFICATION OF EROSION TEST WEDGES

Test Wedge Code	Erosion Coating	Test Wedge Description	Erosion Environment
U-1	None	Uncoated Aluminum 7075-T651	Rainfield
U-2	None	Uncoated Aluminum 7075-T651	Rainfield
U-3	None	Uncoated Aluminum 7075-T651	Rainfield
U-4	None	Uncoated Aluminum 7075-T651	Sand
SP-2A	Anodized	Sanford Plus (0.08 mm thickness) ^a	Rainfield
SP-4A	Anodized	Sanford Plus (0.11 mm thickness) ^a	Rainfield
SP-2B	Anodized	Sanford Plus (0.08 mm thickness) ^a	Sand
SP-4B	Anodized	Sanford Plus (0.11 mm thickness) ^a	Sand
DP-3A	Anodized	Duranodic (0.06 mm thickness) ^a	Rainfield
DP-1A	Anodized	Duranodic (0.09 mm thickness) ^a	Rainfield
DP-3B	Anodized	Duranodic (0.06 mm thickness) ^a	Sand
DP-1B	Anodized	Duranodic (0.09 mm thickness) ^a	Sand
N-1A	Hard Ni	Hard Nickel Plated 16 Hrs. @ 1.86 A/dm ²	Rainfield
N-1B	Hard Ni	Hard Nickel Plated 16 Hrs. @ 1.86 A/dm ²	Sand
N-2A	Hard Ni	Hard Nickel Plated 24 Hrs. @ 1.86 A/dm ²	Rainfield
N-2B	Hard Ni	Hard Nickel Plated 24 Hrs. @ 1.86 A/dm ²	Sand
N-3A	Hard Ni	Hard Nickel Plated 12 Hrs. @ 3.72 A/dm ²	Rainfield
N-3B	Hard Ni	Hard Nickel Plated 12 Hrs. @ 3.72 A/dm ²	Sand
N-4A	Hard Ni	Hard Nickel Plated 16 Hrs. @ 1.86 A/dm ²	Rainfield
N-4B	Hard Ni	Over Zinc-Nickel Alloy With Cu Strike Hard Nickel Plated 16 Hrs. @ 1.86 A/dm ² Over Zinc-Nickel Alloy With Cu Strike	Sand

^a

Identifies hard anodized wedges coated with Sandstrom LC-300.

For sand erosion testing, the facility was used in the sand erosion mode shown in Figure 24. The sand is delivered through a hopper at a constant and reproducible rate of 908 g/min (2 lb/min) into the airstream flowing through a 3.49 cm diameter delivery tube. The air stream exit velocity of 201 m/sec (660 ft/sec) is controlled by the pressure maintained in the chamber. The sand carried by the air stream flows from a 2.22 cm by 4.76 cm elliptical nozzle and impacts the specimen rotating at the required velocity of 274.3 m/sec (900 ft/sec).

Sand Erosion Environment

In the sand erosion exercise discussed above, the particle sizes of the sand ranged from 75 to 1000 microns, the particle size distribution being obtained by mixing various types of sand according to Specification MIL-C-5007C.

In the present study, the sand employed for the erosion testing was obtained from the beach at Fort Story. A sieve analysis was performed on a specimen from this material to determine the particle size distribution and to identify any significant differences from the MIL-C-5007C specification material which had been used earlier. The results of this sieve analysis are given in Table 21. Photomicrographs of random samples of

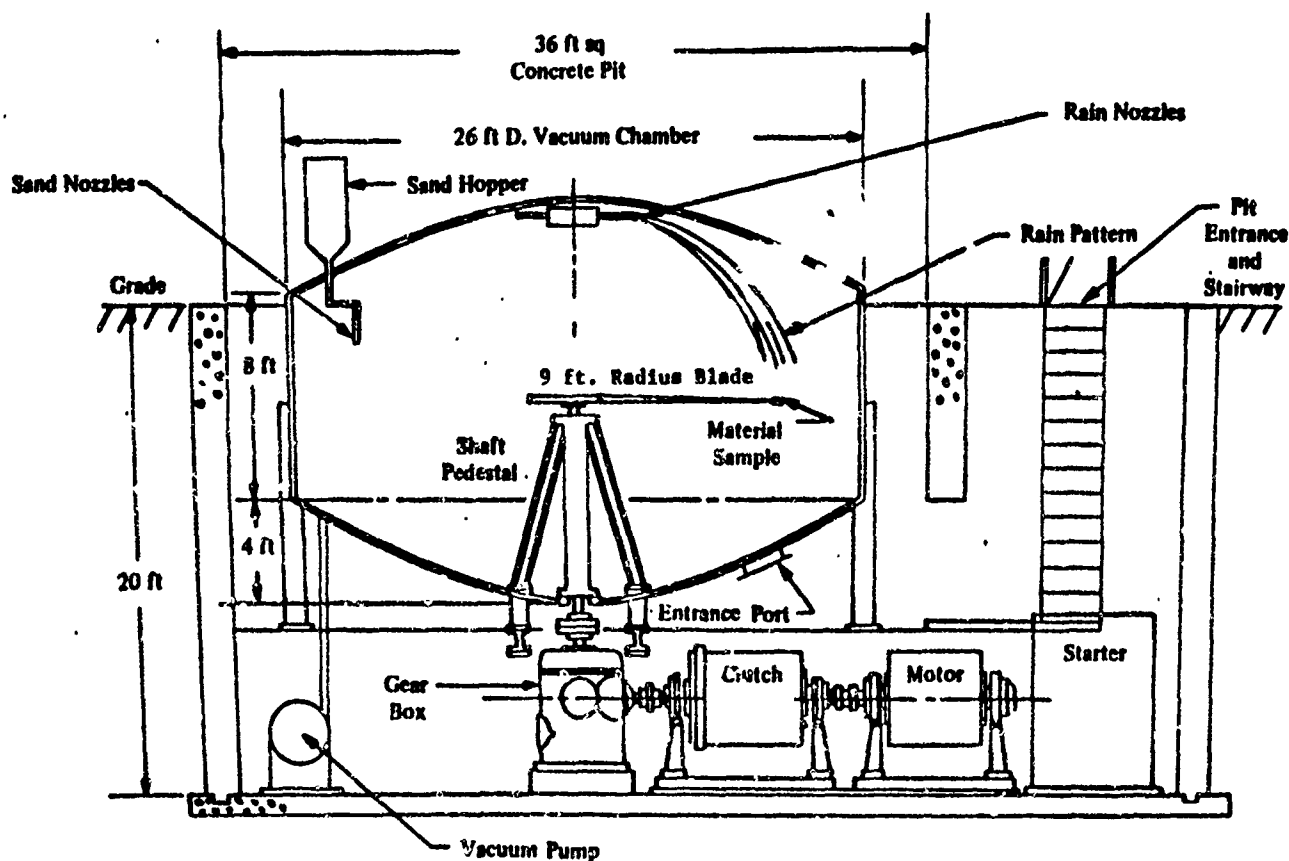


Figure 23. Rain and Particle Erosion Test Facility

these materials are shown in Figure 25. In addition to the presence of a few larger grains than specified, the Fort Story sand exhibited a preponderance of 200 to 400 μm grain sizes. There were also present a number of pebbles greater in size than 9.5 mm (0.375 in). These were removed prior to use of the material in the test facility since it was considered that the presence of these large particles could result in blockage of the sand distribution system.

TABLE 21. COMPARISON OF PARTICLE SIZE DISTRIBUTION:
MIL-C-5007C AND SAND FROM FORT STORY BEACH

MICRONS	NEAREST SCREEN NO.	GRAMS RETAINED ON SCREEN (FORT STORY SAND)	Quantity, percent by weight Finer than size indicated.	
			MIL-C-5007C	FORT STORY SAND
1000	#18 (1000 μm)	0.0 (few grains)	100	100
900	#20 (840 μm)	0.0 (few grains)	98-99	100
600	#30 (590 μm)	1.0	93-97	98.5
400	#40 (420 μm)	7.4	82-86	87.3
250	#70 (210 μm)	46.9	46-50	16.1
125	#120 (125 μm)	10.4	18-22	0.3
75	#200 (75 μm)	no screen	3-7	
	Pan	0.2		
		Total: 65.9 grams		

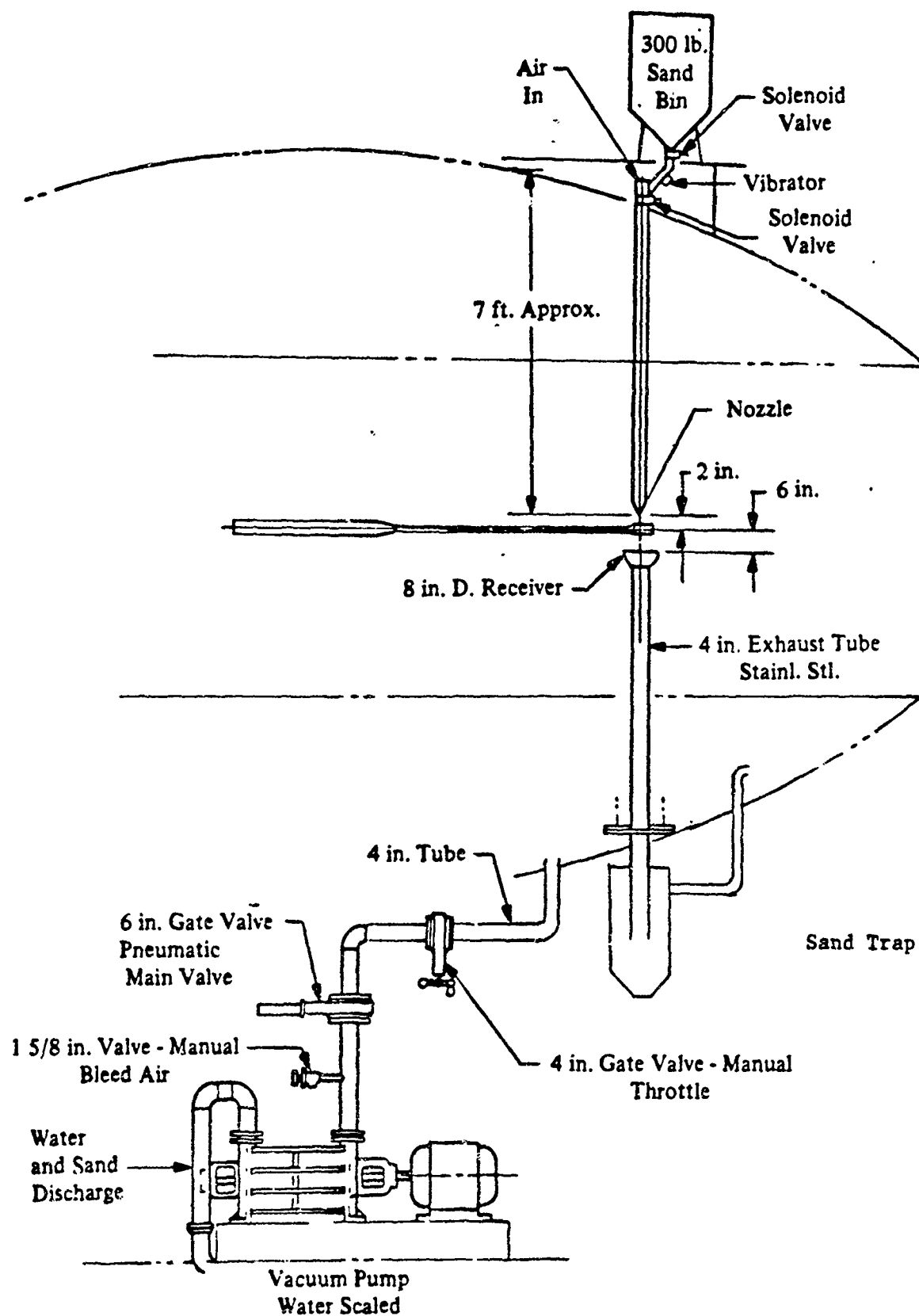
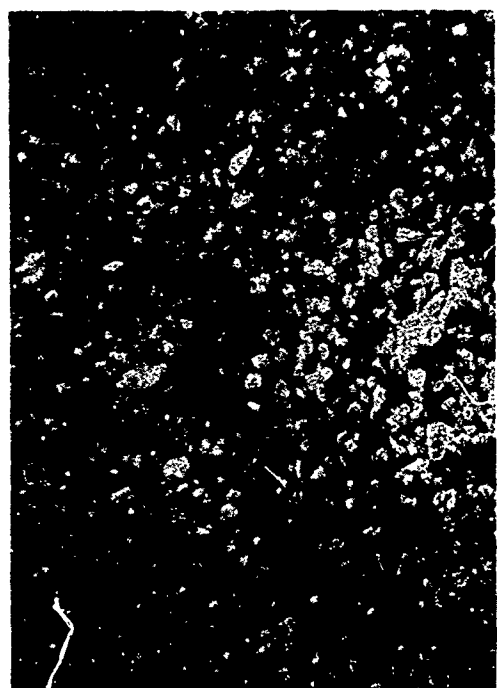


Figure 24. Erosion Test Facility (Sand Erosion Mode)



MIL-C-5007C Sand

7X



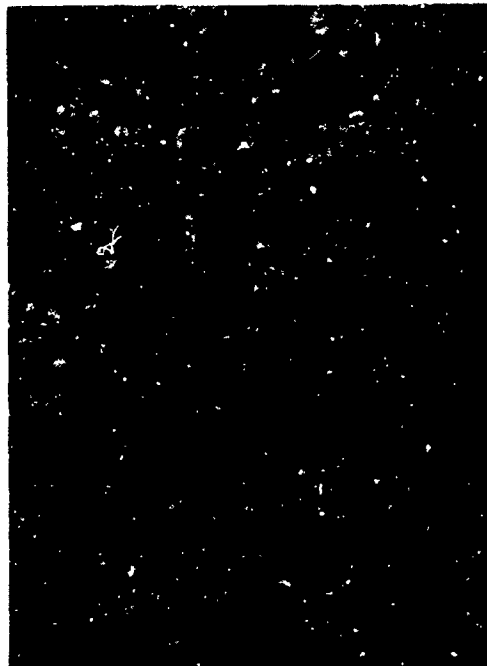
MIL-C-5007C Sand

7X



Fort Story Sand

7X



Fort Story Sand

7X

Figure 25. Photomicrographs of MIL-C-5007C Sand and Sand from Fort Story Beach

Specimen Holders

In view of the protracted exposure times which were anticipated for the rain erosion tests, a configuration was selected for the test specimens which was different from that used in previous studies. While maintaining the contour of the leading edge of the LACV-30 propeller blade, this new test specimen configuration shown in Figure 26 was designed to permit exposure of two or three specimens simultaneously when used in combination with a revised specimen holder. This reduced total program test time by a significant factor. This configuration resulted in the specimens being mounted in a vertical plane, compared to the horizontally mounted specimens in prior work.

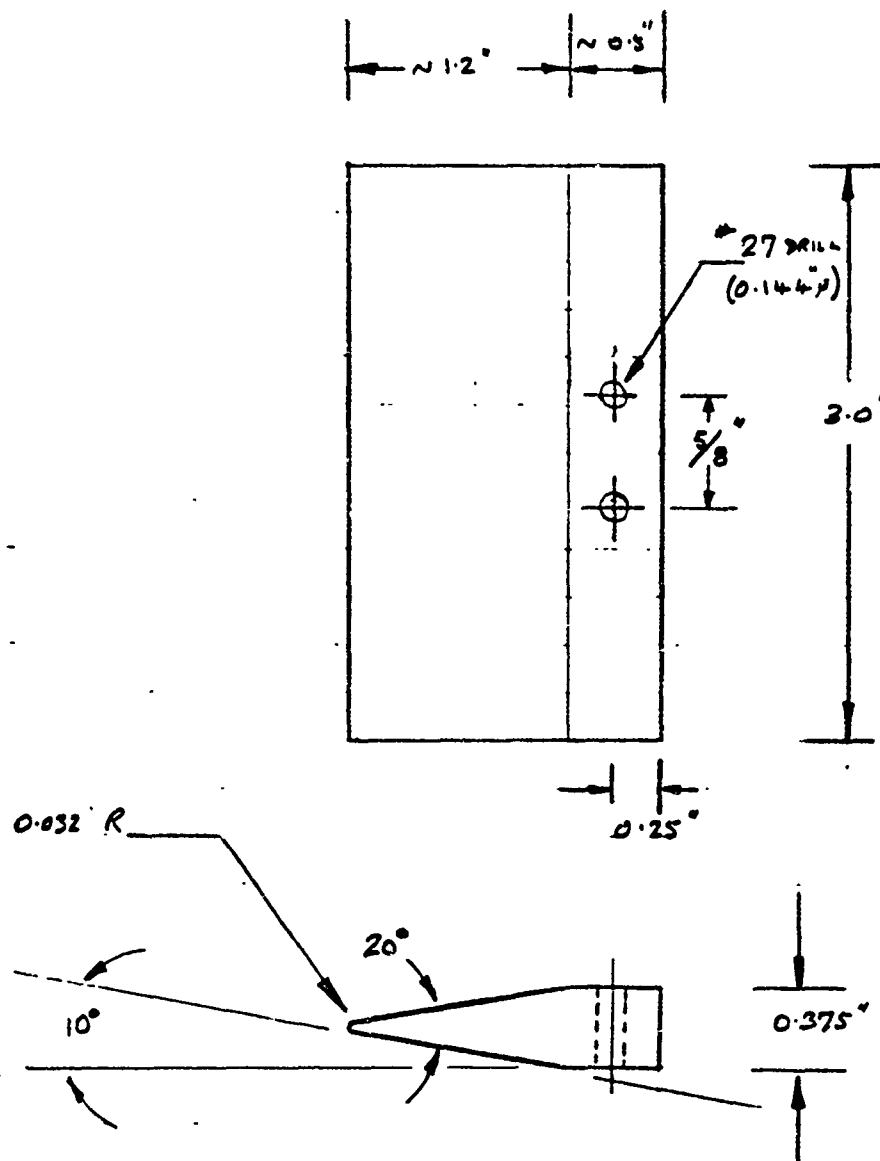


Figure 26. Erosion Test Specimen Configuration

Since the rainfield is a uniform environment within the test chamber, and the vertical velocity of the water droplets is low, in comparison to the velocity of the specimens under test, it is improbable that this feature would have significant effect upon the erosion characteristics of the test specimens. A typical test wedge is shown in Figure 27, and two such wedges mounted in the rain erosion test specimen holder are illustrated in Figure 28. Trial exposures with unprotected specimens revealed that some aerodynamic interference occurred when three specimens were exposed simultaneously, resulting in inconsistent results. It was subsequently determined that exposure of two specimens could be successfully achieved if the center mounting position was vacant. Accordingly, the rain erosion tests were conducted with two specimens mounted in the holder.

A further advantage of this specimen design was that similar wedges could be mounted in a horizontal plane for sand erosion testing when used with a suitable specimen holder, as shown in Figure 29.

Erosion of specimen holders had been anticipated during both protracted rain exposure and sand exposure. In recognition of this problem, extra specimen holders were nickel plated to provide some protection during testing. This was found to be only partially successful, particularly in the case of the sand erosion tests. Subsequently, it was found to be more cost-effective to fabricate simple sacrificial protective sheaths from titanium alloy Ti-6Al-4V; this was found to be particularly effective for rain erosion testing of nickel plated specimens where the test duration was very long (seven hours per test) and the rain erosion protection of the sheath alloy was an advantage.

Rain Erosion Tests and Discussion

Rain erosion testing was performed at a velocity of 274.3 m/sec (900 ft/sec) in a rain field intensity of 3.81 cm/hr (1.5 in/hr) with a nominal droplet size of 1.8 to 2.0 mm. Test duration for the unprotected (base line data) specimens was anticipated to be less than two hours based on results of prior studies and the established rain erosion data for Aluminum 7075-T6 alloy; the test duration for the anodized wedges was expected to be for a similar time span. A test duration of seven hours was projected for the nickel plated wedges based on performance experience from previous studies. Typical examples of unprotected, anodized, and nickel plated wedge specimens are shown in Figures 27, 30 and 31.

Rain erosion testing of unprotected and anodized specimens was terminated after 105 minutes when erosion damage became severe. The eroded specimens are shown in Figures 32 through 36. The damage mode and severe pitting are characteristic of rain erosion. Weight loss data generated during the course of erosion is shown in Table 22 and plotted graphically in Figure 37.

Examination of Figure 37 shows that the performance of all of the anodized specimens was, to various degrees, worse than that of the unprotected specimens.

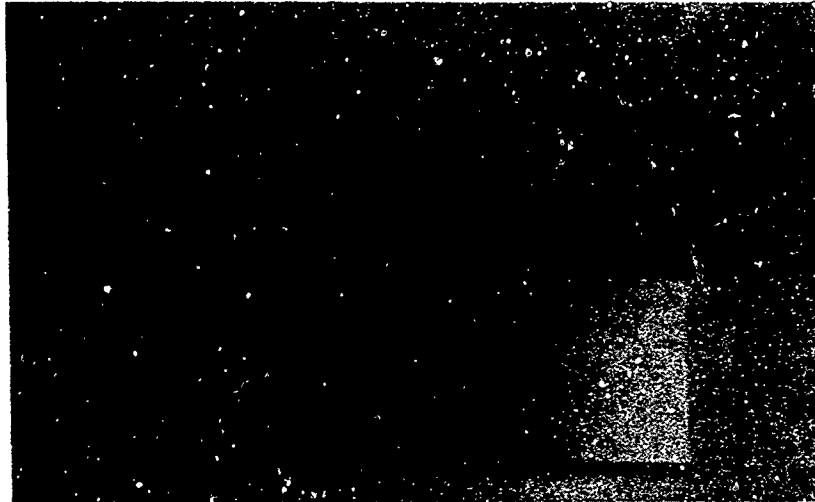


Figure 27. Typical Rain Erosion/Sand Erosion Test Specimen



Figure 28. Two Test Specimens Mounted in Rain Erosion Test Specimen Holder

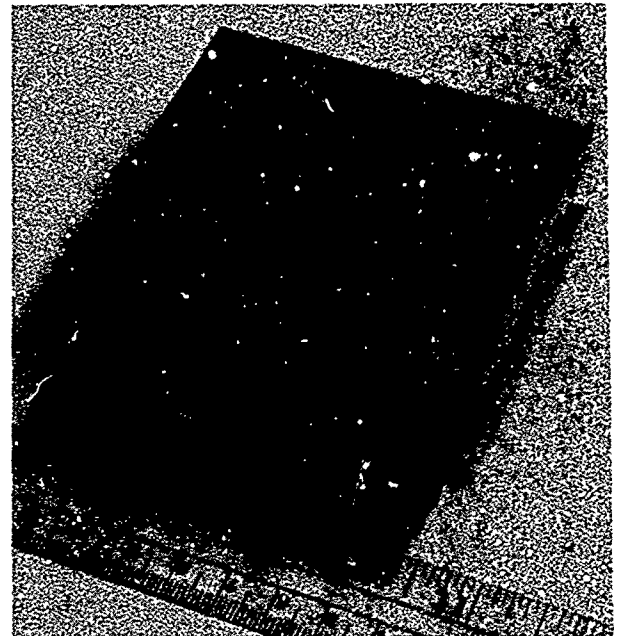
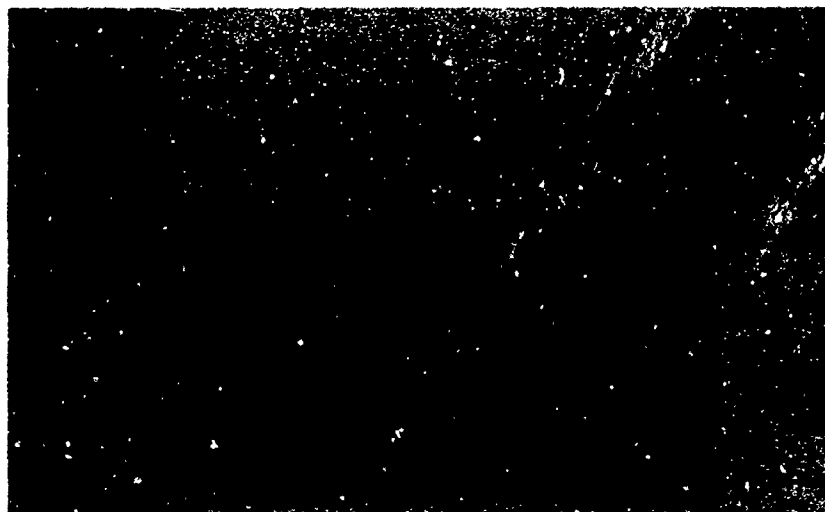
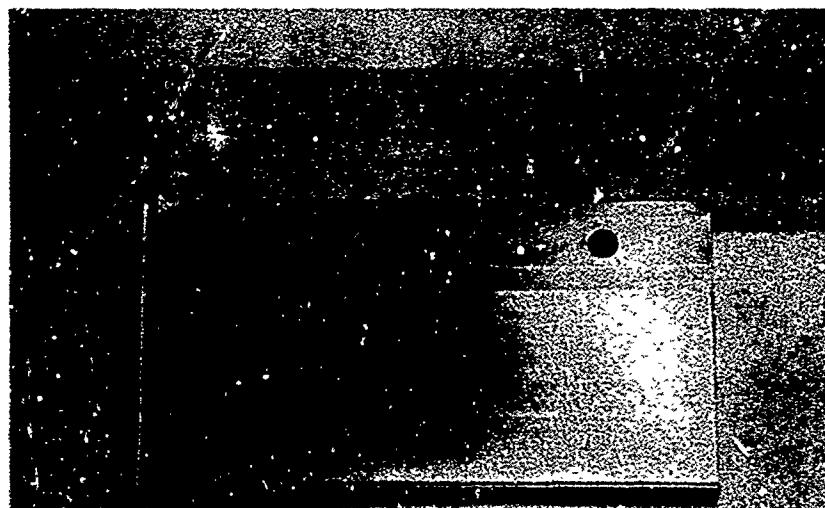


Figure 29. Test Specimen Mounted in Horizontal Plane for Sand Erosion Testing



Wedge No. DP-1A

Figure 30. Typical Anodized Specimen prior to Testing
(Duranodic Anodized 0.09 mm + Sandstrom LC-300 MoS₂)



Wedge No. N-1A

Figure 31. Typical Nickel Plated Specimen prior to Test
(Dilute Phosphoric Acid Anodized + Low pH Nickel +
Hard Nickel Plated at 1.86 amp/dm² for 16 Hours)

Wedge No.
U-1

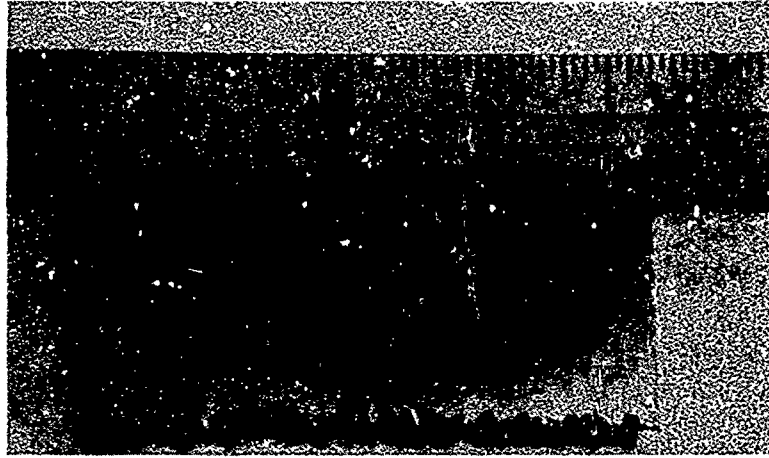


Figure 32. Unprotected Aluminum 7075-T651 Specimen after 105 Minutes Exposure at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in./hr) Rainfield, 1.8 - 2.0 mm Droplet Size

Wedge No.
DP-1A



Figure 33. Duranodic Anodized (0.09 mm) + Sandstrom LC-300 Specimen after 105 Minutes Exposure at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in./hr) Rainfield, 1.8 - 2.0 mm Droplet Size

Wedge No.
SP-2A

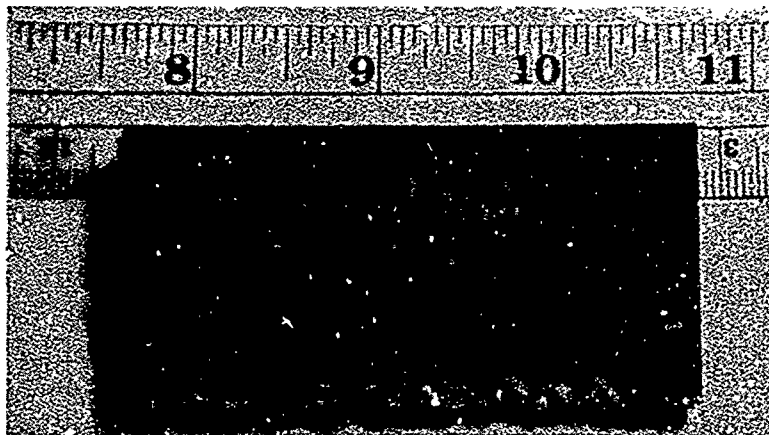


Figure 34. Sanford plus Anodized (0.08 mm) + Sandstrom LC-300 Specimen after 105 Minutes Exposure at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in./hr) Rainfield, 1.8 - 2.0 mm Droplet Size

Wedge No.
DP-3A

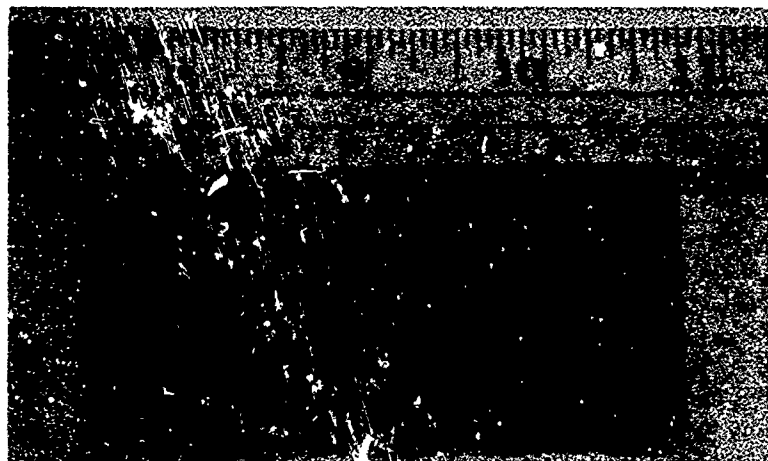


Figure 35. Duranodic Anodized (0.06 mm) + Sandstrom LC-300 Specimen
after 105 Minutes Exposure at 274.3 m/sec (900 ft/sec) in
3.81 cm/hr (1.5 in./hr) Rainfield, 1.8 - 2.0 mm Droplet Size

Wedge No.
SP-4A

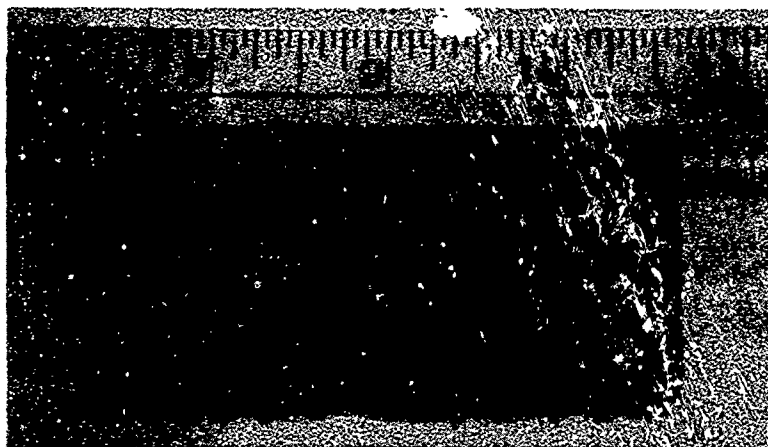


Figure 36. Sanford plus Anodized (0.11 mm) + Sandstrom LC-300 Specimen
after 105 Minutes Exposure at 274.3 m/sec (900 ft/sec) in
3.81 cm/hr (1.5 in./hr) Rainfield, 1.8 - 2.0 mm Droplet Size

TABLE 22. WEIGHT LOSS OF UNPROTECTED AND ANODIZED SPECIMENS DURING EXPOSURE AT 274.3 M/SEC (900 FT/SEC) IN 3.81 CM/HR (1.5 IN/HR) RAINFIELD, 1.8-2.0 MM DROPLET SIZE

Test Wedge Code	Weight, Grams		Weight, Grams		Cumulative Weight Loss, Grams		Weight, Grams		Cumulative Weight Loss, Grams		Weight, Grams		Cumulative Weight Loss, Grams	
	(Before Testing)	(After 45 minutes)	(After 45 minutes)	(After 75 minutes)	Loss, Grams	Weight, Grams	(After 75 minutes)	Loss, Grams	(After 105 minutes)	Weight, Grams	(After 105 minutes)	Loss, Grams	(After 105 minutes)	Weight, Grams
<u>Uncoated Aluminum 7075-T651</u>														
U-1	54.0462	54.9211		53.9113	0.0251				0.1349	53.7215			0.3247	
U-2	54.0530	54.0069		53.8410	0.0461				0.2120	53.6876			0.3654	
U-3	54.3455	54.3039		54.1667	0.0416				0.1788	53.9636			0.3819	
<u>Sanford Plus Anodized + Sandstrom LC-300</u>														
SP-2A ^a	54.1350	53.8703		53.7117	0.2647				0.4233	53.4837			0.6513	
SP-4A ^b	54.4956	54.2210		54.0988	0.2746				0.3968	53.9276			0.5680	
<u>Duranodic Anodized + Sandstrom LC-300</u>														
DP-1A ^c	54.5937	54.4284		54.3433	0.1653				0.2504	54.2204			0.3733	
DP-3A ^d	54.1442	53.9777		53.8190	0.1665				0.3252	53.6642			0.4800	

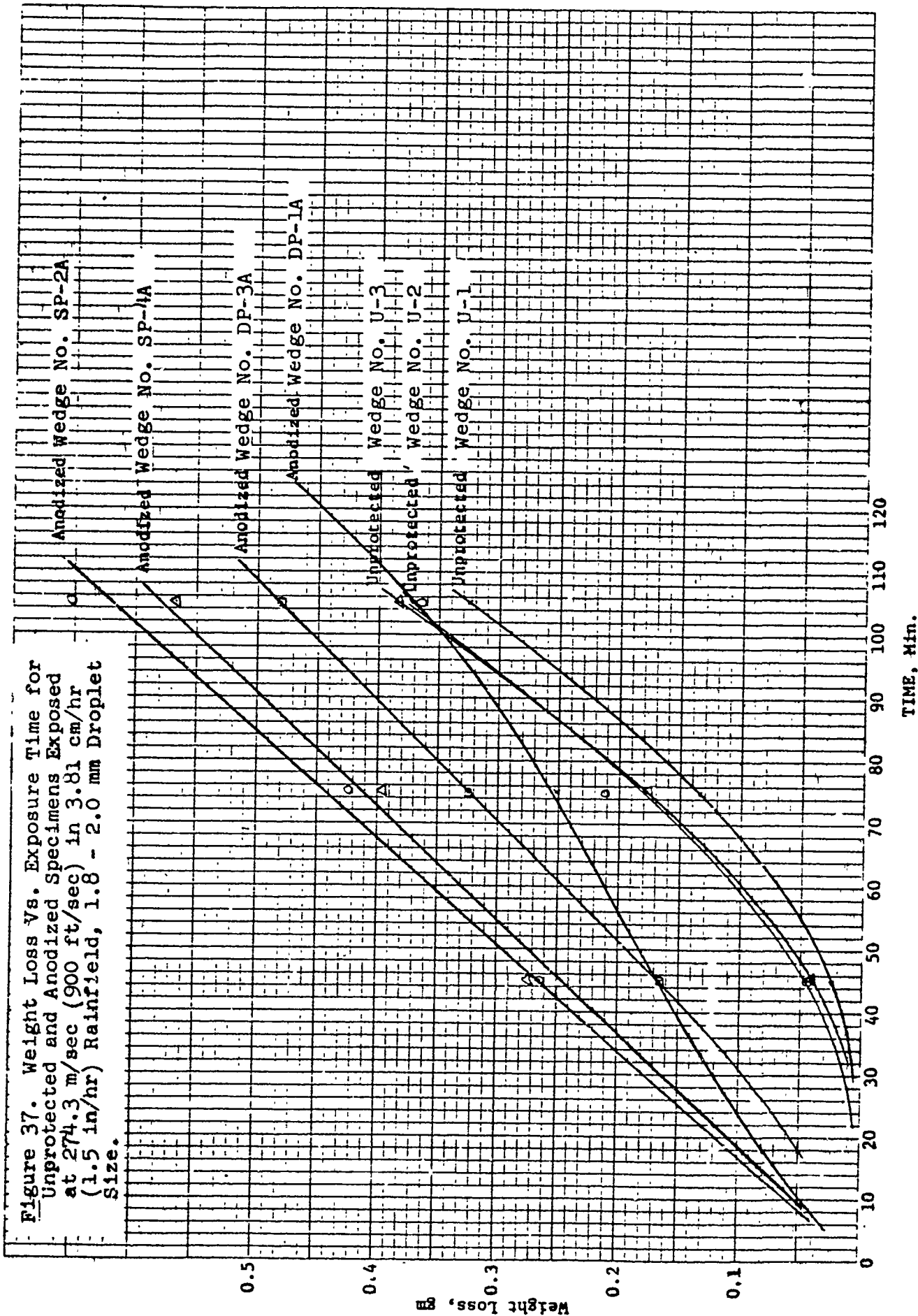
^a Anodic film thickness = 0.08 mm

^b Anodic film thickness = 0.11 mm

^c Anodic film thickness = 0.09 mm

^d Anodic film thickness = 0.06 mm

Figure 37. Weight Loss Vs. Exposure Time for Unprotected and Anodized Specimens Exposed at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in/hr) Rainfield, 1.8 - 2.0 mm Droplet Size.



It is noted that erosion of the anodized specimens tends to be linear -- i.e., of a constant rate throughout the test -- whereas the unprotected specimens appear to be unaffected at the beginning of the test, the erosion rate becoming linear only after about seventy-five minutes. It is a characteristic of the water droplet erosion phenomenon that polished metallic surfaces do not show gross erosion until preliminary pitting occurs on a microscopic scale. This initial pitting phase is known as the "incubation period" and is reflected in the early stages of the erosion curves for the unprotected specimens in Figure 37. Once the incubation period is complete, the erosion rate becomes linear.

In the case of the anodized specimens, there is no incubation period since the anodized surface is, by nature, porous and somewhat brittle. The filling of the pores by sealing and molybdenum disulfide dry film lubricant does not effectively change the nature of the exposed surface in the context of water droplet erosion resistance. The rapid removal of this surface was observed by means of the video system used to monitor the erosion process; the steady removal of the almost black surface to reveal the light colored substrate was clearly evident during the early stages of the test. Examination of Figure 37 reveals that, once the incubation period has passed, the erosion rates for unprotected specimens and anodized specimens are very similar. This is to be expected, since the underlying substrate is the same material in all cases.

Rain erosion testing of hard nickel plated specimens was terminated after seven hours when, with one exception, very little erosion of the wedges was evident. Wedge Number N-3A showed a significantly greater rate of erosion than the remaining three specimens. This was attributed to surface imperfections and some nodule growth on the leading edge. This led to the nucleation of erosion pits and subsequent acceleration of the incubation period. Such surface irregularities were due to lack of plating shield refinement necessary to control high current densities on rather sharp edges. The poorer erosion performance of this particular wedge highlights the necessity for sophisticated shield design.

Nickel plated specimens N-1A, N-2A, N-3A, and N-4A are shown prior to testing in Figures 38, 40, 42, and 44, respectively. The same specimens are shown after seven hours of exposure in Figures 39, 41, 43, and 45. Figure 42 shows the thickening of the plated surface toward one end of Wedge Number N-3A. High current density nodule growth and surface imperfections were associated with this thickening. Erosion of this specimen in the thickened area is evident in Figure 43. A similar phenomenon was observed to a lesser degree in Wedge Number N-4A shown in Figures 44 and 45. Erosion rate of this specimen was somewhat higher than that of Wedge Numbers N-1A and N-2A which exhibited more uniform finish. Inherent roughness from the zinc-nickel alloy plate applied to Wedge Number N-4A evidently influenced the finish obtained on the hard nickel outer plate. Figures 46 and 47 show edge views of eroded Wedge Numbers N-3A and N-4A where the eroded areas are clearly visible. From Figure 46 it appears that nickel plating growth exceeded the designed shield

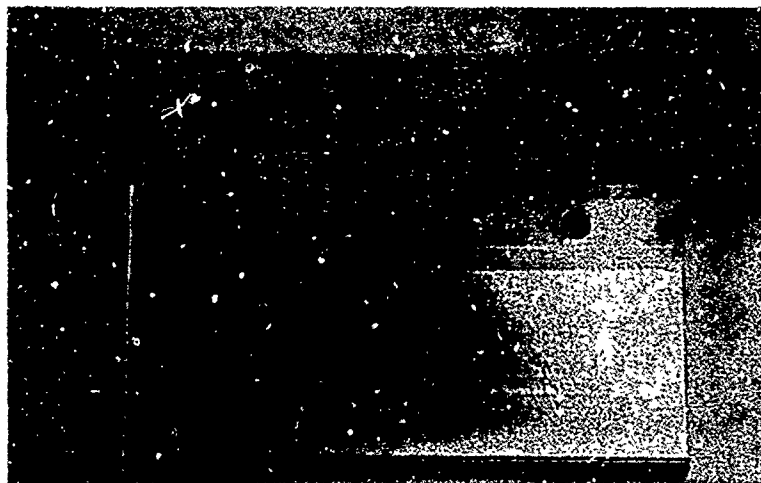


Figure 38. Wedge Number N-1A Processed by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 1.86 amp/dm^2 (20 amp/ft^2) for 16 Hours Before Test

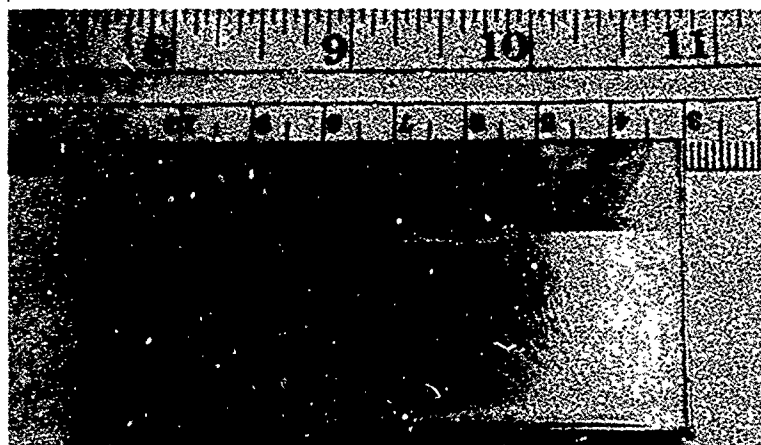


Figure 39. Wedge Number N-1A after Seven Hours Exposure at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in./hr) Rainfield, Nominal Droplet Size $1.8 - 2.0 \text{ mm}$

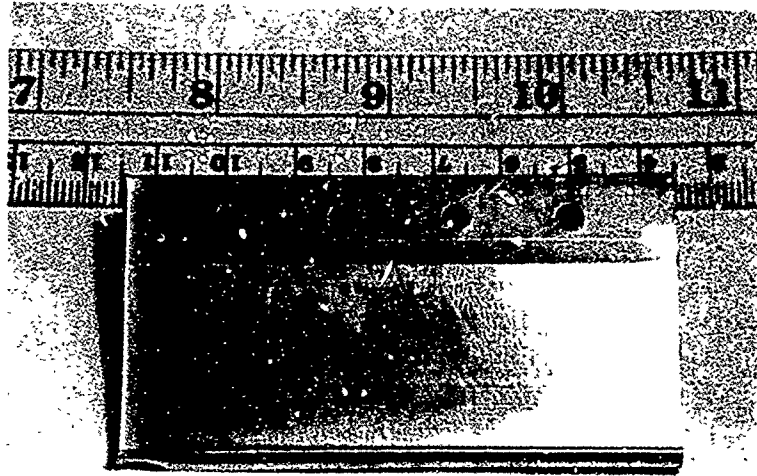


Figure 40. Wedge Number N-2A Processed by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 1.86 amp/dm^2 (20 amp/ft^2) for 24 Hours. Before Test

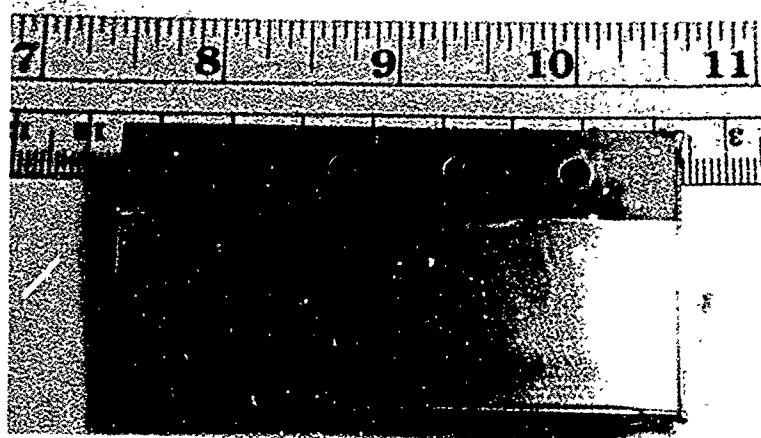


Figure 41. Wedge Number N-2A after Seven Hours Exposure at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in./hr) Rainfield, Nominal Droplet Size $1.8 - 2.0 \text{ mm}$



Figure 42. Wedge Number N-3A Processed by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 3.72 amp/dm^2 (40 amp/ft^2) for 12 Hours. Before Test



Figure 43. Wedge Number N-3A after Seven Hours Exposure at 274.3 m/sec (900 ft/sec) in 281 cm/hr (1.5 in./hr) Rainfield, Nominal Droplet Size $1.8 - 2.0 \text{ mm}$

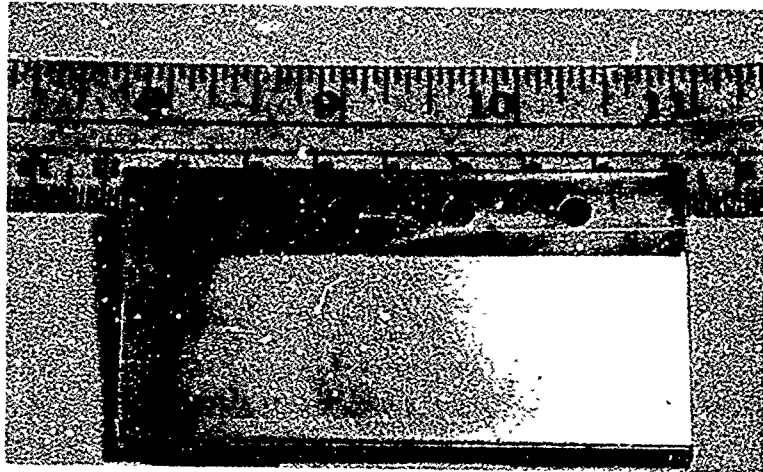


Figure 44. Wedge Number N-4A Processed by Phosphoric Acid Anodizing, Low pH Nickel Plating, Zinc-Nickel Alloy Plating, Copper Striking, and Hard Nickel Plating at 1.86 amp/dm^2 (20 amp/ft^2) for 16 Hours. Before Test

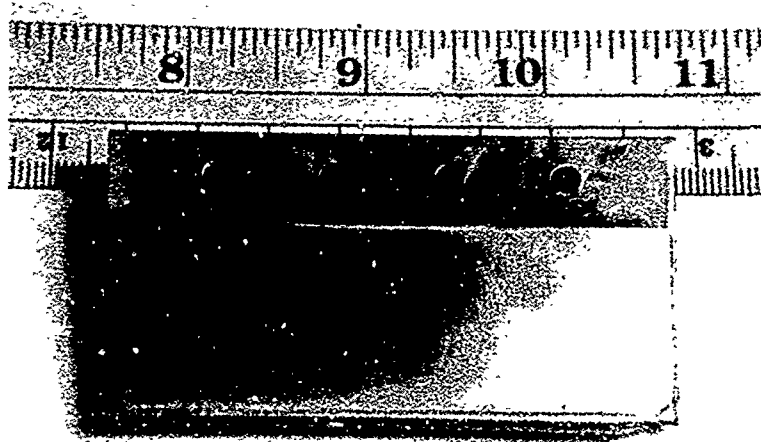


Figure 45. Wedge Number N-4A After Seven Hours Exposure at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in./hr) Rainfield, Nominal Droplet Size $1.8 - 2.0 \text{ mm}$

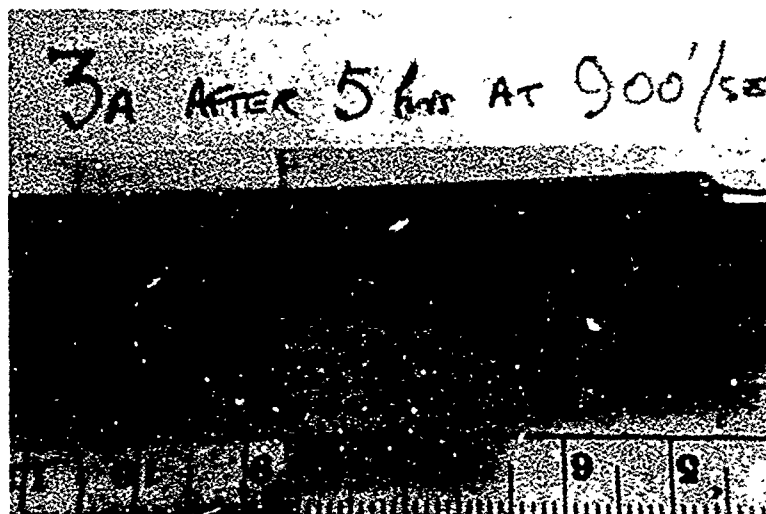


Figure 46. Hard Nickel Plated Wedge Number N-3A Showing Gross Erosion at One End of the Leading Edge. (After Testing)



Figure 47. Hard Nickel Plated Wedge Number N-4A Showing Moderate Erosion of the Leading Edge Associated with Nodule Growth and Surface Imperfections (After Testing)

gap which led to uncontrolled (excessively high) current density. Fortunately, this is not as significant a problem with actual propeller blades where non-contacting shields are employed with a sizable stand-off distance.

Weight loss data for the nickel plated specimens is shown in Table 23. These results are plotted graphically in Figure 48 to show the significantly greater erosion rate of Wedge Number N-3A -- and to a lesser extent, that of Wedge Number N-4A -- compared to the remaining specimens. Only the final seven hour weight loss is plotted since, at one hour increments, small weight gains were observed. At the completion of testing, these weight gains were determined to originate from the deposition of quantities of mineral salts on the specimens as a result of the evaporation of water impinging the wedges. These salts were carefully removed to obtain the weight loss resulting from erosion.

TABLE 23. WEIGHT LOSS OF NICKEL PLATED SPECIMENS DURING EXPOSURE AT 274.3 M/SEC (900 FT/SEC) IN 3.81 CM/HR (1.5 IN/HR) RAINFIELD, 1.8 - 2.0 MM DROPLET SIZE

Test Wedge Code	Weight, Grams (Before Test)	Weight, Grams (After 7 Hrs)	Cumulative Weight Loss, Grams
N-1A ^a	79.4392	79.4104	0.0288
N-2A ^b	87.3276	87.3050	0.0226
N-3A ^c	92.8557	92.5225	0.3332
N-4A ^d	77.3442	77.2409	0.1033

^a Hard nickel plated at 1.86 amp/dm² for 16 hours.

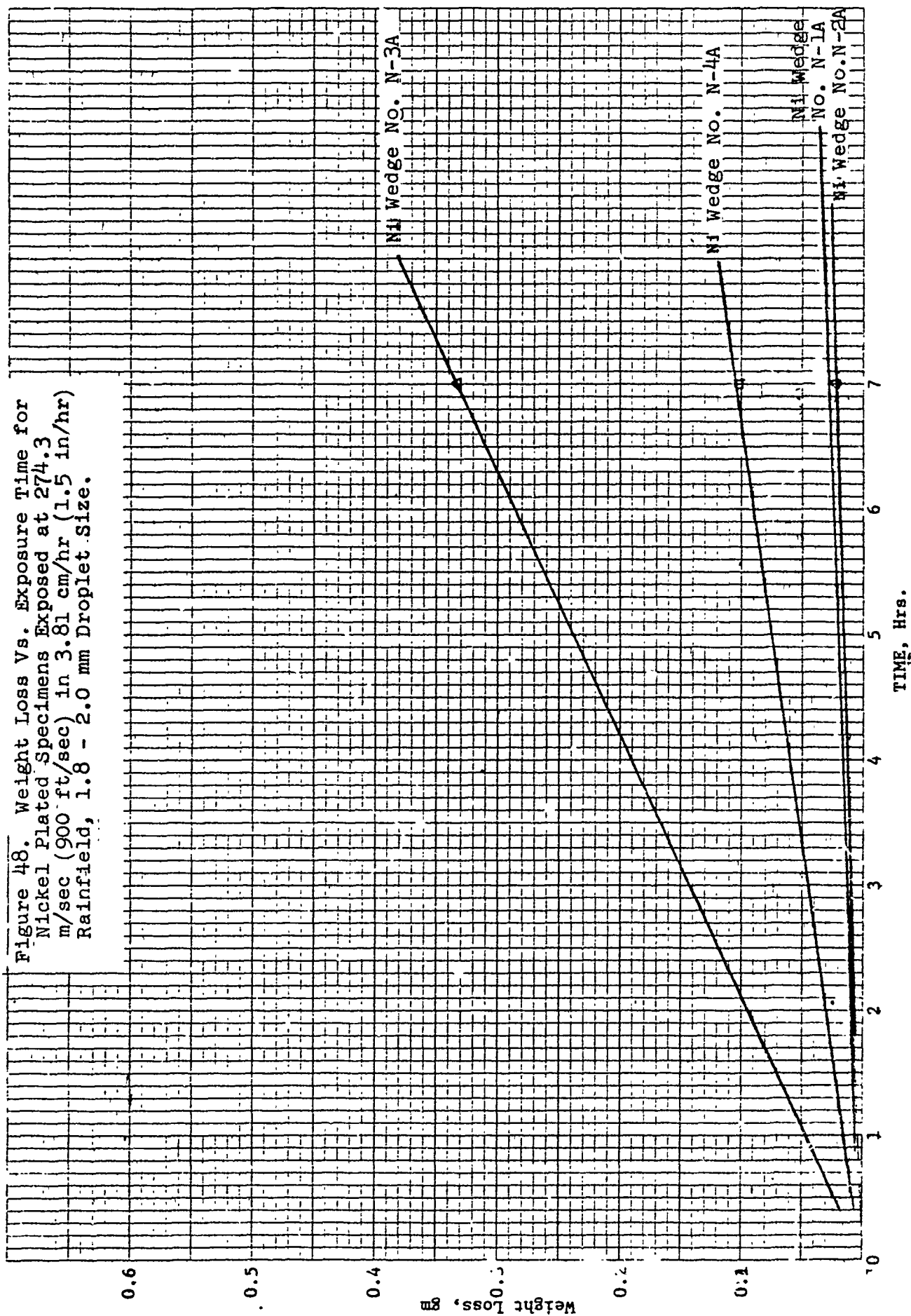
^b Hard nickel plated at 1.86 amp/dm² for 24 hours.

^c Hard nickel plated at 3.72 amp/dm² for 12 hours. Nodular.

^d Hard nickel plated at 1.86 amp/dm² for 16 hours over zinc-nickel alloy. Some roughness.

Examination of the nickel plated specimens subsequent to testing revealed one interesting feature. Some delamination of the nickel plating from the substrate was evident on the trailing edge of all specimens. In all cases, this delamination occurred on the outboard side of the specimens as shown in Figures 49 and 50. These laminations are not believed due to the bonding process involved in fabricating the wedges. The mounting pin holes towards

Figure 48. Weight Loss Vs. Exposure Time for Nickel Plated Specimens Exposed at 274.3 m/sec (900 ft/sec) in 3.81 cm/hr (1.5 in/hr) Rainfield, 1.8 - 2.0 mm Droplet Size.



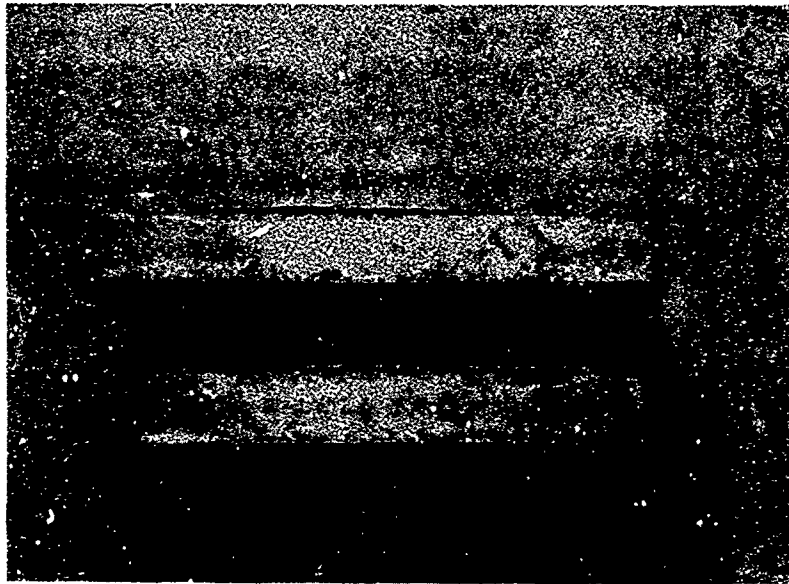


Figure 49. View of Trailing Edges of Nickel Plated Wedge Numbers N-1A and N-2A after Test. Some Delamination of Nickel Plate from Substrate at Outboard Edge is Evident

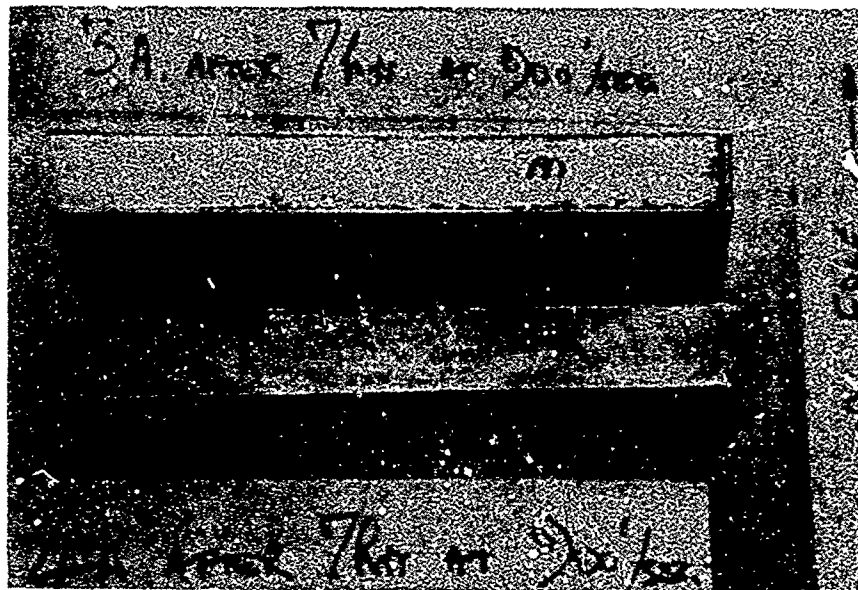


Figure 50. View of Trailing Edges of Nickel Plating Wedge Numbers N-3A and N-4A after Test. Some Delamination of Nickel Plate from Substrate at Outboard Edge is Evident

the aft end of each wedge were of close tolerance which required masking to prevent deposition of nickel into the openings. This was accomplished by filling the holes with wax. Since no plating was desired at the wedge aft face, due to holding fixture tolerances, a plastic shield attachment plate was fastened at this particular face. This plate remained attached through all anodize, rinse, and plating operations. It is reasonable to assume that anodize solution leached from the wedge-shield interface to affect bonding in the immediate region. No special precautions were deemed necessary at that time because the region in question was contained in the specimen holder and not subject to water drop impingement. This problem was unique to the wedges used in the study and due to the need for a contacting shield through all chemical immersions. In actual blade coating, the shields are non-contacting and do not accompany the blade through each process before hard nickel plating.

Sand Erosion Tests and Discussion

Sand erosion testing was performed at a velocity of 274.3 m/sec (900 ft/sec) with the facility operating in the sand erosion mode and using sand from the Fort Story beach as described previously. Test duration for all specimens was sixty minutes.

The unprotected, anodized, and nickel plated specimens are shown after testing in Figures 51 through 59. Significant erosion is apparent in all cases, although the loss of volume is clearly less in the nickel plated specimens. Weight loss and equivalent volume loss data are shown for these specimens in Table 24. These results are plotted graphically as weight loss in Figure 60 and volume loss in Figure 61.

From the weight loss data shown in Figure 60, it is apparent that the performance of all of the anodized specimens was inferior to the remaining specimens. The nickel plated specimens did not appear to be superior to the unprotected Aluminum 7075-T651 in this respect. However, in the context of propeller blade performance, the most important consideration is the change of configuration as a result of erosion, rather than the weight loss. Since the density of nickel is greater than that of the aluminum alloy by a factor of more than three, plotting of the data as volume loss versus time reveals the comparative performance of the coatings as shown in Figure 61. In this figure it is immediately apparent that the nickel plated specimens were superior to the remaining specimens by a factor of approximately four. The poor performance of the anodized coatings may be attributed to the rapid initial removal of the anodized layer. Following this, the rate of erosion will be the same as that of the unprotected specimens.

During the 1977-1978 work, it was determined that the ductility of soft nickel plated specimens had permitted some deformation of the nickel at the leading edge -- resulting in small areas of debonding at the nickel-substrate interface. While no evidence of plastic deformation was seen in the nickel plated specimens on this occasion, metallographic cross-sections were prepared

Wedge No.
U-4

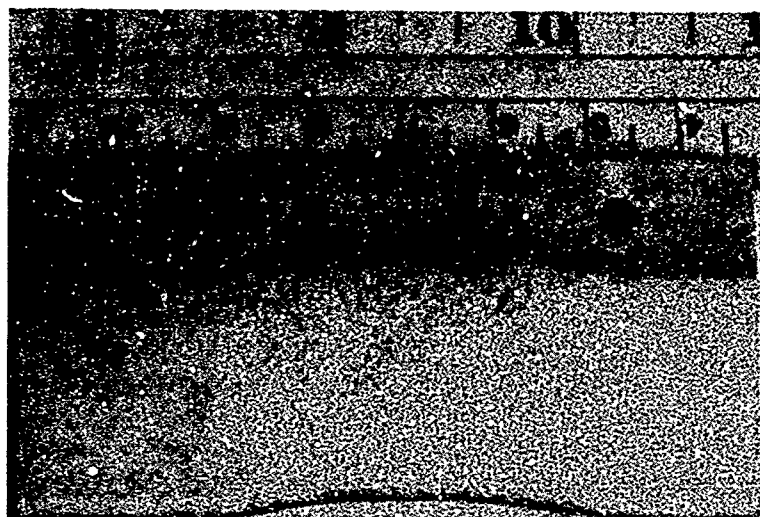


Figure 51. Unprotected Aluminum Wedge No. U-4 after Exposure for 60 Minutes at 274.3 m/sec (900 ft/sec) to Sand Environment; Sand Flow 908 g/min (2 lb/min)

Wedge No.
DP-1B

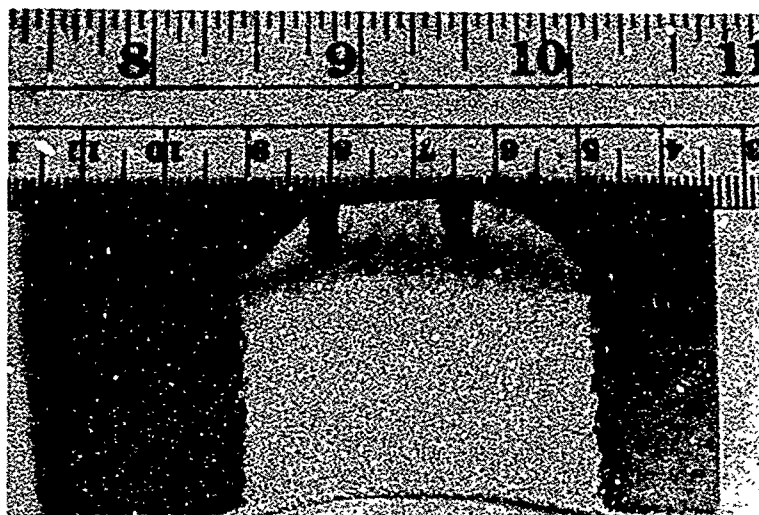


Figure 52. Duranodic Anodized (0.09 mm) + Sandstrom LC-300 Specimen after Exposure for 60 Minutes at 274.3 m/sec (900 ft/sec) to Sand Environment; Sand Flow 908 g/min (2 lb/min)

Wedge No.
SP-2B

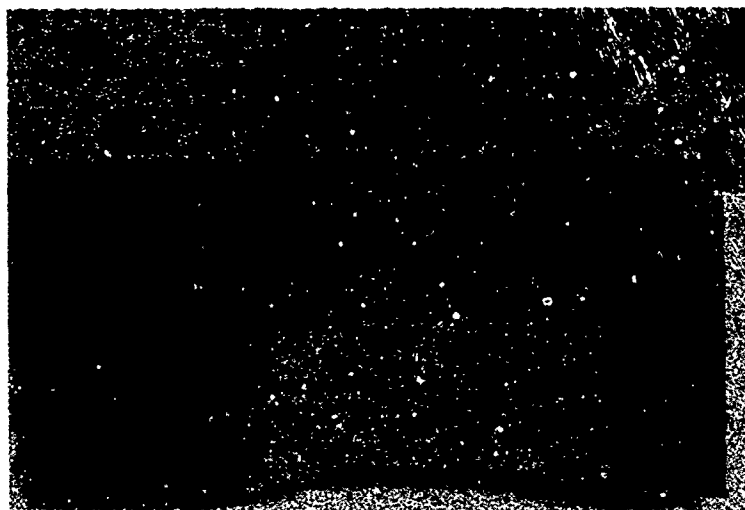


Figure 53. Sanford Plus Anodized (0.08 mm) + Sandstrom LC-300
Specimen after Exposure for 60 Minutes at 274.3 m/sec (900 ft/sec) to
Sand Environment; Sand Flow 908 g/min (2 lb/min)

Wedge No.
DP-3B



Figure 54. Duranodic Anodized (0.06 mm) + Sandstrom LC-300
Specimen after Exposure for 60 Minutes at 274.3 m/sec (900
ft/sec) to Sand Environment; Sand Flow 908 g/min (2 lb/min)

Wedge No.
SP-4B

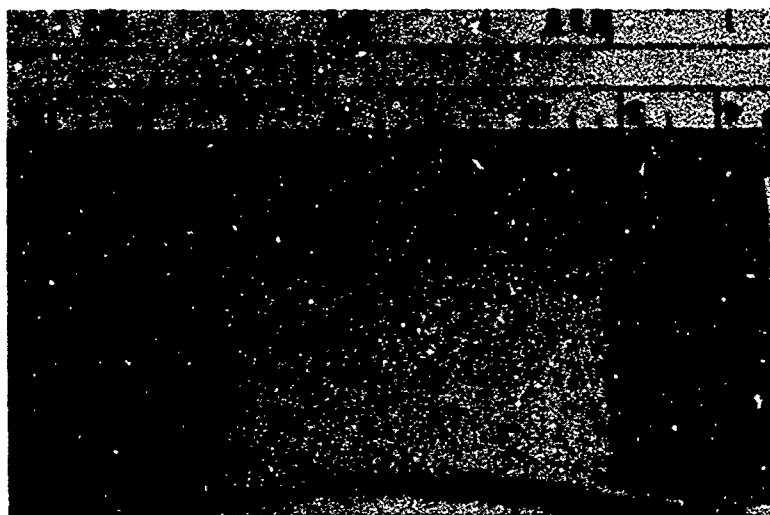


Figure 55. Sanford plus Anodized (0.11 mm) + Sandstrom LC-300
Specimen after Exposure for 60 Minutes at 274.3 m/sec (900
ft/sec) to Sand Environment; Sand Flow 908 g/min (2 lb/min)

Wedge No.
N-1B

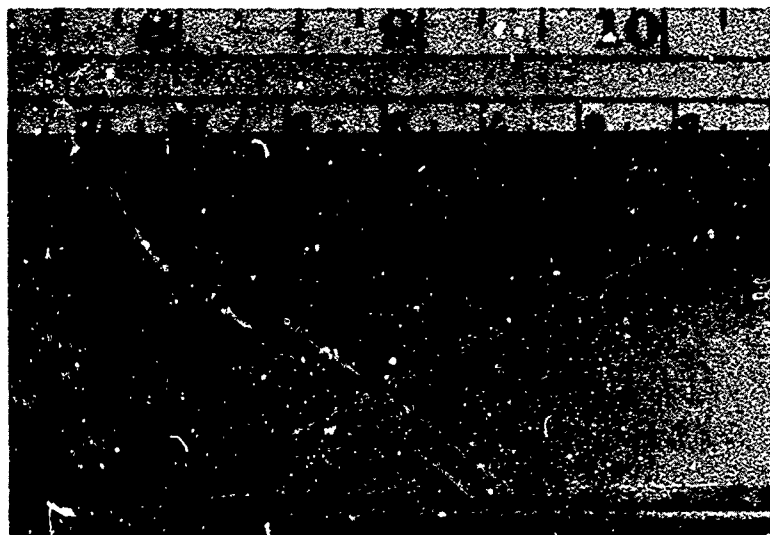


Figure 56. Wedge Number N-1B Processed by Phosphoric Acid
Anodizing, Low pH Plating, and Hard Nickel Plating at 1.86
 amp/dm^2 (20 amp/ft^2) for 16 Hours - after Exposure
for 60 Minutes at 274.3 m/sec (900 ft/sec) to Sand Envi-
ronment; Sand Flow 908 g/min (2 lb/min).

Wedge No.
N-2B



Figure 57. Wedge Number N-2B Processed by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 1.86 amp/dm^2 (20 amp/ft^2) for 24 Hours - after Exposure for 60 Minutes at 274.3 m/sec (900 ft/sec) to Sand Environment: Sand Flow 908 g/min (2 lb/min)

Wedge No.
N-3B

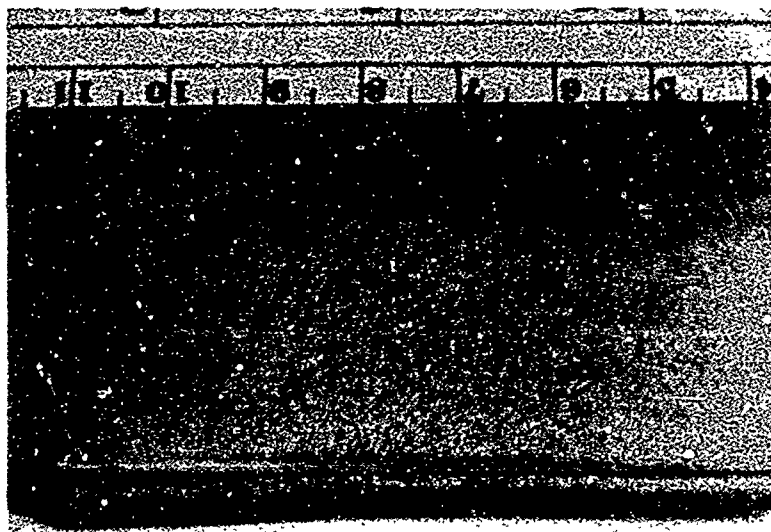


Figure 58. Wedge Number N-3B Processed by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 3.72 amp/dm^2 (40 amp/ft^2) for 12 Hours - after Exposure for 60 Minutes at 274.3 m/sec (900 ft/sec) to Sand Environment; Sand Flow 908 g/min (2 lb/min)

Wedge No.
N-4B

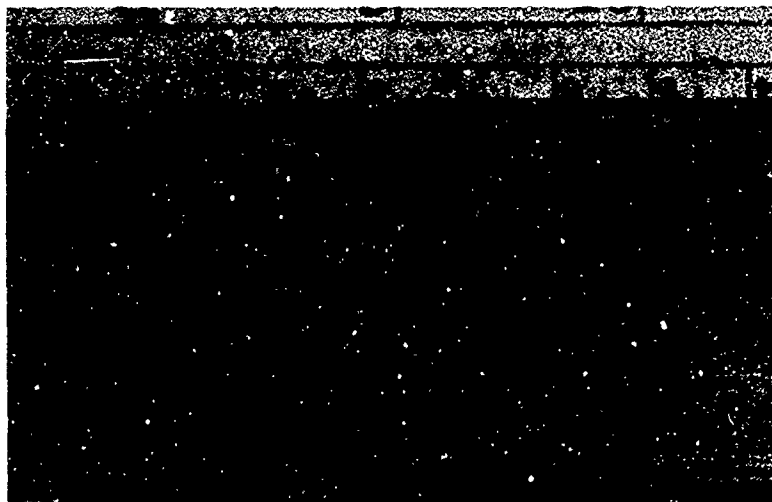


Figure 59. Wedge Number N-4B Processed by Phosphoric Acid Anodizing, Low pH Nickel Plating, Zinc Nickel Alloy Plating, Copper Striking, and Hard Nickel Plating at 1.86 amp/dm^2 (20 amp/ft^2) for 16 Hours - after Exposure for 60 Minutes at 274.3 m/sec (900 ft/sec) to Sand Environment; Sand Flow 908 g/min (2 lb/min)

TABLE 24. WEIGHT AND VOLUME LOSS OF UNPROTECTED, ANODIZED, AND HARD NICKEL PLATED ALUMINUM 7075-T651 TEST WEDGES AFTER EXPOSURE AT 274.3 M/SEC (900 FT/SEC) TO SAND ENVIRONMENT, SAND FLOW 908 G/MIN (2 LB/MIN)

Specimen No.	Weight, gram (before Test)	Weight, gram after 1 hr Exposure	Weight Loss, gram	Equivalent Volume Loss cc
Uncoated U-4	53.8737	52.0860	1.7877	0.65
Anodized DP-1B	54.3787	52.1335	2.2452	0.81
Anodized SP-2B	53.8710	51.6145	2.2565	0.82
Anodized DP-3B	54.1490	51.9037	2.2453	0.81
Anodized SP-4B	54.6564	52.4660	2.1904	0.79
Nickel N-1B	80.0051	78.3922	1.6129	0.18
Nickel N-2B	87.5180	85.7157	1.8023	0.20
Nickel N-3B	93.3670	91.4677	1.8993	0.21
Nickel N-4B	77.4866	75.5029	1.9837	0.22

Figure 60. Weight Loss Vs. Exposure Time.
 Unprotected, Anodized, and Hard Nickel
 Plated Specimens Exposed at 274.3 m/sec
 (900 ft/sec) in Sand Environment. Sand
 Flow Rate: 908 g/min (2 lb/min).

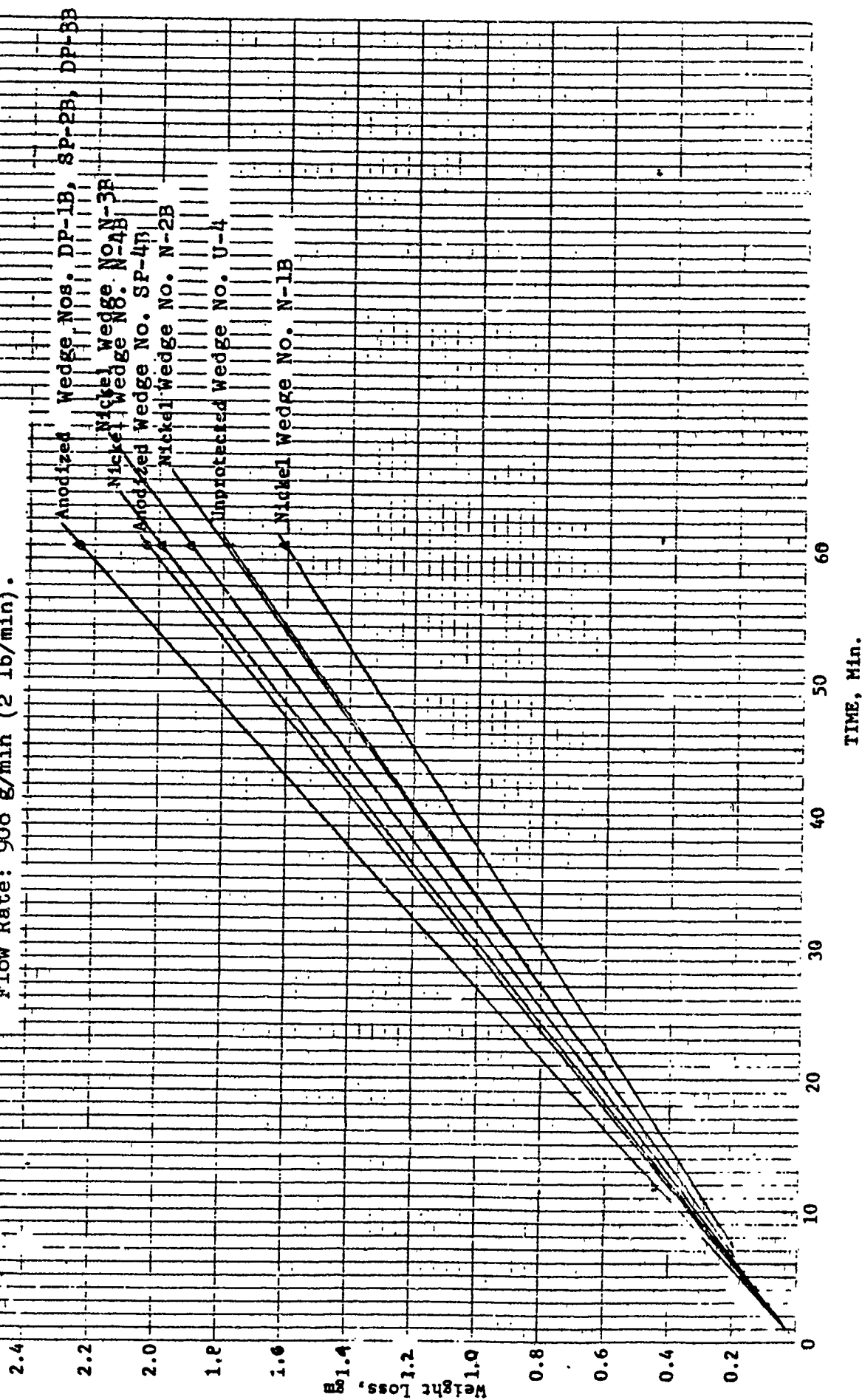
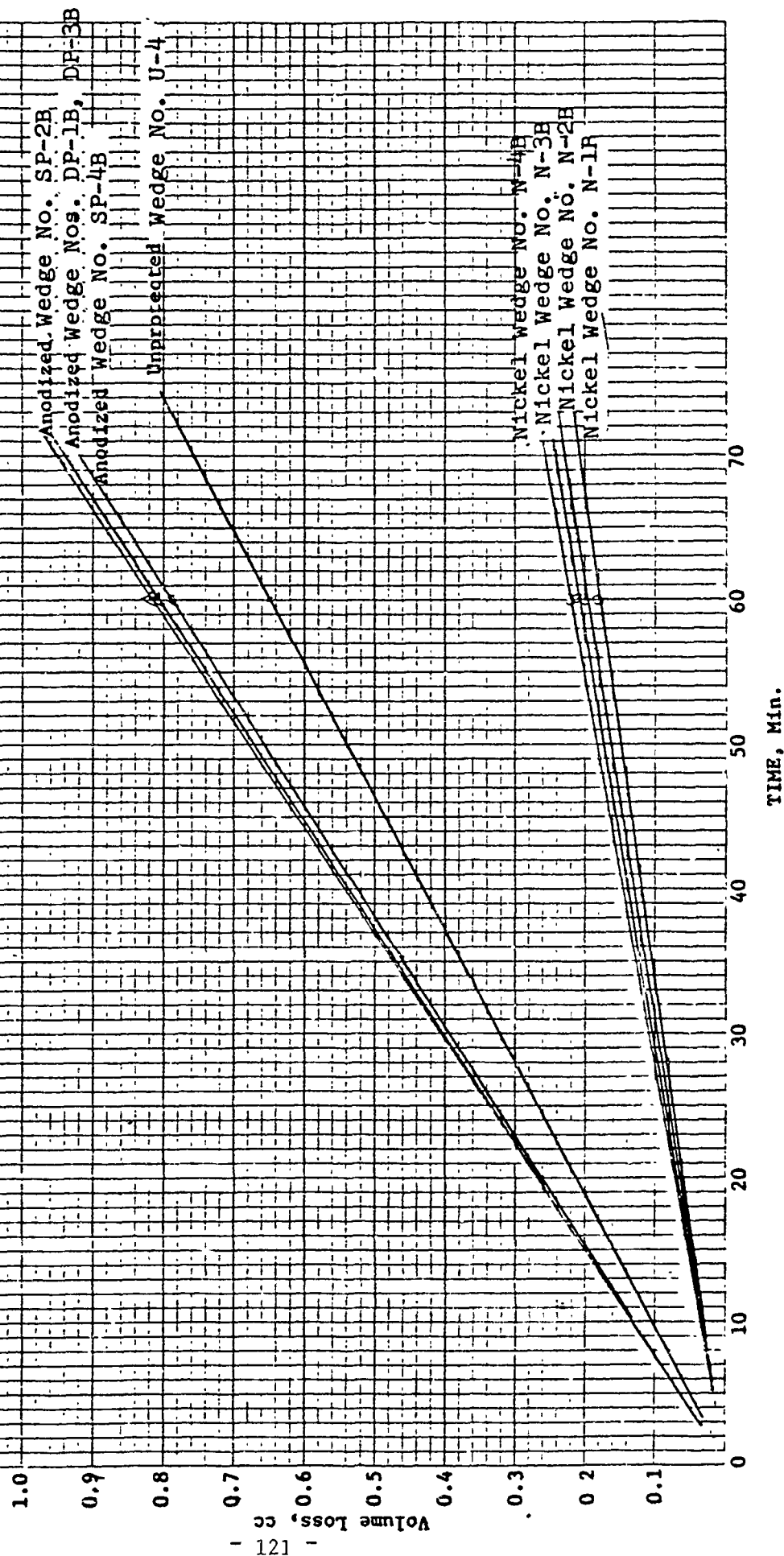


Figure 61. Volume Loss Vs. Exposure Time, Unprotected, Anodized, and Hard Nickel Plated Specimens Exposed at 274.3 m/sec (900 ft/sec) in Sand Environment. Sand Flow Rate: 908 g/min (2 lb/min).



from the leading edges of the wedges to permit examination for evidence of debonding.

Macrographs and micrographs of these specimens are shown in Figures 62 through 69. No evidence of plastic deformation or debonding from the substrate is apparent in Wedge Numbers N-1B, N-2B, or N-3B. In the case of Wedge Number N-4B, one large pore is evident in the macrosection, although there is no appearance of plastic deformation. However, the zinc-nickel layer shows considerable cracking, reflecting what must be a brittle characteristic. This has resulted in considerable debonding between this phase and the overlying copper layer. While this did not appear to impair the erosion resistance of the system, it is regarded as an unfavorable feature which would diminish confidence in the bond strength.

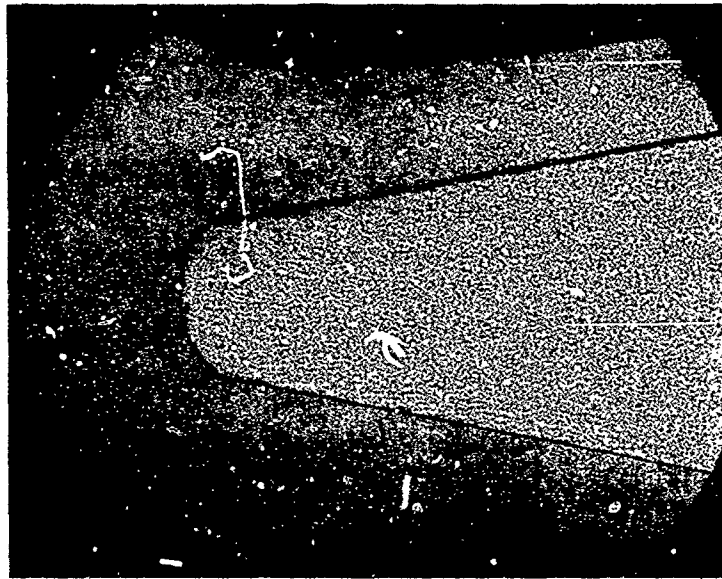
Erosion Study Conclusions

Unprotected, anodized, and hard nickel plated Aluminum 7075-T651 specimens were evaluated at 274.3 m/sec (900 ft/sec) movement in both water droplet and sand environments. This velocity is approximately that experienced by propeller blade tips on the LACV-30.

In the water droplet environment, the nickel plated specimens are clearly superior to the others, although optimum performance is gained only when the surface is devoid of imperfections and nodule growth. The anodized specimens were somewhat inferior to the unprotected Aluminum 7075-T651, largely due to the rapid erosion of the anodized layer (with the dry film lubricant) which eliminated the incubation period normally associated with well finished metallic surfaces.

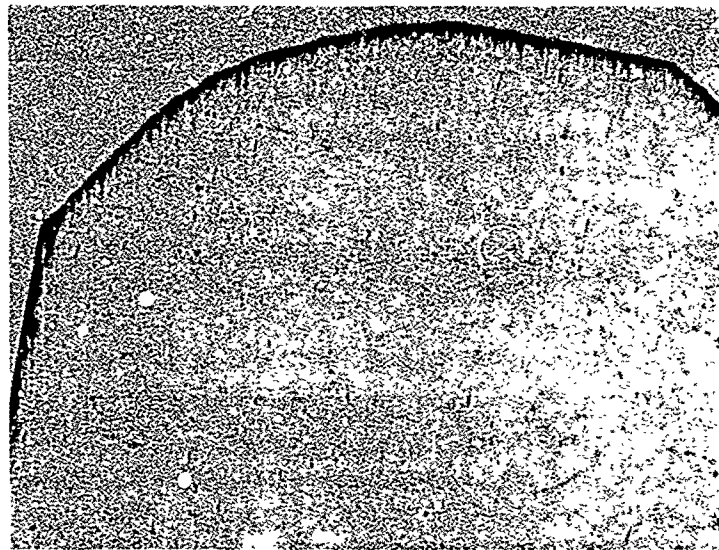
In the sand environment, the hard nickel plated specimens were again superior to the anodized and unprotected specimens by a factor of approximately four, when compared on the basis of volume loss. Again, the performance of the anodized specimens was slightly inferior to the unprotected aluminum. The effects of hard nickel plating variables, such as coating thickness and current density on erosion performance in both sand and rain could not be realistically compared on the particular specimen design used in this study due to the rather sharp angle of the leading edge. There was a tendency for electrodeposits to form a "tear-drop" profile and assume roughness as either current density or plating time (deposit thickness) was increased.

The influence of even slight surface roughness on decreasing the incubation period for water droplet erosion was quite striking. Although most of the leading edge of an actual LACV-30 propeller blade has a substantial "radius" for smooth hard nickel deposition -- even at fairly high current densities or long plating times -- the blade tip is much more similar to the low angle leading edge employed on the test wedges in this study. Roughness has frequently been observed on tips and tip corners of full sized blades after plating, and this is where erosion is most severe. This roughness is undoubtedly an effect of high current density and points to a need for more optimum plating shield design.



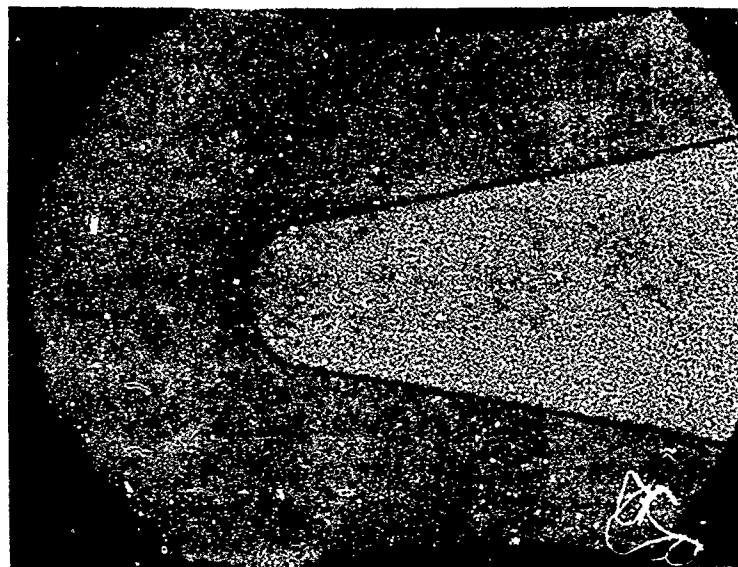
20X

Figure 62. Cross-section of Leading Edge of Wedge Number N-1B after Sand Erosion Testing. Coating was Fabricated by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 1.86 amp/dm^2 (20 amp/ft^2) for 16 Hours



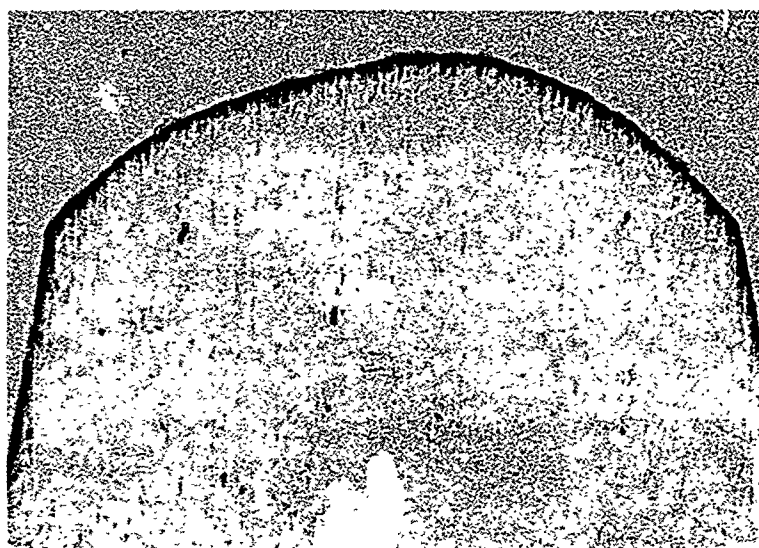
100X

Figure 63. Cross-section of Leading Edge of Wedge Number N-1B after Sand Erosion Testing. View is an Enlargement of the Substrate Tip Area of Figure 62 to Illustrate the Nickel-to-Aluminum 7075 Bondline



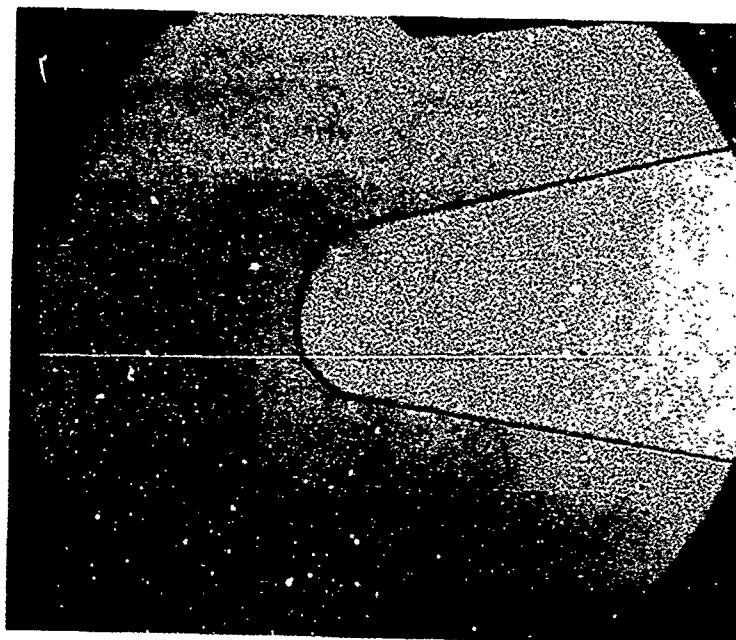
20X

Figure 64. Cross-section of Leading Edge of Wedge Number N-2B after Sand Erosion Testing. Coating was Fabricated by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 1.86 amp dm^2 (20 amps/ft^2) for 16 Hours



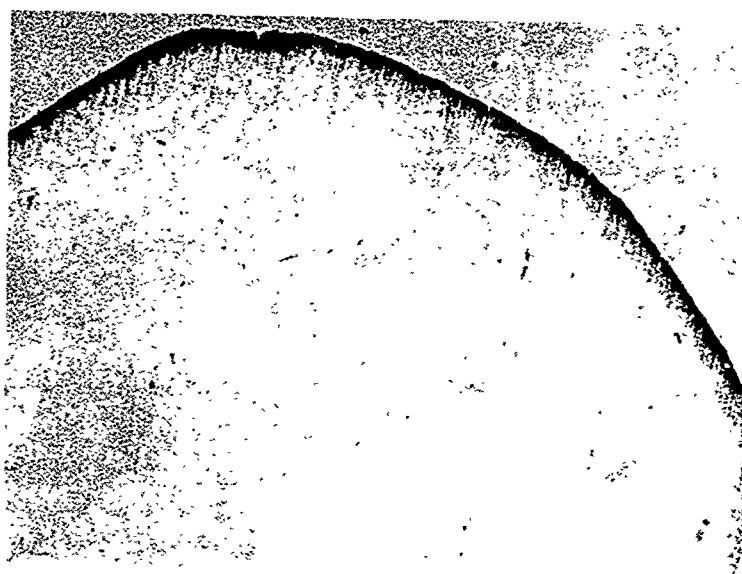
100X

Figure 65. Cross-section of Leading Edge of Wedge Number N-2B after Sand Erosion Testing. View is an Elargement of the Substrate Tip Area of Figure 64 to Illustrate the Nickel-to-Aluminum Bondline



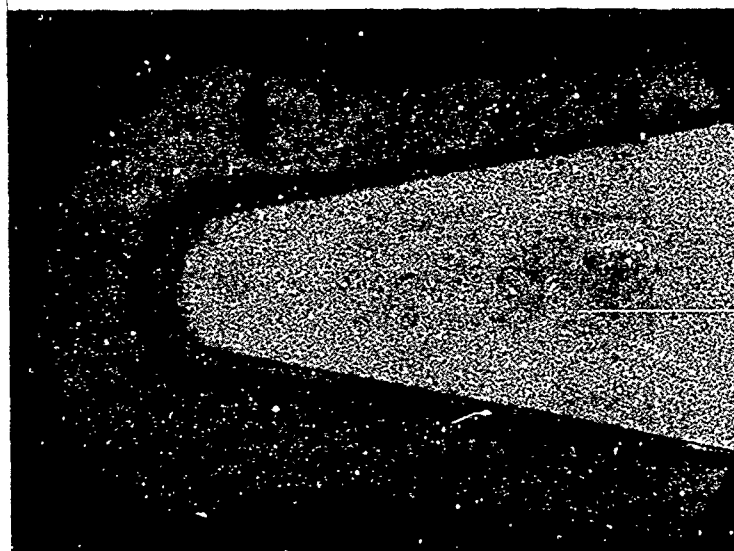
20X

Figure 66 Cross-Section of Leading Edge of Wedge Number N-3B after Sand Erosion Testing. Coating was Fabricated by Phosphoric Acid Anodizing, Low pH Nickel Plating, and Hard Nickel Plating at 3.72 amp/dm^2 (40 amp/ft^2) for 12 Hours



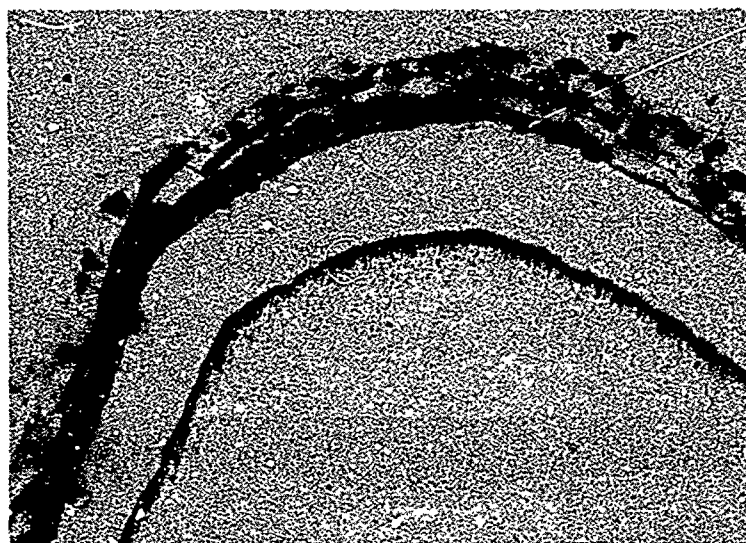
100X

Figure 67. Cross-section of Leading Edge of Wedge Number N-3B after Sand Erosion Testing. View is an Enlargement of the Substrate Tip Area of Figure 66 to Illustrate the Nickel-to Aluminum Bondline



20X

Figure 68. Cross-section of Leading Edge of Wedge Number N-4B after Sand Erosion Testing. Coating was Fabricated by Phosphoric Acid Anodizing, Low pH Nickel Plating, Zinc-Nickel Alloy Plating, Rochelle Copper Striking, and Hard Nickel Plating at 1.86 amp/dm^2 (20 amp/ft^2) for 16 Hours



Hard
Nickel

Copper

Alloy

Low pH
Nickel

Aluminum
100X

Figure 69. Cross-section of Leading Edge of Wedge Number N-4B after Sand Erosion Testing. View is an Enlargement of the Substrate Tip Area of Figure 68 to Illustrate the Brittle Fracturing Within the Zinc-Nickel Alloy and the Copper-Alloy Interface Disbonding

The adjustment of Vickers hardness from around 500, as applied to previous study specimens, to about 400 for this erosion study, appears to have resulted in a significant improvement -- particularly for sand endurance. A quantitative comparison might be inaccurate based on the facts that Fort Story beach sand was used in the present study and the specimen fixturing has been modified.

Results of the erosion studies confirmed previous findings from the previous section on corrosion evaluation -- namely, intermediate coatings, such as the zinc-nickel alloy intermediate layer applied to Wedge Numbers N-4A and N-4B, may be detrimental to the bond integrity of the total coating system. Such coatings may also induce roughness in the hard nickel coat which becomes magnified with thickness to promote more rapid erosion in water droplet environments.

SECTION VII

RECOMMENDATIONS

Having developed and demonstrated successful methods for obtaining optimum hardness and the ability to control this hardness in electro-deposited nickel, and having found a better method for bonding this metal to aluminum substrates while providing good corrosion protection, it now appears appropriate to apply this knowledge to LACV-30 propeller blades for field evaluation. This does not imply that a fully production ready process now exists, since some modifications and scale up development remain which can only be accomplished by working with full sized blades in a production scale facility.

Should it be agreed that this course of action is now appropriate, it is recommended that:

- (1) The dilute phosphoric anodizing process be required to prepare the aluminum blades for bonding. All of the processing parameters for this process are now established. The process imparts good corrosion protection and provides excellent bond strength.
- (2) The low pH nickel sulfamate plate be required over the phosphoric anodized layer to provide a ductile base metal for the hard nickel erosion coating. It is recommended that this layer be at least 0.002 in. thick to assure that it is pore-free.
- (3) The hard nickel electrolyte be operated under the parameters in this program which produced deposits having Vickers Hardness Numbers (VHN's) in the range of 380 to 440 and internal compressive stresses below 10 ksi.
- (4) Further work be performed, using full sized blades, to improve coating distribution by means of better and more flexible shielding. The work here would entail shifting the hard nickel coating distribution so that more is at, or near, the blade tip. Also, shield design should be examined and modified with the objective of producing the heaviest and smoothest possible deposit at the blade tip and leading edge. It is further recommended that scrap propeller blades be coated by use of the modified shields to evaluate the actual coating thicknesses obtained in critical regions such as the tip leading edge.
- (5) Data be gathered during the course of this scale-up, particularly in the forms of stress measurements and hardness test results to confirm indications from the current study that stress, hardness, and hardening agent activity are closely related.

REFERENCES

- (1) Weaver, J. H., "Electrodeposited Nickel Coatings for Erosion Protection", Air force Materials Laboratory, Technical Report AFML-TR-70-111, July 1970, p. 18.
- (2) Schmitt, G. F. Jr., "Liquid and Solid Particle Impact Erosion", Wear Control Handbook, (Publisher Unknown), pp. 271-2.
- (3) Private Communication from M. Ishibashi, Mitsui Engineering & Shipbuilding Co., Ltd., Tokyo, Japan (1979).
- (4) Bell Aerospace Textron Report No. 0500-927014, "Independent Research and Development - 1979", Project No. 7919.
- (5) Brenner, A. and Senderoff, S., "A Spiral Contractometer for Measuring Stress in Electrodeposits", Proceedings of the 35th Annual Convention, American Electroplaters' Society, Atlantic City, New Jersey (1948) pp. 53-78.
- (6) Marti, J. L. and Lanza, G. P., "Hardness of Sulfamate Nickel Deposits", Plating (April 1969).
- (7) Klingenmaier, O. J., "The Effect of Anode Efficiency on the Stability of Nickel Sulfamate Solutions", Plating (November 1965) pp. 1138-41.
- (8) Knapp, B. B., "Notes on Nickel Plating from Sulfamate Solutions", Plating (December 1971) pp. 1187-93.
- (9) Reference (6).
- (10) Marti, J. L., "The Effect of Some Variables upon Internal Stress of Nickel as Deposited from Sulfamate Electrolytes", Plating (January 1966).
- (11) Reference (6).
- (12) Bocker, J. and Bolch, Th., "Nickel Electroforming - Some Aspects for Process Control", AES International Symposium on Electroforming/Deposition Forming, Los Angeles, California (March 1983).
- (13) Wernick, S. and Pinner, R., Surface Treatment of Aluminum, 3d Ed., Robert Draper Ltd., Teddington, England (1964) pp. 582-4.
- (14) "Chemical Milling Solution Produces Smooth Surface Finish on Aluminum", NASA Tech Brief No. 66-10312 (July 1966).
- (15) Enthronics Data Sheet, "Actane 70", Enthone Incorporated, West Haven, Connecticut 06508.
- (16) Enthronics Data Sheet, "Alumon", Enthone Incorporated, West Haven, Connecticut 06508.

- (17) "The Clepo Bondal Process for Plating on Aluminum and Its Alloys", Frederick Gumm Chemical Company, Inc., Lyndhurst, New Jersey 07071.
- (18) "Alumon, Process for Electroplating Upon Aluminum", Enthone Incorporated, West Haven, Connecticut (1963).
- (19) Reference (17).
- (20) Malone, G. A., "Nickel Plating of Voyageur ACV Propeller Blades to Improve Their Erosion Resistance", Transport Canada Report No. TP 3147 (April 1981).
- (21) Wittrock, H. J., "Adhesion of Sulfamate Nickel Electrodeposits on Aluminum-Zinc-Magnesium Alloys Anodized in Phosphoric Acid", Plating and Surface Finishing (January 1980) pp. 44-7.
- (22) Thomas, D. E., "Adhesion Failure of Electrodeposited Coatings on Anodized Aluminum Coatings", The Second AES Plating on Difficult-to-Plate Materials Symposium, March 1982, St. Louis, Missouri.
- (23) Private Communication from J. C. Cahill, Frederick Gumm Chemical Company, Inc., Lyndhurst, New Jersey 07071 (1982).
- (24) Mansfield, F.; Hengstenberg, D. H.; and Kenkel, J. V., "Galvanic Corrosion of Aluminum Alloys: Effect of Dissimilar Metal", Corrosion 30:10, pp. 343-53.
- (25) Dini, J. W. and Johnson, H. R., "Electrodeposition of Zinc-Nickel Alloy Coatings", Sandia Laboratories Report No. 77-8511, Sandia Laboratories, Livermore, California.
- (26) Safranek, W. H., "Plating on Zinc Alloy Die Castings", Modern Electroplating, 3d Ed., Edited by F. A. Lowenheim, John Wiley & Sons, Inc., New York City, New York (1973) pp. 605-17.
- (27) "Ecolozinc 2001", R.O. Hull and Company, Inc., Cleveland, Ohio 44102.
- (28) Wernick, S. and Pinner, R., Surface Treatment of Aluminum, 3rd Ed., Robert Draper Ltd., Teddington, England (1964) p. 636.
- (29) "Clepo Acid Zinc Process SR-420", Frederick Gumm Chemical Company, Inc., Lyndhurst, New Jersey 07071.
- (30) Safranek, W. H. and Faust, C. L., "Improved Electroplated Finishes for Zinc Die Castings", Plating (October 1958) p. 1029.
- (31) Shibuya, A.; Kurimoto, T.; and Noji, K., "Corrosion Resistance of Ni-Zn Alloy Plated Steel Sheet", Proceedings of Interfinish '80 (1980) pp. 128-32.

- (32) Dini, J. W. and Johnson, H. R., "Electrodeposition of Zinc-Nickel Alloy Coatings", Sandia Laboratories Report No. SAND 77-8511, Sandia Laboratories, Livermore, California, p. 16.
- (33) Tsuji, H. and Kamitani, H., "Electrodeposition and Passivation of Bright Zinc-Nickel Alloys", 69th AES Annual Technical Conference (June 1982) San Francisco, California.
- (34) Sanford, P. L., U.S. Patent No. 2,743,221 (April 1956).
- (35) Franklin, J. B., U.S. Patent Nos. 2,897,125 (July 1959), 2,905,600 (September 1959), 2,977,294 (March 1961), and 3,020,213.
- (36) "Specifications for LC-300", Sandstrom Products Company, Port Byron, Illinois 61275.