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OPTIMIZATION AND EVALUATION OF ALUMINIMUM SEALING

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FOREWORD

This is the final report of work done under Air Force Materials Laboratory Contract AF 33(615)-2747, "Optimization and Evaluation of Aluminum Sealing" for the period 1 June 1965 to 15 December 1966. The contract was initiated under Project Number 7381, Task Number 738107. The program was monitored by 1/Lt Jay A. Wein, and by Mr B. Cohen, Systems Support Branch, Materials Applications Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

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This technical report has been reviewed and is approved.

W. P. CONRARDY, Chief
Systems Support Branch
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ABSTRACT

Preliminary studies showed that outstanding corrosion resistance to humid N_2O_4 and salt fog could be achieved on sulfuric acid anodized 7075-T6 aluminum alloys when sealed first with nickel acetate followed by sodium dichromate. In this study, the nickel acetate-sodium dichromate sealing procedure, termed duplex sealing, was investigated in detail for 2024-T3, 7075-T6, 7178-T6 and 7079-T6 aluminum alloys to identify the treatment combinations giving optimum corrosion resistance. The process variables studied were seal solution immersion times, temperatures and concentrations. Factorial designed experiments were used, followed by statistical analyses of the corrosion resistance of the treatment combinations. The nickel acetate seal temperature was found to be the predominant variable affecting corrosion resistance. The lowest temperature, 180°F, resulted in the best corrosion resistance. Based on these studies, maximum corrosion resistance was achieved by sealing first in 1.25 w/o nickel acetate for ten minutes at 180°F followed by a two minute seal in 4.15 w/o sodium dichromate at 180°F. In duplex sealing, the chromium concentration in the sealed anodic film is not related to the chromate yellow color of the anodized alloy. High nickel acetate seal temperatures inhibit stable chemisorption or reaction of the chromate with the anodic film. Under such conditions, the chromium content is very low, even though the samples are intensely colored. Sulfuric acid anodizing times as short as five minutes, when duplex sealed, were resistant to 5% salt fog for times in excess of 1,000 hours. Based on limited fatigue data, duplex sealed sulfuric acid anodized high strength aluminum alloys are comparable to Type II, MIL-A-8625 process conditions. The paint adhesive qualities of duplex sealed high strength alloys is excellent. After 14 days exposure to 100% relative humidity at 95°F, 100% adhesion of the zinc chromate primer was observed on all samples.

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SECTION I

INTRODUCTION

1.1 BACKGROUND

Corrosion during service and storage is an important problem in the effectiveness of our defense system. In many of our military aircraft and missile systems, high strength aluminum alloys are extensively used. In the bare state, these alloys are susceptible to corrosion and hence are usually protected by anodizing or conversion film coatings. Paint systems are frequently applied to further enhance corrosion resistance.

The work described in this report is an extension of a preliminary investigation that was undertaken in connection with some unusual corrosion problems that were encountered on Titan Missile Decoy Systems. Components used on the Titan were required to survive a combined exposure of humid N_2O_4 for one hour plus 240 hours 5% sodium chloride salt fog exposure. Variable and unsatisfactory corrosion resistance was repeatedly encountered on 7075-T6 aluminum base alloys when anodized and sealed in accordance to MIL-A-8625 Type II coatings (sulfuric acid process with sodium dichromate seal). Complete breakdown of the film occurred as measured by electrical conductivity and a yellow, wax-like residue was present after the humid N_2O_4 exposure. This residue, identified by X-ray diffraction, was found to be $Al(NO_3)_3 \cdot 9H_2O$ with some chromate contamination from the dichromate seal. This compound partially melts in its own water of hydration at room temperature and is sufficiently viscous to prevent operation of close tolerance components.

A cursory investigation was undertaken to gain further understanding of the variations observed in N_2O_4 corrosion of anodized 7075-T6 aluminum alloys and, hopefully, to find some combination of anodizing and seal process conditions that would solve this problem.

This investigation, described in Section III, resulted in the development of a dual process using a nickel acetate, $Ni(C_2H_3O_2)_2$, followed by a sodium dichromate, $Na_2Cr_2O_7$, seal that has shown remarkable corrosion resistance. Test coupons of 7075-T6 aluminum alloy processed by this method, termed duplex sealing for convenience in this report, have survived the one hour moist N_2O_4 exposure and over 3,000 hours of 5% salt spray (Federal Test Method 141) exposure without corrosion.

1.2 OBJECTIVES

In the above described cursory investigation, only a single set of process conditions were used and only the 7075-T6 alloy. The first objective of this study was, then, to fully evaluate the duplex seal process and optimize the process conditions and procedures for sealing sulfuric acid anodized

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high strength aluminum alloys (7075-T6, 2024-T3, 7079-T6 and 7178-T6) to provide improved salt fog corrosion resistance.

As a second objective, because of the known degradation of fatigue properties of high strength aluminum base alloys after anodizing, the fatigue behavior of duplex sealed alloys was determined with anodic films of various thicknesses. Since fatigue life degradation is approximately proportional to anodizing times, as will be shown later, the possibility of achieving equal or superior corrosion resistance with improved fatigue response was an attractive goal.

Since painting is often required, the third objective was to determine the effect of duplex sealing on the paint adhesive qualities.

SECTION II

REVIEW OF LITERATURE ON SEALING OF ANODIZED ALUMINUM

2.1 ANODIZING

The literature on the anodizing of aluminum base alloys is legion, yet we still do not have a complete understanding of the complex surface chemistry of this process. In general, except for a few papers, the investigators in this field have concentrated more on the details of the anodizing process rather than those of sealing. Perhaps this is because the results are more tractable.

The anodizing of aluminum is treated in detail in two fairly recent books.[1,2] Wernick and Pinner[1] state that "the mechanism of anodic oxidation is very complex and is still largely controversial". It is well recognized in the literature that the nature of the anodic film produced depends to a surprising degree on the chemical composition of the electrolyte. Since here we are concerned with sulfuric acid anodizing and its sealing, only that phase of the literature will be reviewed.

There is general agreement[1,2,3] that the sulfuric acid anodic film is composed of two identifiably different type films. The inner layer, termed dielectric or barrier layer, has a thickness of about 10 Å/volt while the outer layer, comprising 98 to 99.5% of the total film thickness, is porous and cellular. As was pointed out by Hunter and Towner,[4] the two films are not separable and distinct layers in the sense that they can be separated or that a definite line of demarcation exists between them. The two films are identifiable, however, by virtue of their differences in solid state properties. The barrier layer is capable of electrolytic rectification, whereas the porous layer offers little or no resistance to current flow in either direction.

The structure morphology of the anodic films has been examined extensively by electron microscopy. The initial study by Keller, et al.,[5] developed the hexagonal cell model (Figure 1) and defined the basic dimensions of the pores within the outer porous layer. Keller's technique,[5] while well adapted to phosphoric acid anodic films, has resolution difficulties of the structural details of the finer pore size sulfuric acid anodic films. These difficulties, summarized by Paoline, et al.,[6] include:

(1) Small size of pores formed in H_2SO_4 makes direct counting very difficult, if not impossible.

(2) Direct counting requires very thin films detached from the metal substrate and partially dissolved to widen the pores. Small size of pores results in some dissolution of walls between cells.

(3) Thin films required are produced by short time anodizing (45 seconds) and may not have the same structural morphology as normal anodic films.

(4) Density of pore wall uncertain, ranging from 3.2 (Russell) to 2.77 (Prati).

(5) Pores may not be cylindrical.
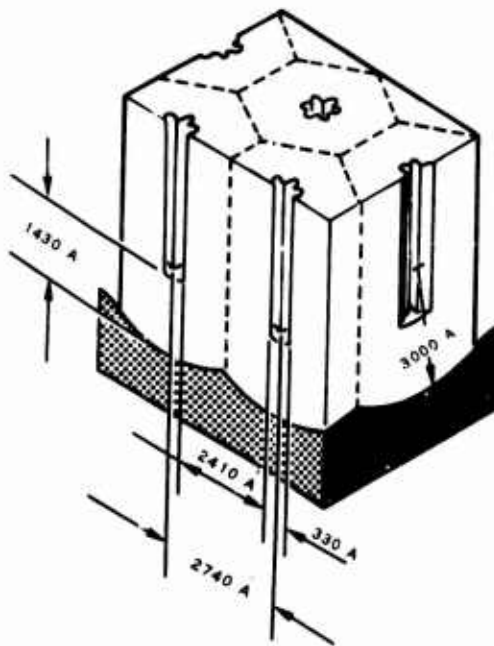
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FIGURE 1. HEXAGONAL CELL MODEL, ANODIC ALUMINUM FILM, AFTER KELLER[5]

Paolini's findings,[6] based on the combined results of surface area measurement using the Brunauer, Emmett and Teller (BET) method, and gravimetric and electronoptic techniques, suggest that the pores in H_2SO_4 anodic films are very slightly truncated conics (as shown in Figure 2) with an average density of 2.78 g/cc for 30 minute films.
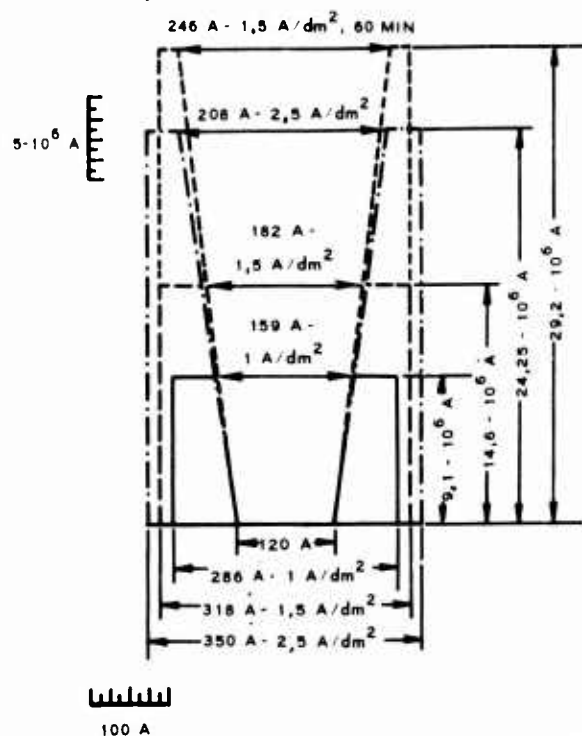
FIGURE 2. CELL MODEL, ANODIC ALUMINUM FILM, AFTER PAOLINI[6]

Recent work by G. A. Dorsey, Jr.,[7,8,9] is an illuminating study of the chemi-
cal composition of anodically formed films. He used the infrared reflectance
technique to measure the adsorption bands of anodic films using different
electrolytes, process and seal conditions. All results were carefully com-
pared with reference standards of the various numerous aluminum hydrates.[10]
The infrared adsorption spectra analysis demonstrated that the barrier layer
could be distinguished from the porous layer even when both are present by a
characteristic infrared adsorption at 900-1000 cm^{-1} of the barrier layer.
It was concluded from these data that the barrier layer is a trihydrate,
$Al(OH)_3$, with some structural modification. Using deuterosulfuric acid in
heavy water, it was shown[9] that hydrogen is an integral component of the
anodic barrier layer. The suggested structure of the barrier layer included
both tri-and di-valent aluminum in a polymeric form, as shown in Figure 3.

Many points concerning the chemical constitution of the porous layer remain
to be resolved. However, it should be recognized from Dorsey's work that
the anodic film is not simple Al_2O_3 but some complex polymer-like mixture
of the various hydrated compounds of aluminum. Adsorption spectra found[7]
suggest the presence of AlO(OH) Bohemite and/or Diaspore in addition to the

tri-hydrate. The presence of absorption bands in the wavenumber range of 1200-1325 cm^{-1} suggests the possible presence of Al = O linkage and would indicate the presence of an adsorptive or reactive material with limited cross-linkage.

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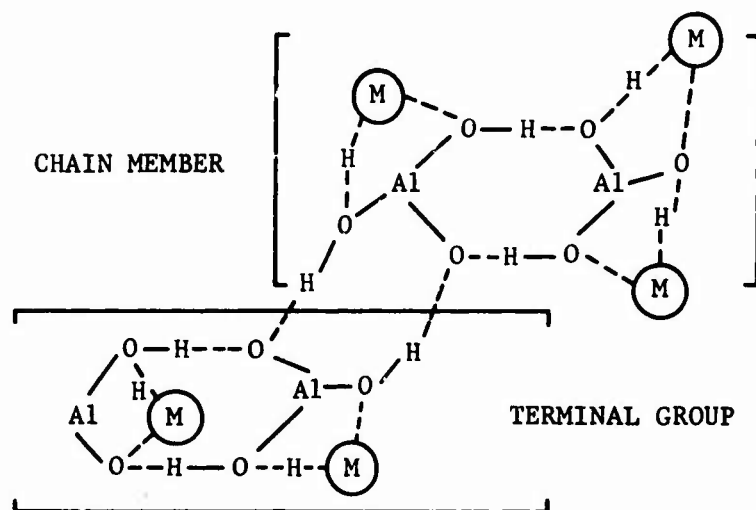
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FIGURE 3. PROPOSED STRUCTURE OF BARRIER LAYER AFTER DORSEY[8,9]

Further studies by Dorsey using deutero-sulfuric acid heavy water as an anodizing bath and infrared absorption analysis of the films formed sub- stantiates the polymeric tri-hydrate structure of the barrier layer. Dorsey suggests from these data that the primary phase of the barrier layer is a cyclic aluminic acid tri-hydrate. The secondary barrier phase may be a decyclized form of the primary, having more terminal groupings with a lower molecular weight of the polymer cross-linked chain.

Prior to sealing, it appears reasonable to assume we have a complex, highly hydrated polymer-like alumina gel containing very fine pores in its outer surface. Surface areas are large,[6] ranging from about 590 to 1230 cm^2/cm^2 in 20% H_2SO_4 electrolytes after anodizing for 30 minutes. Based on the infrared adsorption spectra, this coating will have a relatively high chemical activity in terms of its ability to chemisorb or react with suitable anions and cations during the sealing process.

2.2 SEALING OF ANODICALLY FORMED FILMS ON ALUMINUM AND ITS ALLOYS

The effect of sealing anodically formed films on aluminum to improve their corrosion resistance and/or organic dye stability has been known for many years. The sealing process, according to the generally accepted theories,[2,11,12] is the result of a "plugging" of the pores present in the outer layer of the film either by hydration of the anodic film and presumed swelling or by precipitation of some insoluble compound in the pores. It is generally agreed that the efficaciousness of anodic films against corrosion depends on the perfection of the seal. Unfortunately, no universally acceptable technique is known that will quantitatively measure the degree of sealing or predict corrosion performance over a range of corrosive environmental conditions in a short time.

The rationale for the selection of seal solutions has not clearly been defined in the literature. The successful seal solutions, other than hot water or steam, that have been reported are either "inhibitors" such as alkali dichromates or "precipitators" such as nickel, barium or lead acetates.

In the case of steam[13,14] or hot water[15] sealing, it is generally stated that hydration and presumably swelling of the anodic film is responsible for the "pore plugging". In view of the infrared adsorption work[7,9] cited in Section 2.1, this concept must be questioned, since the anodic films as formed are virtually fully hydrated. The infrared spectra[7] on sealed and unsealed H_2SO_4 anodized films show no significant differences in their adsorption spectra. Such would not be the case if hydration of the magnitude required to "plug" pores was responsible for the film property changes observed in hot water or steam sealing. As a possible hypothesis, it seems reasonable to assume that the exposure of the anodic film to hot water or steam may simply provide an environment that allows for greater surface mobility and/or molecular re-arrangement of the gel-like film that reduces its chemical reactivity by cross-linkage and/or slight additional hydration on selected reactive sites. Much work remains to be done in this area to resolve this enigma.

The "inhibitor" type seals include sodium or potassium dichromates, alkali silicates and possibly the alkali molybdates.

Dichromate sealing processes[16,17,18] are believed to be effective not only because of the inhibitor action of the chromates but also by reaction with the anodic film to form oxydichromate or oxychromates. Dichromate sealing

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practice in the United States per MIL-A-8625 uses 5% dichromate at a pH range of 5.0 to 6.5, whereas Russian practice utilizes a 10% potassium dichromate at a pH of about 6.3 to 6.4. While the Russian method has not been extensively used in this country, it is apparently finding application in England. Superior corrosion resistance is claimed[1] but quantitative data are lacking. Likewise, direct experimental evidence for the formation of the oxy-chromate compounds proposed[18] has not been reported. (Tyukina's proposed mechanism of formation is based only on compositional and pH changes in the seal solution rather than direct observation on the sealed film.)

Alkali metal silicates were first patented by Dunham[16] and Edwards[17] as sealants on conversion coatings and anodized aluminum alloys. According to Edwards, a $Na_2O:SiO_2$ ratio of 1:3 or higher is preferable.

One of the problems associated with alkali silicate seals is that they form a cloudy, loose coating that can be removed rather easily by wiping. In a recent United States Patent by Cohn,[19] a number of techniques are described to circumvent this problem. One method uses two stages of sealing. The first stage involves sealing at 120°F for two to five minutes in a 10g/l solution of sodium silicate with a $Na_2O:SiO_2$ ratio of 1:2 or 1:3.2, followed by a second stage immersion in solution of the same composition at 190°F to 200°F for five minutes. Superior corrosion resistance to copper acidified salt spray and 3% caustic solution at 80°F was claimed for this sealing process. One of the most notable effects of silicate seals is in the increase in abrasion resistance.

Molybdate and chromate molybdate seals have been used most extensively in the automotive industry on anodized 5000 series aluminum alloys[20,21,22]. On long term road exposure tests, the chromate molybdate seals showed better performance than hot water or nickel acetate seals.[21]

Seal solutions of the metal acetate type (e.g., Ni, Co, Ba, and Pb) are thought[23-28] to function by chemisorption and hydrolysis of the metal ion, resulting in the precipitation of a hydroxide in the pore of the outer anodic layer. Nickel sulfate and formates[29] have been used instead of nickel acetate. Seals of this class are most widely used for dyed anodic finishes since they improve color fastness without color modification.

In sealing, an unusually large number of process variables seem to influence the corrosion resistance. The recognized variables[12,20,21] include:

(1) Surface finish of the Al metal.

(2) Anodizing electrolyte composition and process conditions.

(3) Post anodizing - pre-sealing conditioning.

(4) Composition and concentration of inorganic seal solution(s).

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(5) pH of seal solutions.

(6) Purity of water used.

(7) Sealing time.

(8) Post seal drying process.

(9) Post seal aging time prior
     to corrosion evaluation.[29]

The problem is further compounded by the fact that item (2) includes the
variables solution concentration, time of anodizing temperature of electro-
lyte and current density as a minimum. Thus, a total of some 12 variables
must be examined if all effects are to be evaluated.

Additional complications are encountered since it is well recognized[1,2,20,21,29]
that the service and accelerated exposure tests usually do not give correlat-
able results with different seal solutions.

To summarize briefly, our understanding of the anodizing process is substanti-
ally better than that of sealing. The work of Dorsey[7,8,9] is possibly the
most significant work performed on anodizing in the past decade. Many of our
prior concepts must be revised to accommodate his experimental findings. At
present, our knowledge of the sealing process of anodic films is incomplete
as many of the models proposed lack experimental verification. Much could be
gained by infrared adsorption studies and perhaps some resolution of the
problem of non-correlation of results between accelerated and service tests
could be achieved.

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SECTION III

EXPERIMENTAL

3.1 PRELIMINARY INVESTIGATION OF DUPLEX SEALING

A preliminary investigation was undertaken to devise an anodizing and sealing process for 7075-T6 aluminum alloys that would withstand combined corrosion of humid N_2O_4 and 5% NaCl salt fog.

All test coupons (1" x 4") were prepared from a single .040" sheet of 7075-T6 aluminum alloy. Each specimen was identified as to its position within the sheet. Samples were randomized to minimize any possible compositional or microstructural variation in the sheet.

All anodizing electrolytes and seal solutions were freshly prepared from reagent grade chemicals with deionized water. The anodizing conditions used are summarized in Table I.

TABLE I. ANODIZING CONDITIONS - PRELIMINARY INVESTIGATION

Temperature Levels	60, 70 and 80°F
Anodizing Time	30 and 45 minutes
Voltage	10, 12 and 15
H_2SO_4 Concentration	15, 20 and 25 wt.%

All combinations and permutations of the above were used, resulting in 54 variations in the anodizing conditions. Ten coupons were anodized under each condition for subsequent sealing. Ten sealing conditions were used in the preliminary study (Table II).

All anodized and sealed 7075-T6 coupons were simultaneously exposed to humid N_2O_4. The stainless steel, N_2O_4 exposure chamber (16" diameter by 68" long) was equipped to inject a "slug" of N_2O_4 at time zero and add H_2O vapor at a uniform rate during the first 45 minutes of the one-hour exposure. Approximately 2 ml. of N_2O_4 and 2 ml. of H_2O were added per liter volume of the chamber. Temperature of exposure was maintained constant at 70°F ± 3°F.

After the one-hour N_2O_4 exposure and post exposure visual inspection, the test samples were subjected to salt spray test in accordance with Federal Test Method 141 using 5% NaCl salt solution.

All samples were examined after each 24-hour salt spray exposure period. Samples showing one or more pits were removed at that time to prevent extensive substrate corrosion. The appearance of one corrosion spot or pit on the coupon was considered to be a failure since rapid corrosion occurs on the 7075 alloy once the anodic film is destroyed.

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TABLE II. PRELIMINARY INVESTIGATION - SEAL PROCESSES USED ON 7075-T6 TYPE II ANODIZED SAMPLES.

Seal No.	Sealant I	w/o	Sealant II	w/o	Time, Minutes I	Time, Minutes II	Temperature, °F
*1	$Na_2Cr_2O_7$	5	---	-	30	--	208 - 210
2	$Na_2Cr_2O_7$	5	---	-	10	--	208 - 210
3	$Na_2Cr_2O_7$	5	Deionized H_2O	-	3	10	208 - 210
4	$Na_2Cr_2O_7$	5	$Ni(C_2H_3O_2)_2$	5	3	10	208 - 210
5	$Ni(C_2H_3O_2)_2$	5	$Na_2Cr_2O_7$	5	5	10	208 - 210
6	$Ba(C_2H_3O_2)_2$	5	$Na_2Cr_2O_7$	5	10	10	208 - 210
7	Electroless Gold Soln.	1	Deionized H_2O	-	3	3	208 - 210
8	Deionized H_2O	-	---	-	10	--	208 - 210
**9	Alodine Conversion Ctg.	-	Deionized H_2O	-	3	10	Room Temp., 208 - 210
10	$Ni(C_2H_3O_2)_2$	5	---	-	30	--	208 - 210

* MIL-A-8625, Type II.

** No Deoxidizer Used.

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The results of the combined corrosion effects of N_2O_4 - salt spray are summarized in Table III.

TABLE III. CORROSION EVALUATION OF 540 ANODIZED
SAMPLES 7075-T6 Al VERSUS SEAL PROCESS

Corrosion Environment: 1 Hour Humid N_2O_4 Plus 240
Hours 5% NaCl Fog (Federal
Test Method 141)

Seal Process (Table II)	Number of Corroded Samples	Percent Failure
1	50	92.6
2	52	96.2
3	42	84.0
4	47	87.0
5	3	5.5
6	26	48.2
7	51	94.4
8	52	96.2
9	53	98.2
10	51	94.4

In an attempt to further evaluate the corrosion resistance of seal process No. 5, i.e., nickel acetate - sodium dichromate, salt spray tests were continued in 72 hour increments. Exposure times in excess of 2000 hours were achieved before corrosion failures occurred.

The yellow, wax-like residue present on anodized aluminum after N_2O_4 exposure was identified as $Al(NO_3)_3 \cdot 9H_2O$ by X-ray diffraction. Such residue was present on all anodized and seal test coupons except Seal Process No. 5.

Of all anodizing and seal conditions investigated, only Seal No. 5, nickel acetate - dichromate, produced samples that showed no signs of fading, discoloration or corrosion after the N_2O_4-salt spray exposure. Of the 54 samples in this seal group, only 13 samples met these criteria. These were predominantly from the 15% H_2SO_4 and electrolyte at the lower anodizing voltages, i.e., 10 and 12 volts.

Generally, aside from the above effect, no major statistical significance of the anodizing conditions was apparent for the 540 factorial replica.

Longer anodizing times and lower bath temperatures resulted in slightly improved corrosion behaviour during the first 48 hours of salt spray exposure but this effect was not significant at longer NaCl exposure times.

The most important finding of this preliminary investigation was the remarkable corrosion resistance of the duplex seal using first, 5% nickel acetate for 10 minutes followed by the 5% $Na_2Cr_2O_4$ seal (Seal Process No. 5). The sequence of sealing is important. In Seal Process No. 4, the order was reversed and very poor corrosion resistance was observed. Likewise, a comparison of $Na_2Cr_2O_7$ seal (Seal Process No. 1--corresponds to MIL-A-8625) or nickel acetate (Seal Process No. 1C) resulted in very poor corrosion resistance.

The above promising results provided a base for the development of optimized process conditions for the duplex (nickel acetate - dichromate) sealing of Type II anodized aluminum.

3.2 SELECTION OF OPTIMUM SEAL PROCESS CONDITIONS

3.2.1 ANODIZING PROCESS

Earlier work described in Section 3.1 indicated that minor variations in the sulfuric acid anodizing conditions had little or no effect on the corrosion resistance after sealing. Thus, anodizing conditions of 17 w/o H_2SO_4 at 70°F $\pm$ 1°F for 30 minutes at 12.0 $\pm$ 0.5 amps/ft^2 current density were maintained throughout this investigation.

a. Material. Sufficient 4' x 12' sheets of each of 7075-T6, 2024-T3 and 7078-T6 aluminum alloys with the analysis given in Table IV were purchased in one lot for the entire program. Each sheet was sheared into 3" x 10" test coupons for subsequent processing.

b. Cleaning. All 3" x 10" test coupons were used with the 'as received' mill finish. Test coupons were placed on titanium anodizing racks as shown in Figure 4 and solvent vapor degreased in trichlorethylene in accordance with Aeronutronic Process Specification (APS) CL-0101. (See Appendix A.) After vapor degreasing, all coupons were cleaned in a non-etching alkaline cleaner (Amchem 106 cleaner at 160-180°F), rinsed in deionized water, deoxidized using Amchem No. 1 deoxidizer and rinsed in accordance with APS-CL-0103. (See Appendix A.)

c. Anodizing. The cleaned, racked test coupons were anodized in 17 w/o H_2SO_4 at 70°F $\pm$ 1°F for 30 minutes at 12 $\pm$ 0.5 amps/ft^2. After anodizing, the test coupons were rinsed first in tap water (overflow rinse) then in deionized water (spray rinse). All coupons were air dried prior to sealing.

Typical coating weights achieved on each of the high strength alloys used are summarized in Tables XXXI and XXXIV.

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TABLE IV. ANALYSIS OF ALUMINUM ALLOYS

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ni	Ti
					w/o Elements				
2024	.14	.26	4.81	.57	1.48	.05	.09	.006	.03
7075	.25	.24	1.50	.08	2.60	.?6	5.41	.007	.04
7178	.26	.30	2.01	.05	2.59	.20	6.52	.004	.04
7079	.13	.20	.70	.20	3.45	.21	4.24	.003	.03
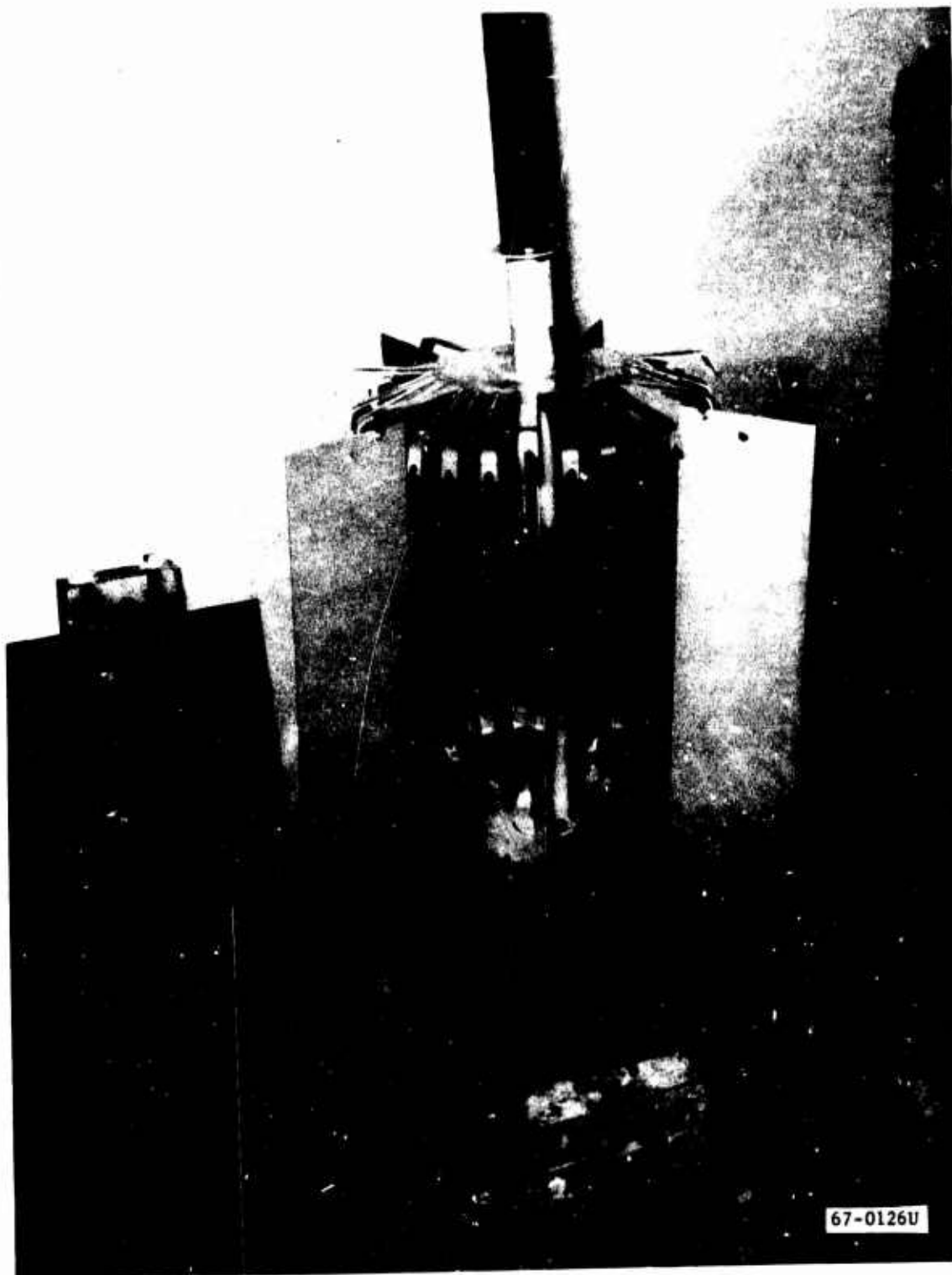
FIGURE 4.   TITANIUM ANODIZING RACK

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3.2.2 SEALING PROCESS OPTIMIZATION

a. <u>Selection of Process Parameters</u>. Based on the preliminary work already described, it is doubtful that the optimum process conditions were selected for the nickel acetate - dichromate sealing of the 7075-T6 aluminum alloy. Because of the number of variables involved in sealing and the lack of complete understanding of the sealing mechanism of anodic films, a factorial design statistical approach was used to attempt to identify the optimum process conditions for maximum salt spray corrosion resistance.

The process variations[12,20,21] that are believed of first order importance in the duplex sealing process are the immersion times, temperatures and concentrations of the $Ni(C_2H_3O_2)_2$ and $Na_2Cr_2O_7$ seal solutions.

Initially, the seal conditions listed in Table V were used (all samples anodized as in 3.2.1.c.).

TABLE V. FACTORIAL DESIGN NO. 1 - DUPLEX SEALING PROCESS

$Ni(C_2H_3O_2)_2$ Wt.%	---- 0.5; 2.5; 10.0
Time in $Ni(C_2H_3O_2)_2$ (minutes)	---- 2, 5, 10, 20 and 30
$Ni(C_2H_3O_2)_2$ Seal Temperature, °F	---- 180, 208
$Na_2Cr_2O_7$, Wt.%	---- 2.5; 10.0
Time in $Na_2Cr_2O_7$ (minutes)	---- 2, 5, 10, 20 and 30
$Na_2Cr_2O_7$ Seal Temperature, °F	---- 180, 208

After the initial 75 samples were anodized and duplex sealed, X-ray fluorescent analysis was run to determine the nickel/chromium ratio in the coating.

These data showed that nickel was absorbed very rapidly by the anodic film and that its concentration increased with time. In contrast, the chromium content remained nearly constant or decreased under the seal conditions listed in Table V. As these data suggested that the major portion of physical or chemical adsorption occurred in times less than two minutes, samples were prepared to better assess the Ni/Cr ratio effect at shorter times. Test coupons were anodized and sealed, as summarized in Table VI. The X-ray fluorescent results are shown in Figure 5.

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TABLE VI.   SEAL CONDITIONS USED FOR METAL ION CONCENTRATION MEASUREMENT

Sample Number	5 w/o Ni(C2H3O2)2 @ 210°F	5 w/o Na2Cr2O7 @ 210°F
N - 1	1	-
N - 5	5	-
N -10	10	-
D - 1	-	1
D - 5	-	5
D -10	-	10
ND- 1	1	1
ND- 5	5	5
ND-10	10	10

From Figure 5, it is apparent that both nickel and chromium are rapidly
adsorbed by the anodic film when used individually as sealants. However,
when $Ni(C_2H_3O_2)_2$ seal is used first, followed by $Na_2Cr_2O_7$, the level of
concentration of chromium is about one half that of $Na_2Cr_2O_7$ used alone.
This suggests that there may be some competition for adsorption sites by
Ni^{++} and $Cr_2O_7^=$ on the surface of the film or in the pores. Alternately,
it could result from pore plugging by nickel as a hydroxide with a re-
sultant decrease in the surface area and hence, fewer available sites for
chromate absorption.

It was also observed, as shown in Figure 6, that the nickel and chromium
concentration in the anodic film was dependent on both the $Ni(C_2H_3O_2)_2$ and
$Na_2Cr_2O_7$ concentration at constant immersion times. Again, the nickel
shows a much greater tendency to react with or chemisorb on the anodic film
than the chromium.

Based on these findings, it seemed advisable to modify the process parameters
investigated to identify the optimum conditions to produce a wider range of
Ni/Cr ratios in the film.

The process conditions selected for Factorial Matrix No. 2 are listed in
Table VII. Using this matrix, a total of 4,500 samples per alloy studied
would be required. To simplify the problem of maintaining identity, the
samples were encoded to identify the alloy, process conditions and sample
number. The system used is illustrated on the following page.

FIGURE 5. Ni/Cr CONCENTRATION AFTER 30 SEC SEAL VERSUS SEAL SOLUTION CONCENTRATION
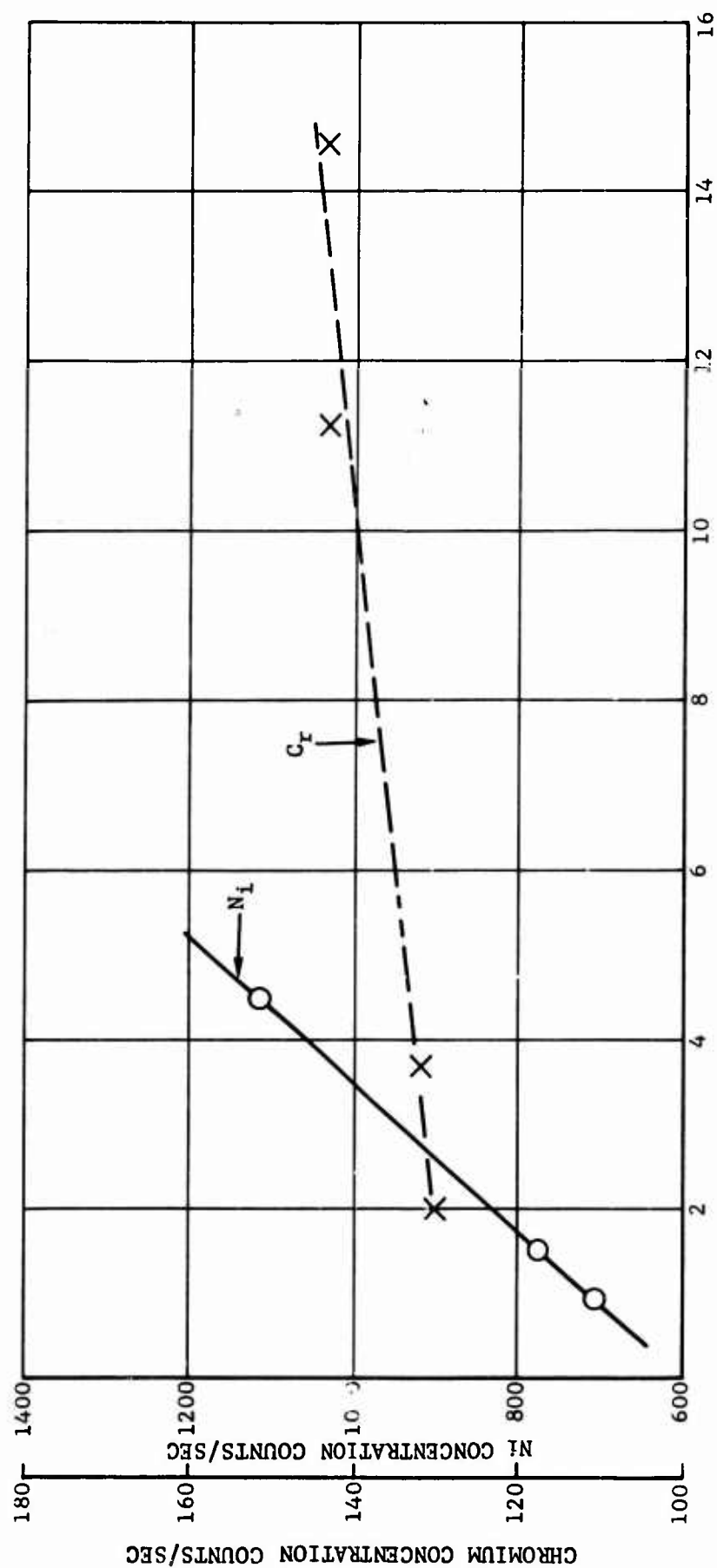
W/O Ni($C_2H_3O_2$)$_2$ Na$_2$Cr$_2$O$_7$ SEAL SOLUTION

F09874 U
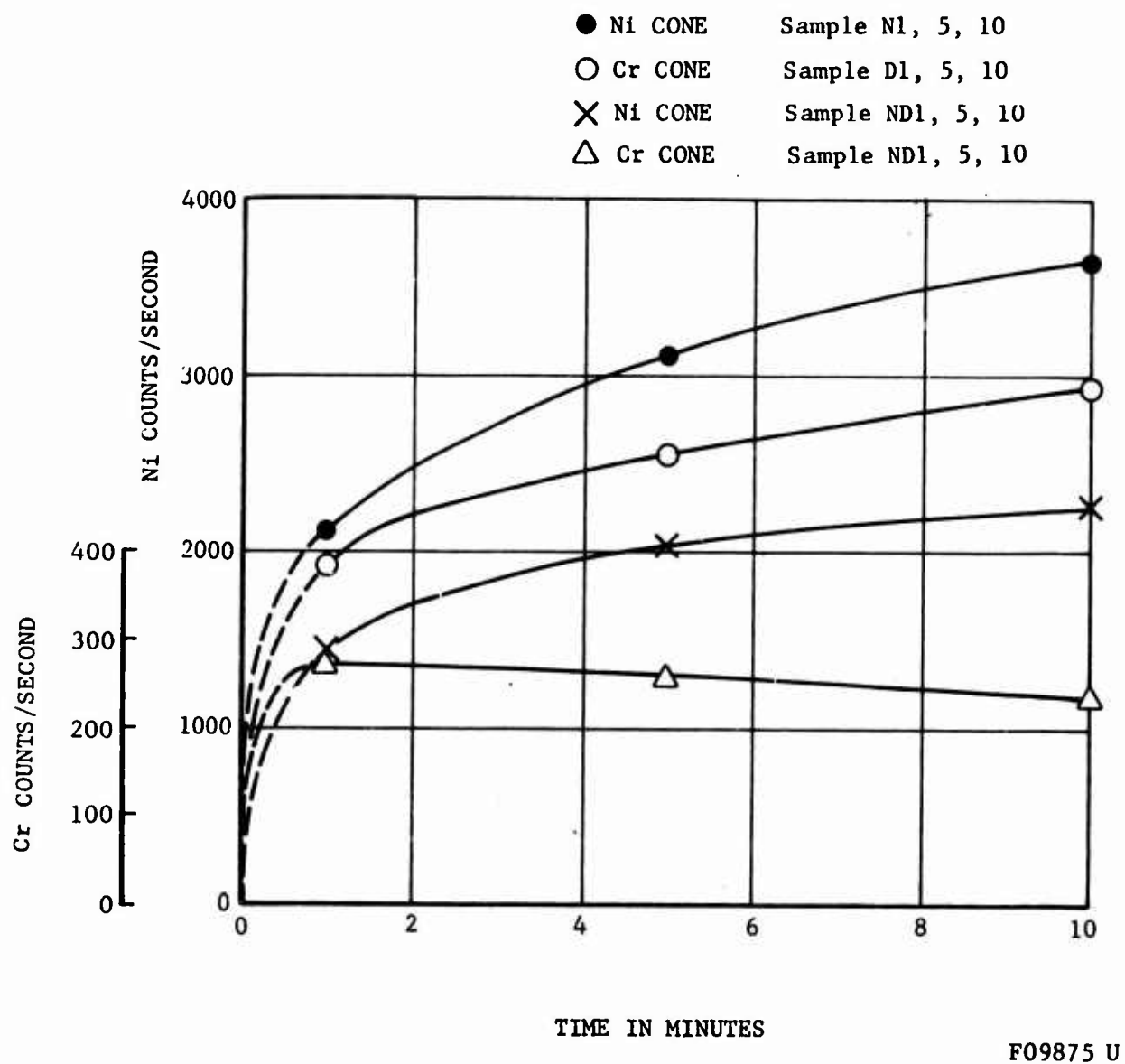
FIGURE 6.   IMMERSION TIME IN 5 W/O SEAL SOLUTION AT 200°F

TABLE VII. SELECTED RANGE OF PROCESS VARIATIONS - FACTORIAL MATRIX NO. 2

	Nickel Acetate $Ni(C_2H_3O_2)_2$	Symbol	Sodium Dichromate $Na_2Cr_2O_7$	Symbol
Temperature, °F	180	T_1	180	T_2
	200	T_3	200	T_4
	212	T_5	212	T_6
Seal Immersion Time	10 sec.	τ_1	2 min.	τ_2
	30 sec.	τ_3	5 min.	τ_4
	2 min.	τ_5	10 min.	τ_6
	5 min.	τ_7	20 min.	τ_8
	10 min.	τ_9	30 min.	τ_{10}
Seal Solution Concentration	1.25 w/o ≈ .375 M Ni^{++}	C_1	1.03 w/o ≈ .75 M Cr_2O_7 .217 M Cr^{+6}	C_2
	2.5 w/o ≈ .75 M Ni^{++}	C_3		
	5.0 w/o ≈ 1.5 M Ni^{++}	C_5	2.06 w/o ≈ 1.5 M Cr_2O_7 .434 M Cr^{+6}	C_4
	10.0 w/o ≈ 3.0 M Ni^{++}	C_7	4.12 w/o ≈ 3.0 M Cr_2O_7 .868 M Cr^{+6}	C_6
			6.17 w/o ≈ 4.5 M Cr_2O_7 1.3 M Cr^{+6}	C_8
			10.0 w/o ≈ 7.3 M Cr_2O_7 3.5 M Cr^{+6}	C_{10}

```
24   -3   6   5   0   1   6   -1
 |    |   |   |   |   |   |    |
 |    |   |   |   |   |   |    └─ Sample No. with indicated
 |    |   |   |   |   |   |       treatment.
 |    |   |   |   |   |   └─ Na₂Cr₂O₇ Seal Conc. C₆
 |    |   |   |   |   └─ Ni(C₂H₃O₂)₂ Seal Conc. C₁
 |    |   |   |   └─ Na₂Cr₂O₇ Seal Time: τ₁₀
 |    |   |   └─ Ni(C₂H₃O₂)₂ Seal Time: τ₅
 |    |   └─ Na₂Cr₂O₇ Seal Temp. °F, T₆
 |    └─ Ni(C₂H₃O₂)₂ Seal Temp. °F, T₃
 └─ Alloy Designation:  2024-T3
```

The diagram labels read, from top to bottom:

- Sample No. with indicated treatment.
- $Na_2Cr_2O_7$ Seal Conc. C_6
- $Ni(C_2H_3O_2)_2$ Seal Conc. C_1
- $Na_2Cr_2O_7$ Seal Time: τ_{10}
- $Ni(C_2H_3O_2)_2$ Seal Time: τ_5
- $Na_2Cr_2O_7$ Seal Temp. °F, T_6
- $Ni(C_2H_3O_2)_2$ Seal Temp. °F, T_3
- Alloy Designation: 2024-T3

    b. __Sealing Procedure__. In order to minimize possible process variations other than time, temperature and seal solution concentration, all sealing was done on a laboratory scale. The equipment used is shown in Figure 7. Seal solutions of the appropriate concentration were made up using distilled water and reagent grade chemicals. Each lot of solution was replaced after the sealing of fifty 3" x 10" test coupons to minimize concentration changes or possible contamination. The process steps used are summarized in Figure 8.

After sealing, all samples were aged a minimum of 96 hours prior to salt fog exposure. Before exposing to the salt fog, a 1/2" x 3" tab was sheared from the bottom end of each 3" x 10" coupon for coating weight determination and X-ray fluorescent analysis of the Ni/Cr ratio.

Identical procedures were used in the preparation of paint adhesion and fatigue test samples.

The test series to study the influence of thinner anodic coatings on corrosion resistance were prepared as described but with shorter anodizing times.

    c. __Salt Fog Corrosion Evaluation__. Aluminum alloy test coupons (3" x 10" x 0.040") of 2024-T3, 7075-T6, 7178-T6 and 7079-T6 anodized as sealed under the process conditions defined by Factorial Matrix Nos. 1 or 2, were exposed to 5% NaCl salt fog in accordance with Federal Test Method 141.

To accommodate the large number of samples used in this investigation, two 30 cubic foot salt fog cabinets were fitted with slotted Lucite racks to support the test coupons as required. This arrangement is shown in Figure 9.

Operating conditions and NaCl concentrations were monitored daily by the Aeronutronic Quality Control Department to insure that all necessary parameters required by Federal Test Method 141 were met.
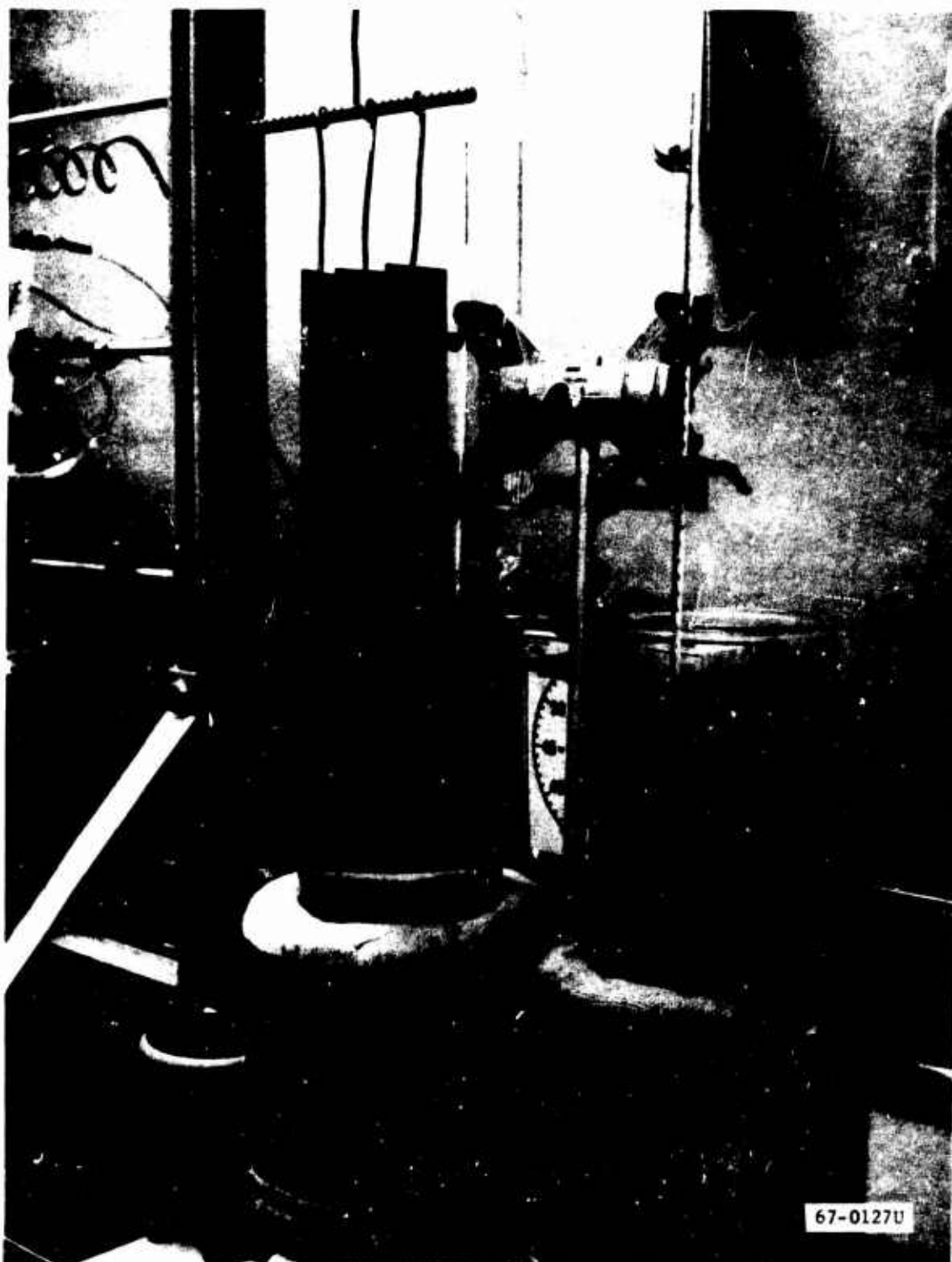
FIGURE 7. TEMPERATURE CONTROLLED NICKEL ACETATE AND
SODIUM DICHROMATE SEALING APPARATUS

Dry 3" x 10" Coupons From Anodizing

Maximum Aging Time Prior To Seal - 24 Hrs.

↓

A.R. Ni(C$_2$H$_3$O$_2$)$_2$
Distilled Water
$\longrightarrow$
Ni(C$_2$H$_3$O$_2$)$_2$ Seal Solution

Temp. Control to $\pm$1°F

Time Control to $\pm$2 Sec.

↓

Overflow Rinse

↓

Distilled Water Rinse

↓

A.R. Na$_2$Cr$_2$O$_7$
Distilled Water
$\longrightarrow$
Na$_2$Cr$_2$O$_7$ Seal Soln.

Temp. Control to $\pm$1°F

Time Control to $\pm$2 Sec.

↓

Overflow Rinse

↓

Distilled Water Rinse

↓

Oven Dry @ 160°F $\pm$5°F

↓

To Salt Spray
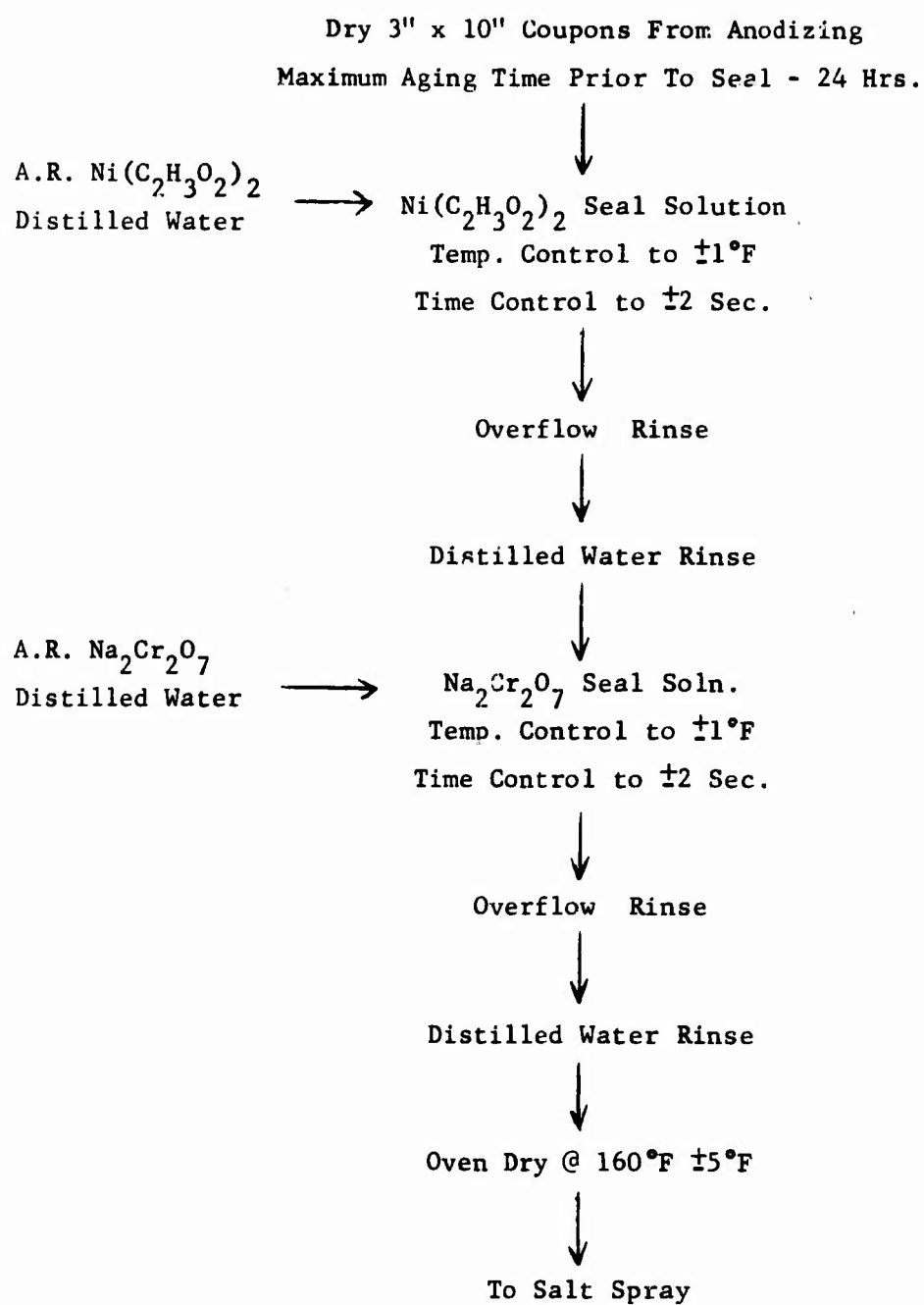
FIGURE 8.   DUPLEX SEALING PROCESSING SEQUENCE

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67-0410U
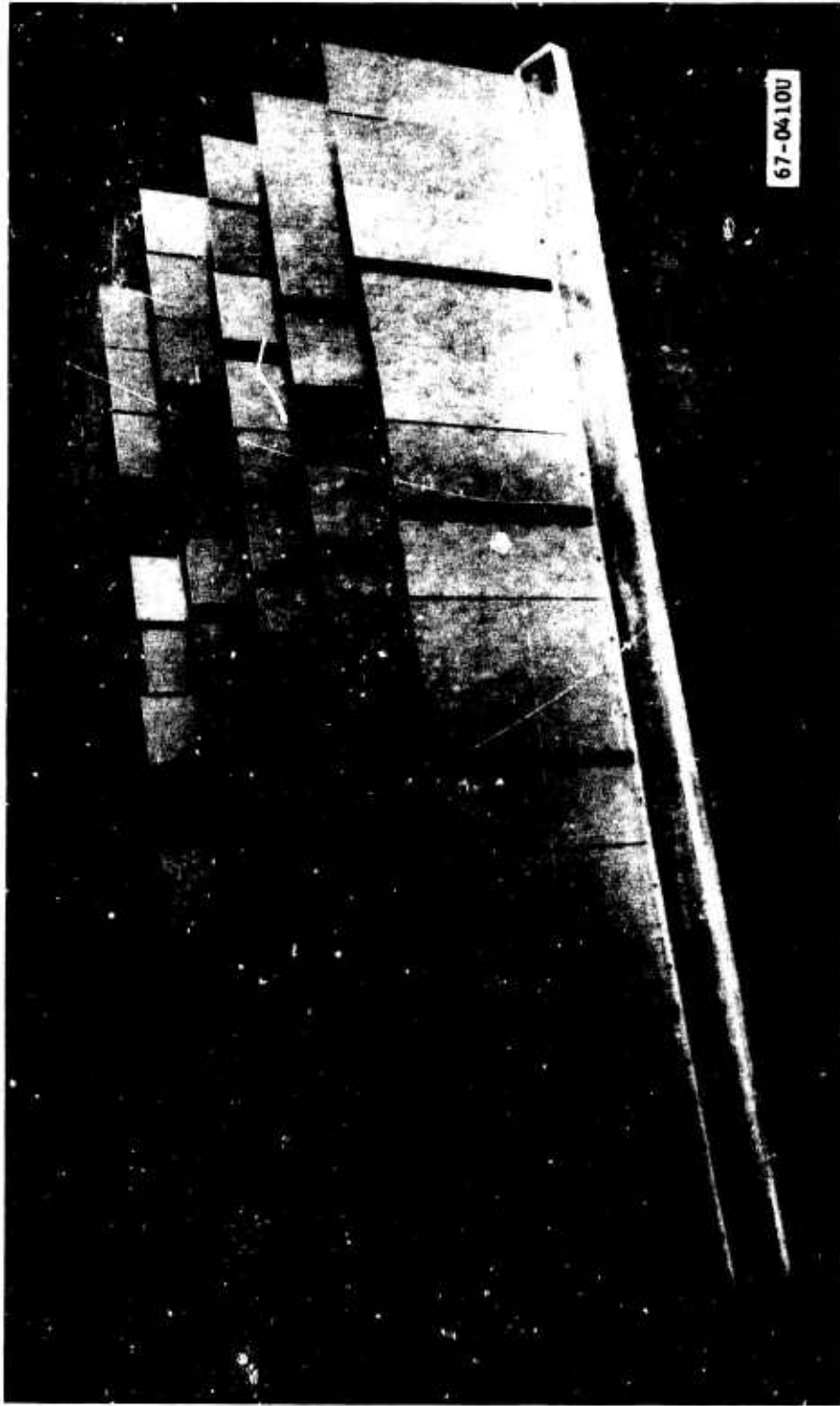
FIGURE 9. LUCITE RACK CONTAINING DUAL SEAL SAMPLES

After each 10-day salt fog exposure, the sealed anodized samples were re-moved, washed with tap water, spray rinsed in distilled or deionized water and air dried prior to corrosion evaluation. After evaluation, the samples were returned to salt fog exposure for an additional 10-day exposure cycle.

d. <u>Corrosion Evaluation</u>. The assessment of corrosion damage is always highly subjective. In this investigation, various techniques were tried in an attempt to quantify the evaluation, but the results achieved were not conclusive.

Failure of the duplex sealed anodic film generally proceeds in the following sequence:

(1) During the first 10-day salt fog exposure, leaching of the chromate ion occurs, reducing the color intensity. This effect is predominant on the upward facing side of the sample. The rate of change of color, i.e., the comparison of the as sealed color versus the color after ten day's exposure appears significant. Samples showing greatest rate of color change have shorter mean failure times.

(2) Small discolored areas or micropits detectable at 4 to 8X magnification increase in frequency and size as salt fog exposure times are increased.

(3) Break-through of the anodic film in localized areas produces a macropit and characteristic white corrosion products of the aluminum alloy.

The first method used to assess corrosion utilized a modified "blood-counting" procedure in which a 1/4" square grid of No. 40 copper wires supported on a milled aluminum frame was overlaid on the 3" x 10" test coupons. (See Figure 10.) The number of squares containing micropits could be counted rapidly at 8X magnification and an average number of pits per square estimated.

The second method used was that of evaluating the rate of change of color. Color comparison standards were prepared using 2024-T3 alloy, sulfuric acid anodized for 30 minutes and then sealed in 5% $Na_2Cr_2O_7$ at 212°F for various times. Process conditions for preparation of the color comparison standards are given in Table VIII.

-25-
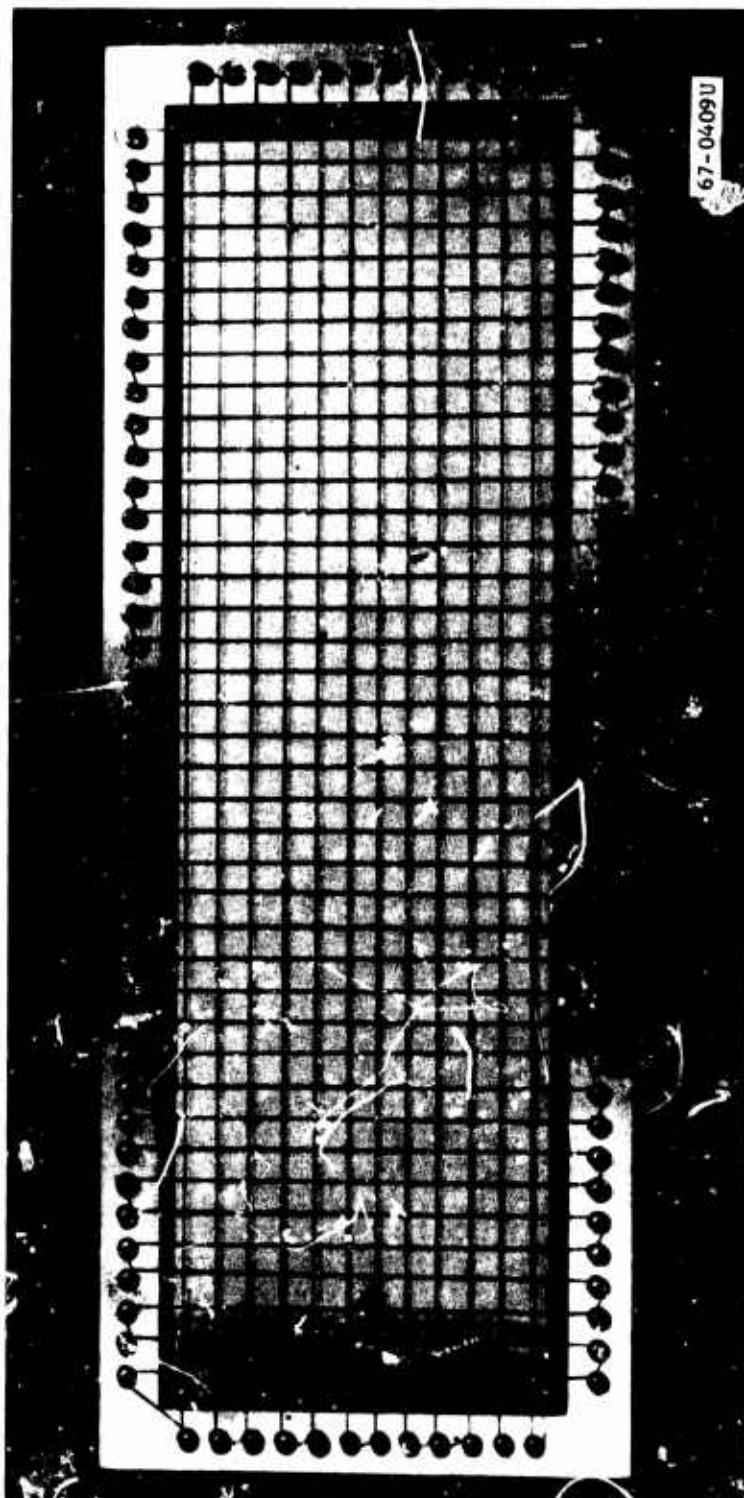
FIGURE 10. GRID OF COPPER WIRE ON MILLED ALUMINUM FRAME

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TABLE VIII. COLOR COMPARISON STANDARDS
2024-T3, TYPE II, 30-MINUTE
ANODIZE TIME.

Color No.	Seal Time, 5% $Na_2Cr_2O_7$ @ 212°F
0	Water Seal at 212°F
1	0.5 sec.
2	1.0 sec.
3	30.0 sec.
4	2.0 min.
5	5.0 min.
6	10.0 min.
7	15.0 min.
8	30.0 min.
9	1.0 hr.
10	2.0 hr.

The third method of evaluation was the appearance of massive corrosion identified by the presence of typical white corrosion products on the surface of the test coupon. One such spot per panel was judged failure in this analysis.

The number of 10-day cycles to failure are presented in Tables IX to XX, using the factorial design arrangement to simplify the analysis. Each table is for the identified concentration of the $Ni(C_2H_3O_2)_2$ and $Na_2Cr_2O_7$ arranged in increasing order of concentration. Since each alloy will be considered separately, the tables are grouped by alloy. As statistical terminology will be used in the analysis of these data, the following definitions are presented for clarity.

Factor:

Any feature of the experimental conditions which may be assigned at will from one trial to another.

Quantitative Factor:

One whose values can be pre-arranged in order of magnitude— in this experiment, temperature, T, seal immersion time, , seal solution concentration, C, and alloy composition.

Qualitative Factor:

One whose values can be arranged in order of magnitude, but no a priori reasons for such an arrangement exists.

Levels of Factors:

Preselected values chosen for a trial; for example, 180°F, 200°F and 212°F.

Treatment:

Set of levels employed in a given trial.

Response:

Numerical results of a trial based on a given treatment— in this series, the number of 10-day cycles in 5% NaCl salt fog to failure.

Effect of a Factor:

Change in response produced by a change in the level of the factor.

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Other terminology will be required, but it will be defined at the first point of usage for reader convenience.

Initially, let us consider only one alloy system for detailed analysis. The other three alloys will be evaluated by identical methods, but only the summary findings will be presented.

As a first approximation of the response to the various levels of factors, the method of averaging is useful. This entails simply determination of the average response of a single factor at all levels of the other factors of the experiment. For example, using Table IX, we have the average response of T_1 ($Ni(C_2H_3O_2)_2$) seal temperature over all levels of temperature of the dichromate seal, at all immersion times for the indicated concentration of the seal solutions (C_1C_6 for Table IX).

Thus,

$$T_{1_{(C_1C_6)}} = \frac{1}{27} (21 + 21 + 21 + \cdots + 15) + (21 + 19 + 6 \cdots + 21) + (21 + 8 + \cdots 21)$$

$$T_{1_{(C_1C_6)}} = 15.5$$

This process is repeated for each factor at various concentrations of the seal solution. The summary results are presented using this method in Tables XXI, XXII and XXIII.

TABLE IX. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 2024-T3, C_1C_6, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5		Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	21	21	21	21	7	15	21	21	10	17.6
	τ_6	21	19	8	21	7	21	21	21	10	16.6
	τ_{10}	21	6	7	6	6	11	21	21	6	11.7
τ_5	τ_2	21	4	19	21	21	10	18	7	6	14.1
	τ_6	5	8	8	21	15	15	21	12	6	12.3
	τ_{10}	18	12	18	17	7	12	7	6	3	11.1
τ_9	τ_2	21	12	21	21	19	21	21	8	21	18.3
	τ_6	19	21	8	19	8	14	21	7	21	15.3
	τ_{10}	15	21	21	21	8	21	21	21	7	17.3
Average Response:		18.0	13.8	14.6	18.7	10.9	15.6	19.1	13.8	10.0	

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TABLE X.   NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 2024-T3, C_1C_8, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
T_1	τ_2	17	3	18	13	10	21	18	18	9	14.1
	τ_6	3	5	9	19	21	21	19	9	3	12.1
	τ_{10}	9	3	3	5	9	21	21	4	9	9.3
T_5	τ_2	3	5	3	5	9	9	18	21	21	10.4
	τ_6	3	5	3	5	9	21	17	4	6	8.1
	τ_{10}	3	3	5	3	21	21	9	6	16	9.3
T_9	τ_2	5	5	9	6	21	21	21	21	8	13.0
	τ_6	3	5	3	5	21	21	21	21	21	13.4
	τ_{10}	3	5	3	9	18	21	18	21	21	13.2
Average Response:		5.4	4.3	6.2	7.8	15.4	19.7	18.0	13.8	12.7	

TABLE XI. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 2024-T3, C_3C_6, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	19	4	6	5	4	4	21	4	9	8.4
	τ_6	19	4	4	4	5	6	6	6	5	6.6
	τ_{10}	21	4	4	4	4	6	21	5	6	8.3
τ_5	τ_2	21	4	4	4	4	4	6	6	6	6.6
	τ_6	21	4	8	4	4	5	21	4	6	8.6
	τ_{10}	13	4	4	5	5	6	5	21	6	7.7
τ_9	τ_2	21	4	4	17	21	21	13	18	4	13.7
	τ_6	6	5	4	6	12	21	13	4	4	8.3
	τ_{10}	6	4	5	21	12	21	21	21	19	14.4
Average Response:		16.3	4.1	4.8	7.8	7.9	10.4	14.1	9.9	7.2	

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TABLE XII. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 2024-T3, C_3C_8, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	15	21	5	17	21	3	21	3	13	13.2
	τ_6	4	21	3	21	9	3	8	3	16	9.8
	τ_{10}	3	3	6	3	21	21	18	3	21	11.0
τ_5	τ_2	3	3	4	3	18	3	3	16	5	6.4
	τ_6	4	4	3	3	21	3	21	6	21	9.6
	τ_{10}	4	21	3	3	21	3	21	21	18	12.8
τ_9	τ_2	9	21	21	21	16	13	4	21	13	15.4
	τ_6	21	21	21	4	21	19	21	16	12	17.3
	τ_{10}	3	21	3	21	21	16	4	21	12	13.6
Average Response:		7.3	15.1	7.7	10.7	18.8	9.3	13.4	12.2	14.6	

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TABLE XIII. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7075-T6, C_1C_6, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	7	21	21	21	5	21	21	21	7	16.1
	τ_6	19	21	7	9	4	19	21	11	3	12.7
	τ_{10}	19	9	21	21	5	7	6	5	12	11.7
τ_5	τ_2	21	21	21	21	6	7	6	3	3	12.1
	τ_6	8	21	21	21	7	7	4	3	4	10.7
	τ_{10}	21	21	21	13	7	7	6	3	6	11.7
τ_9	τ_2	21	21	21	21	7	7	19	8	18	15.9
	τ_6	19	21	7	21	9	15	5	21	6	13.8
	τ_{10}	15	21	21	21	10	8	8	6	7	13.0
Average Response:		11.7	19.7	17.9	18.8	6.7	10.9	10.7	9.0	7.3	

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TABLE XIV. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7075-T6, C_1C_8, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	21	3	9	9	21	21	21	21	9	15.0
	τ_6	6	.5	5	9	21	6	21	21	9	11.4
	τ_{10}	9	21	3	5	6	21	6	9	8	9.8
τ_5	τ_2	21	3	5	6	9	21	9	21	17	12.4
	τ_6	21	9	3	5	10	6	9	9	5	8.5
	τ_{10}	3	3	3	5	6	5	9	6	6	5.1
τ_9	τ_2	9	7	5	9	18	21	19	9	9	11.8
	τ_6	9	9	21	6	9	21	21	21	9	14.0
	τ_{10}	5	9	ᴱ	9	9	21	21	21	9	12.1
Average Response:		11.6	7.7	6.6	7.0	12.1	15.9	15.1	15.3	9.0	

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TABLE XV. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7075-T6, C_3C_6, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	21	21	4	5	6	21	21	21	4	13.8
	τ_6	21.	4	4	4	4	5	5	6	5	8.3
	τ_{10}	5	4	5	4	6	5	21	5	6	6.8
τ_5	τ_2	17	4	4	4	5	5	5	21	6	7.9
	τ_6	5	4	21	4	5	5	8	6	7	7.2
	τ_{10}	5	4	4	4	7	6	5	21	5	6.8
τ_9	τ_2	5	5	4	21	13	21	13	18	19	13.2
	τ_6	5	4	4	5	21	21	13	21	21	12.8
	τ_{10}	5	5	4	21	9	21	19	21	21	14.0
Average Response:		5.9	6.1	6.0	8.0	10.3	12.2	12.2	15.6	10.4	

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TABLE XVI. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7075-T6, C_3C_8, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	4	21	21	4	6	3	3	3	3	7.6
	τ_6	3	21	3	21	3	3	3	3	14	8.2
	τ_{10}	3	3	3	21	3	3	3	3	4	5.1
τ_5	τ_2	4	3	3	3	6	3	3	10	21	6.2
	τ_6	3	21	3	3	3	3	7	21	3	7.4
	τ_{10}	3	3	3	3	3	3	4	21	21	7.1
τ_9	τ_2	4	4	21	3	21	3	21	21	4	11.3
	τ_6	4	4	8	5	21	21	21	21	21	14.0
	τ_{10}	3	21	21	3	21	5	21	3	12	12.2
Average Response:		3.4	11.2	9.6	7.3	9.7	5.2	9.6	11.8	11.4	

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TABLE XVII. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7178-T6, C_1C_6, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	11	3	21	21	21	21	21	21	11	16.8
	τ_6	14	21	12	21	7	?	21	19	6	15.6
	τ_{10}	21	3	21	21	6	7	21	8	12	14.7
τ_5	τ_2	21	21	18	21	15	8	19	4	7	14.9
	τ_6	3	21	21	21	21	18	21	7	8	15.7
	τ_{10}	12	16	19	13	19	21	21	9	7	15.2
τ_9	τ_2	17	14	21	21	18	21	21	11	18	18.0
	τ_6	11	21	19	21	19	21	21	10	18	17.9
	τ_{10}	21	7	21	21	21	21	21	11	14	17.6
Average Response:		14.6	14.1	19.2	20.1	16.3	17.7	20.8	12.2	11.2	

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TABLE XVIII. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7178-T6, C_1C_8, 5% NaCl, FEDERAL TEST METHOD 14i.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
T_1	τ_2	9	5	21	18	21	21	21	21	21	17.6
	τ_6	21	5	3	9	21	21	21	9	6	12.9
	τ_{10}	9	21	3	9	7	21	21	21	9	13.4
T_5	τ_2	9	9	9	7	9	21	21	21	9	12.8
	τ_6	3	3	3	5	10	9	21	7	6	7.4
	τ_{10}	3	3	5	3	6	21	9	7	7	7.1
T_9	τ_2	10	3	9	9	21	21	21	21	21	15.1
	τ_6	7	9	9	9	21	21	21	21	18	15.1
	τ_{10}	9	3	3	9	21	21	21	21	21	14.3
Average Response:		8.9	6.8	7.2	8.7	15.2	19.7	19.7	16.6	13.1	

TABLE XIX. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7178-T6, C_3C_6, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	19	4	8	5	5	5	4	6	5	6.8
	τ_6	21	4	4	4	21	4	6	5	4	8.1
	τ_{10}	21	5	4	4	5	5	4	5	4	6.3
τ_5	τ_2	6	4	5	4	21	5	8	6	5	7.2
	τ_6	21	4	4	4	5	5	5	21	6	8.3
	τ_{10}	21	4	4	4	21	5	5	21	6	10.1
τ_9	τ_2	5	4	4	7	21	4	6	4	21	8.4
	τ_6	8	4	4	8	21	4	21	21	21	12.4
	τ_{10}	5	4	4	5	21	4	21	21	21	11.8
Average Response:		14.1	4.1	4.6	5.0	15.7	4.6	8.9	12.2	10.4	

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TABLE XX. NUMBER OF 10-DAY EXPOSURE CYCLES TO FAILURE: 7178-T6, C_3C_8, 5% NaCl, FEDERAL TEST METHOD 141.

		T_1			T_3			T_5			Average Response
		T_2	T_4	T_6	T_2	T_4	T_6	T_2	T_4	T_6	
τ_1	τ_2	21	21	6	21	21	3	21	3	21	15.3
	τ_6	3	21	21	21	21	3	21	4	21	15.1
	τ_{10}	21	3	3	21	21	21	21	21	21	17.0
τ_5	τ_2	3	3	3	3	21	3	21	21	21	11.0
	τ_6	3	21	3	4	21	3	3	3	3	7.1
	τ_{10}	3	4	21	3	21	3	21	21	21	13.1
τ_9	τ_2	4	21	8	21	21	21	21	21	21	17.7
	τ_6	3	21	21	4	21	21.	21	21	21	17.1
	τ_{10}	4	6	21	?.	21	17	21	21	21	17.0
Average Response:		7.2	13.4	11.9	13.2	21.0	10.6	19.0	15.1	19.0	

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TABLE XXI. AVERAGE RESPONSE OF 2024-T3 AT VARIOUS $Ni(C_2H_3O_2)_2$ AND $Na_2Cr_2O_7$ SEAL CONCENTRATIONS AT ALL IMMERSION TIMES AND TEMPERATURES.

	C_1C_6	C_1C_8	C_3C_6	C_3C_8
T_1	15.5	5.3	8.4	10.0
T_3	15.1	14.3	8.7	12.9
T_5	14.3	12.9	10.4	13.4
T_2	18.6	10.4	12.7	10.5
T_4	12.8	11.2	7.3	15.3
T_6	13.4	12.9	7.5	10.5
τ_1	15.3	11.8	7.8	11.3
τ_5	12.5	9.3	7.6	9.6
τ_9	17.0	13.2	12.1	15.4
τ_2	16.7	12.5	9.6	11.7
τ_6	14.7	11.2	7.8	12.0
τ_{10}	13.4	10.6	10.1	12.5
Avg.	14.9	11.3	9.1	12.1

TABLE XXII. AVERAGE RESPONSE OF 7075-T6 AT VARIOUS $Ni(C_2H_3O_2)_2$ AND $Na_2Cr_2O_7$ SEAL CONCENTRATIONS AT ALL IMMERSION TIMES AND TEMPERATURES.

	C_1C_6	C_1C_8	C_3C_6	C_3C_8
T_1	16.4	8.6	7.3	8.1
T_3	12.1	11.6	10.2	7.4
T_5	9.0	13.1	12.7	10.9
T_2	13.7	11.2	10.0	6.8
T_4	11.8	11.7	10.6	10.9
T_6	12.0	10.5	9.5	8.7
τ_1	13.5	12.1	9.6	7.0
τ_5	11.5	8.7	7.3	6.9
τ_9	14.2	12.6	13.3	12.5
τ_2	14.7	13.1	11.6	8.4
τ_6	12.4	11.3	9.4	9.8
τ_{10}	12.1	9.0	9.2	8.1
Avg.	12.8	11.1	10.0	8.8

TABLE XXIII.   AVERAGE RESPONSE OF 7178-T6 AT VARIOUS $Ni(C_2H_3O_2)_2$ AND $Na_2Cr_2O_7$ SEAL CONCENTRATIONS AT ALL IMMERSION TIMES AND TEMPERATURES.

	C_1C_6	C_1C_8	C_3C_6	C_3C_8
T_1	16.0	7.6	9.3	10.8
T_3	18.0	14.5	8.4	14.9
T_5	14.7	16.5	10.5	17.7
T_2	18.5	12.4	9.3	13.1
T_4	14.2	12.9	10.7	16.5
T_6	16.0	13.2	6.5	13.8
τ_1	15.7	14.6	7.1	15.8
τ_5	15.3	9.1	8.5	10.4
τ_9	17.8	14.8	10.9	17.3
τ_2	16.6	15.2	7.5	14.7
τ_6	16.4	11.8	9.6	13.1
τ_{10}	15.8	11.6	9.4	15.7
Avg.	16.2	12.8	8.9	14.4

Summarizing the average response, we have

	C_1C_6	C_1C_8	C_3C_6	C_3C_8
2024-T3	14.9	11.3	9.6	12.1
7075-T6	12.8	11.1	10.0	8.8
7178-T6	16.3	12.9	9.0	14.5

The corrosion resistance of all three alloys is substantially better under the seal solution concentration levels C_1C_6 (1.25 w/o $Ni(C_2H_3O_2)_2$ 4.12 w/o $Na_2Cr_2O_7$) than at C_1C_8 or C_3C_6. The C_1C_6 condition is somewhat better than C_3C_8, but results are not as sharply defined.

It is interesting to note that the response of all three alloys is approximately the same for various levels of concentration. The only exception is the poor response of 7075-T6 in C_3C_8.

Using this method, some preliminary idea of optimum process conditions can be obtained by selecting various combinations of the process variables based on the average summed responses. These selections are presented in Table XXIV.

To fully assess the statistical significance of the results, it is necessary to perform a more detailed analysis. A large percentage of the corrosion exposure samples had not failed after 5,000 hours exposure (21 ten-day salt fog cycles). However, to quantitatively analyze the results, it was necessary to assume failure at that point.

Since the 2024, 7075 and 7178 alloys appear to respond in an analogous fashion, the statistical significance of the results will be improved by considering the three alloys simultaneously in the factorial analysis.

It is also assumed, based on the results presented above, that treatment combination C_1C_6 is clearly superior to all others investigated and concentration can then be eliminated from the analysis.

TABLE XXIV. SUMMARY OF RESPONSES TO VARIOUS TREATMENT COMBINATIONS

Alloy	Treatment	Σ Resp.	Treatment	Σ Resp.	Treatment	Σ Resp.	Treatment	Σ Resp.
2024-T3	$T_1T_2T_9T_2C_1C_6$	17.0	$T_3T_2T_9T_2C_1C_6$	16.9	$T_1T_6T_9T_2C_1C_6$	15.7	$T_3T_6T_9T_6C_1C_6$	15.6
7075-T6	$T_1T_2T_9T_2C_1C_6$	14.7	$T_1T_6T_9T_2C_1C_6$	14.3	$T_1T_6T_1T_2C_1C_6$	14.2	$T_3T_2T_9T_2C_1C_6$	13.7
7178-T6	$T_3T_2T_9T_2C_1C_6$	17.7	$T_3T_2T_9T_6C_1C_6$	17.7	$T_1T_2T_9T_2C_1C_6$	17.2	$T_3T_2T_1T_2C_1C_6$	17.2

e. <u>Detailed Statistical Analysis</u>. Preliminary analysis of the factorial design used in this study indicated a strong probability of interaction of the various treatments. Because of the long times involved in sample preparation and corrosion evaluation plus interaction effects, the complete factorial design was analyzed using confounding. Confounding is the process by which unimportant comparisons are deliberately confused for the purpose of assessing the more important comparisons with greater precision. Such a procedure is necessary whenever the number of observations capable of being carried out under strictly comparable conditions is less than the number required for the whole design.

Table XXV represents the average responses of the 2024-T3, 7075-T6 and 7173-T6 alloys under each set of process conditions. For example, $a_0 b_0 c_0 d_0$ value of 13 is the average response of samples

$$24\text{-}121216\text{-}1 = 21$$

$$75\text{-}121216\text{-}1 = 7$$

$$78\text{-}121216\text{-}1 = \underline{11}$$

$$39 \div 3 = 13$$

Each average response is rounded to the neares_ integer to simplify the calculations.

In Table XXV, the notations are changed to simplify the identification of the linear and quadratic terms. In addition, standard tables are available for the arrangement sequence of 3^4 factorial designs using the notation in Table XXV.

The method developed by Yates will be used to analyze the data in Table XXV.[28] Table XXVI summarizes the arrangement, treatment combinations and the calculations.

In Table XXVI, Column (1), the treatment combinations are systematically arranged in accordance with the Yates method of analysis. Column (2) is the average response of the 2024-T3, 7075-T6 and 7178-T6 anodized duplex sealed samples. Column (3) is obtained by summing each group of three values in Column (2); i.e., 13 + 21 + 20 = 54; 18 + 5 + 17 = 40; 20 + 19 + 17 = 56, etc. This gives the first 27 values in Column (3). The second group is obtained by the difference between the third number minus the first; i.e., $y_3 - y_1$. For example, treatment combinations d_1, $a_1 d_1$, $a_2 d_1$, etc., are 20-13 = 7; 17-18 = -1; 17-20 = -3, etc. The last 27 numbers of Column (3) are obtained using the values of Column (2) according to the equation $y_1 - 2y_2 + y_3$. For example, treatment combinations d_2, $a_1 d_2$, $a_2 d_2$ are 13-(2 x 21)+ 20 = -9; 18-(2 x 5)+ 17 = 25; 20-(2 x 19)+ 17 = -1, etc. This process is repeated n times where n is the number of factors considered (in this case, 4) to obtain the values in columns (4), (5) and (6).

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TABLE XXV. AVERAGE RESPONSE OF 2024, 7075 AND 7178 AT CONCENTRATION $c_1 c_6$

		$d_0(T_1)$			$d_1(T_3)$			$d_2(T_5)$		
		$c_0(T_2)$	$c_1(T_4)$	$c_2(T_6)$	$c_0(T_2)$	$c_1(T_4)$	$c_2(T_6)$	$c_0(T_2)$	$c_1(T_4)$	$c_2(T_6)$
$a_0(\tau_1)$	$b_0(\tau_2)$	13	15	21	21	11	19	21	21	9
	$b_1(\tau_6)$	18	20	9	17	6	20	21	17	6
	$b_2(\tau_{10})$	20	6	20	16	6	9	16	15	10
$a_1(\tau_5)$	$b_0(\tau_2)$	21	15	19	21	14	8	14	5	5
	$b_1(\tau_6)$	5	17	17	21	14	13	15	7	6
	$b_2(\tau_{10})$	19	16	19	14	11	13	11	6	5
$a_2(\tau_9)$	$b_0(\tau_2)$	20	16	21	21	15	16	20	9	19
	$b_1(\tau_6)$	17	21	11	20	12	17	16	13	15
	$b_2(\tau_{10})$	17	16	21	21	13	17	17	13	9

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TABLE XXVI. YATES' ANALYSIS OF AVERAGE RESPONSE DATA FROM TABLE XXV.

(1)	(2)	(3)	(4)	(5)	(6)	Divisor	
1	13	54	150	450	1197	-	
a_1	21	40	142	406	40	54	26.6
a_2	20	56	158	341	144	162	12.8
b_1	18	46	172	18	-54	54	54.0
$a_1 b_1$	5	58	102	27	20	36	11.1
$a_2 b_1$	17	38	132	-5	-30	108	8.3
b_2	20	61	151	6	24	162	3.6
$a_1 b_2$	19	37	106	19	16	108	2.4
$a_2 b_2$	17	60	84	119	6	324	.1
c_1	15	63	3	-7	-99	54	181.5
$a_1 c_1$	15	58	12	-26	17	36	8.0
$a_2 c_1$	16	51	3	-21	9	108	.75
$b_1 c_1$	20	40	8	0	7	36	1.36
$a_1 b_1 c_1$	17	32	17	19	3	24	.38
$a_2 b_1 c_1$	21	30	2	1	-44	72	26.8
$b_2 c_1$	6	43	-5	-4	9	108	.75
$a_1 b_2 c_1$	16	50	-18	-11	-16	72	3.6
$a_2 b_2 c_1$	16	39	18	-15	72	216	24.0
c_2	21	55	15	45	147	162	133.4
$a_1 c_2$	19	52	-2	-14	7	108	.45
$a_2 c_2$	21	44	-7	-7	-21	324	1.36
$b_1 c_2$	9	35	4	12	+4	108	.14
$a_1 b_1 c_2$	17	37	-15	9	-46	72	29.3
$a_2 b_1 c_2$	11	34	30	-5	18	216	1.5
$b_2 c_2$	20	33	31	-48	117	324	42.2
$a_1 b_2 c_2$	19	27	52	31	10	216	.46
$a_2 b_2 c_2$	21	24	36	23	18	648	.5

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TABLE XXVI. (CONTINUED)

(1)	(2)	(3)	(4)	(5)	(6)		Divisor
d_1	21	7	2	8	-1053	54	20,533
$a_1 d_1$	21	-1	-8	-40	24	36	16.0
$a_2 d_1$	21	-3	-1	-67	-18	324	1.0
$b_1 d_1$	17	1	-12	0	108	36	324.0
$a_1 b_1 d_1$	21	1	-10	-6	-51	24	108.4
$a_2 b_1 d_1$	20	10	-4	23	63	72	55.13
$b_2 d_1$	16	0	-11	-22	-168	108	261.3
$a_1 b_2 d_1$	14	2	-1	26	14	72	2.7
$a_2 b_2 d_1$	21	1	-9	5	-99	216	45.4
$c_1 d_1$	11	0	-10	-3	-75	36	156.25
$a_1 c_1 d_1$	14	3	9	+8	23	24	22.0
$a_2 c_1 d_1$	15	5	1	2	27	72	10.1
$b_1 c_1 d_1$	6	4	5	11	5	24	1.0
$a_1 b_1 c_1 d_1$	14	6	3	6	-24	16	36.0
$a_2 b_1 c_1 d_1$	12	7	11	-13	+2	48	.08
$b_2 c_1 d_1$	6	-3	2	-9	-9	72	1.1
$a_1 b_2 c_1 d_1$	11	-3	10	-28	-10	48	2.1
$a_2 b_2 c_1 d_1$	13	8	-11	-7	-96	144	64.
$c_2 d_1$	19	-1	8	17	-1	108	0.009
$a_1 c_2 d_1$	8	-5	-11	-16	67	324	13.9
$a_2 c_2 d_1$	16	1	-1	8	-49	216	11.1
$b_1 c_2 d_1$	20	-12	9	-9	-34	72	16.1
$a_1 b_1 c_2 d_1$	13	-4	-1	12	-2	48	.08
$a_2 b_1 c_2 d_1$	17	-2	-19	-19	-32	144	7.1
$b_2 c_2 d_1$	9	10	-2	95	-133	216	81.9
$a_1 b_2 c_2 d_1$	13	9	-4	-22	+28	144	5.4
$a_2 b_2 c_2 d_1$	17	-1	-9	-1	-10	432	.23

TABLE XXVI. (CONTINUED)

(1)	(2)	(3)	(4)	(5)	(6)	Divisor	
d_2	21	-9	30	24	-21	162	2.72
a_1d_2	14	25	-32	100	-41	108	15.6
a_2d_2	20	-1	47	23	87	324	19.8
b_1d_2	21	1	-2	-18	24	108	5.3
$a_1b_1d_2$	15	7	6	-24	-37	72	19.0
$a_2b_1d_2$	16	-10	-18	49	3	216	.04
b_2d_2	16	4	-5	12	66	324	13.4
$a_1b_2d_2$	11	-14	-5	4	-11	216	.56
$a_2b_2d_2$	17	3	3	-37	-87	648	11.7
c_1d_2	21	0	6	17	21	108	4.1
$a_1c_1d_2$	5	-5	9	4	35	72	16.3
$a_2c_1d_2$	9	9	-3	-17	-69	216	22.0
$b_1c_1d_2$	17	-2	-1	-27	-17	72	4.0
$a_1b_1c_1d_2$	7	-10	-1	10	-14	48	4.1
$a_2b_1c_1d_2$	13	-3	+11	-29	38	144	10.0
$b_2c_1d_2$	15	19	+10	29	57	216	15.0
$a_1b_2c_1d_2$	6	11	-6	-8	-52	144	18.8
$a_2b_2c_1d_2$	13	0	-9	-3	138	432	44.0
c_2d_2	9	13	-60	141	-153	324	72.2
$a_1c_2d_2$	5	7	-25	-32	79	216	28.9
$a_2c_2d_2$	19	11	35	8	-33	648	1.7
$b_1c_2d_2$	6	20	19	-15	-9	216	.375
$a_1b_1c_2d_2$	6	16	15	12	-76	144	40.1
$a_2b_1c_2d_2$	15	16	-3	13	42	432	4.1
$b_2c_2d_2$	10	18	10	21	213	648	70.0
$a_1b_2c_2d_2$	5	9	4	-14	-26	432	1.6
$a_2b_2c_2d_2$	9	9	9	11	60	296	2.8

The divisor in Column 7 can be shown to be given by the formula

Divisor $= 2^m 3^{n-p}$

where:

m = order of interaction.

p = number of linear terms in the interaction,
        e.g., identified by subscript (1).

n = number of factors examined.

The analysis of variance of Table XXVI is given in Table XXVII. The variance ratio is useful in the assessment of the statistical significance of the values obtained for the main effect and two and three factor interactions. Usually, the higher level interactions are relatively small and can be used to determine the error and statistical significance. In this case, a number of four factor interactions has higher than expected values and, hence, tend to reduce the statistical significance of the results when evaluated by the "F" test. One of the problems of these data is the fact that even after 210 days exposure (5,000 hours) an unusually large number of the test coupons had not failed. As was pointed out earlier, there is no a priori way that a quantitative estimate can be made of their time to failure. Thus, grouping this large number of samples at 21, i.e., 210 days exposure, produces an abnormal statistical distribution in the time to failure.

In spite of this problem, a number of significant features of duplex sealed sulfuric acid anodized, high strength aluminum alloys can be determined.

First using the "F" test to determine the statistical significance, each treatment combination involving 1, 2 or 3 factors has one degree of freedom; hence, $\emptyset_1 = 1$. Summing the 4 factor interactions, 16 degrees of freedom are present; hence, $\emptyset = 16$. From tables of the Probability Points of the Variance Ratio Tables (F - Distribution) for $\emptyset_1/\emptyset_2 = 1/16$, we have[29]

Probability Point	F Value
(P)	
0.1	3.05
0.05	4.49
0.01	8.53

Thus, the variance ratio will be highly significant when the variance ratio is equal to or greater than

$$F \times \frac{\text{Mean Square of Four Factor Interaction}}{\emptyset_2}$$

$$8.53 \times 15.03 = 128.2 \qquad 1\% \text{ level}$$

$$4.49 \times 15.03 = 67.5 \qquad 5\% \text{ level}$$

$$3.05 \times 15.03 = 45.8 \qquad 10\% \text{ level}$$

Examining the data given in Table XXVII for the analysis of variance, it is immediately apparent that the seal temperature of the $Ni(C_2H_3O_2)_2$ is highly significant in the corrosion resistance of the duplex sealed anodized alloys. The variance ratio of 1366 is approximately one order of magnitude greater than the required value of 128.2 for the 1% level. Since the value of d_1 in Column (6) of Table XXVI is a large negative number, the higher levels of $Ni(C_2H_3O_2)_2$ seal temperatures have a very adverse effect on the corrosion resistance of the duplex sealed alloys. This result was at least partially anticipated from the predominance of the T_1 condition in the treatment combinations shown in Table XXIV. This finding suggests that nickel acetate seal temperatures below 180°F, the lowest value examined in this study, may be even better.

The consequence of a high nickel acetate seal temperature is evident from the X-ray fluorescent analysis for chromium and nickel of the duplex sealed samples. These data for C_1C_6 (1.25 w/o $Ni(C_2H_3O_2)_2$ and 4.12 w/o $Na_2Cr_2O_7$ seal solutions) are summarized in Table XXVIII.

The nickel concentration of the sealed films is approximately constant at 180°F to 212°F for comparable immersion times as shown in Figure 11. The nickel concentration increases very rapidly with immersion time following the general equation

$$e^{C_{Ni}} = k\, e^{T_{Ni}}$$

Chromium is also very rapidly reactant with, or is chemisorbed by, the anodic film; however, the maximum concentration reached is very dependent on the nickel acetate seal temperature.

The treatment combinations 16-5016 and 56-9016 are excellent examples of this effect. Thus, as the nickel acetate seal temperature is increased, the chromium concentration decreases drastically. An increase in $Ni(C_2H_3O_2)_2$ seal temperature from 180°F to 212°F decreases the chromium concentration about one order of magnitude.

X-ray fluorescent analysis data as well as the analysis of variance of the factorial design clearly show that $Na_2Cr_2O_7$ immersion time and temperature a relatively unimportant in terms of corrosion performance over the range of variables investigated.

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TABLE XXVII. ANALYSIS CF VARIANCE

Main Effect		Mean Square Divisor	Variance Ratio
$Ni(C_2H_3O_2)_2$	Linear a_1	26.6	1.87
	Quadratic a_2	128.0	8.5
$Na_2Cr_2O_7$	Linear b_1	54.0	3.6
	Quadratic b_2	3.6	0.2
$T_{Na_2Cr_2O_7}$	Linear c_1	181.5	12.07
	Quadratic c_2	133.4	8.87
$T_{Ni(C_2H_3O_2)}$	Linear d_1	20,533.	1366.
	Quadratic d_2	2.72	.18

Two Factor Interactions:

$L_{Ni} \times L_{Cr}$	a_1b_1	11.1	.7
$Q_{Ni} \times L_{Cr}$	a_2b_1	8.3	.6
$L_{Ni} \times Q_{Cr}$	a_1b_2	2.4	.2
$Q_{Ni} \times Q_{Cr}$	a_2b_2	0.1	.06
$L_{Ni} \times L_{T_{Cr}}$	a_1c_1	8.0	5.3
$Q_{Ni} \times L_{T_{Cr}}$	a_2c_1	.75	0.05
$L_{Ni} \times Q_{T_{Cr}}$	a_1c_2	.45	0.03
$Q_{Ni} \times Q_{T_{Cr}}$	a_2c_2	1.36	0.09

TABLE XXVII. (CONTINUED)

Two Factor Interactions:		Mean Square Divisor	Variance Ratio
$L_{Ni} \times L_{T_{Ni}}$	$a_1 d_1$	16.0	1.1
$Q_{Ni} \times L_{T_{Ni}}$	$a_2 d_1$	1.0	0.07
$L_{Ni} \times Q_{T_{Ni}}$	$a_1 d_2$	15.6	1.0
$Q_{Ni} \times Q_{T_{Ni}}$	$a_2 d_2$	19.8	1.3
$L_{Cr} \times L_{T_{Cr}}$	$b_1 c_1$	1.36	0.09
$Q_{Cr} \times L_{T_{Cr}}$	$b_2 c_1$	.75	0.05
$L_{Cr} \times Q_{T_{Cr}}$	$b_1 c_2$	.14	0.01
$Q_{Cr} \times Q_{T_{Cr}}$	$b_2 c_2$	42.2	2.8
$L_{Cr} \times L_{T_{Ni}}$	$b_1 d_1$	324.	21.5
$Q_{Cr} \times L_{T_{Ni}}$	$b_2 d_1$	261.	17.3
$L_{Cr} \times Q_{T_{Ni}}$	$b_1 d_2$	5.3	.35
$Q_{Cr} \times Q_{T_{Ni}}$	$b_2 d_2$	13.4	.9
$L_{T_{Cr}} \times L_{T_{Ni}}$	$c_1 d_1$	156.2	10.4
$Q_{T_{Cr}} \times L_{T_{Ni}}$	$c_2 d_1$	0.01	0

TABLE XXVII. (CONTINUED)

Two Factor Interactions:		Mean Square Divisor	Variance Ratio
$L_{T_{Cr}} \times Q_{T_{Ni}}$	$c_1 d_2$	4.1	.27
$Q_{T_{Cr}} \times Q_{T_{Ni}}$	$c_2 d_2$	72.2	4.8

Three Factor Interactions:

$L_{Ni} \times L_{Cr} \times L_{T_{Cr}}$	$a_1 b_1 c_1$	.38	0.03
$L_{Ni} \times L_{Cr} \times Q_{T_{Cr}}$	$a_1 b_1 c_2$	29.3	1.95
$L_{Ni} \times Q_{Cr} \times L_{T_{Cr}}$	$a_1 b_2 c_1$	3.6	0.2
$L_{Ni} \times Q_{Cr} \times Q_{T_{Cr}}$	$a_1 b_2 c_2$	.46	0.03
$Q_{Ni} \times L_{Cr} \times L_{T_{Cr}}$	$a_2 b_1 c_1$	26.8	1.78
$Q_{Ni} \times L_{Cr} \times Q_{T_{Cr}}$	$a_2 b_1 c_2$	1.5	0.1
$Q_{Ni} \times Q_{Cr} \times L_{T_{Cr}}$	$a_2 b_2 c_1$	24.0	1.6
$Q_{Ni} \times Q_{Cr} \times Q_{T_{Cr}}$	$a_2 b_2 c_2$	.5	0.03
$L_{Ni} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$a_1 c_1 d_1$	22.	1.5
$L_{Ni} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$a_1 c_1 d_2$	16.3	1.1
$L_{Ni} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$a_1 c_2 d_1$	13.9	0.9
$L_{Ni} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$a_1 c_2 d_2$	28.9	1.9

TABLE XXVII. (CONTINUED)

Three Factor Interactions:		Mean Square Divisor	Variance Ratio
$Q_{Ni} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$a_2c_1d_1$	10.1	0.7
$Q_{Ni} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$a_2c_1d_2$	22.0	1.5
$Q_{Ni} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$a_2c_2d_1$	11.1	0.7
$Q_{Ni} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$a_2c_2d_2$	1.7	0.1
$L_{Ni} \times L_{Cr} \times L_{T_{Ni}}$	$a_1b_1d_1$	108.4	7.2
$L_{Ni} \times L_{Cr} \times Q_{T_{Ni}}$	$a_1b_1d_2$	19.0	1.3
$L_{Ni} \times Q_{Cr} \times L_{T_{Ni}}$	$a_1b_2d_1$	2.7	0.2
$L_{Ni} \times Q_{Cr} \times Q_{T_{Ni}}$	$a_1b_2d_2$	0.56	0.04
$Q_{Ni} \times L_{Cr} \times L_{T_{Ni}}$	$a_2b_1d_1$	55.1	3.7
$Q_{Ni} \times L_{Cr} \times Q_{T_{Ni}}$	$a_2b_1d_2$	0.04	0
$Q_{Ni} \times Q_{Cr} \times L_{T_{Ni}}$	$a_2b_2d_1$	45.4	3.0
$Q_{Ni} \times Q_{Cr} \times Q_{T_{Ni}}$	$a_2b_2d_2$	11.7	0.8
$L_{Cr} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$b_1c_1d_1$	1.0	0.04
$L_{Cr} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$b_1c_1d_2$	4.0	4.9

TABLE XXVII. (CONTINUED)

Three Factor Interactions:		Mean Square Divisor	Variance Ratio
$L_{Cr} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$b_1c_2d_1$	16.1	0.7
$L_{Cr} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$b_1c_2d_2$	.4	0.02
$Q_{Cr} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$b_2c_1d_1$	1.1	0.04
$Q_{Cr} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$b_2c_1d_2$	15.0	0.31
$Q_{Cr} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$b_2c_2d_1$	81.9	3.3
$Q_{Cr} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$b_2c_2d_2$	70.0	2.8

Four Factor Interactions:

Interaction		Mean Square Divisor
$L_{Ni} \times L_{Cr} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$a_1b_1c_1d_1$	36.0
$Q_{Ni} \times L_{Cr} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$a_2b_1c_1d_1$	0.08
$L_{Ni} \times Q_{Cr} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$a_1b_2c_1d_1$	2.1
$Q_{Ni} \times Q_{Cr} \times L_{T_{Cr}} \times L_{T_{Ni}}$	$a_2b_2c_1d_1$	64.0
$L_{Ni} \times L_{Cr} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$a_1b_1c_2d_1$	0.08
$Q_{Ni} \times L_{Cr} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$a_2b_1c_2d_1$	7.1
$L_{Ni} \times Q_{Cr} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$a_1b_2c_2d_1$	5.4
$Q_{Ni} \times Q_{Cr} \times Q_{T_{Cr}} \times L_{T_{Ni}}$	$a_2b_2c_2d_1$	.23

TABLE XXVII. (CONTINUED)

Four Factor Interactions:		Mean Square Divisor
$L_{Ni} \times L_{Cr} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$a_1 b_1 c_1 d_2$	4.1
$Q_{Ni} \times L_{Cr} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$a_2 b_1 c_1 d_2$	10.0
$L_{Ni} \times Q_{Cr} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$a_1 b_2 c_1 d_2$	18.8
$Q_{Ni} \times Q_{Cr} \times L_{T_{Cr}} \times Q_{T_{Ni}}$	$a_2 b_2 c_1 d_2$	44.0
$L_{Ni} \times L_{Cr} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$a_1 b_1 c_2 d_2$	40.1
$Q_{Ni} \times L_{Cr} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$a_2 b_1 c_2 d_2$	4.1
$L_{Ni} \times Q_{Cr} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$a_1 b_2 c_2 d_2$	1.6
$Q_{Ni} \times Q_{Cr} \times Q_{T_{Cr}} \times Q_{T_{Ni}}$	$a_2 b_2 c_2 d_2$	2.8

Sum, Four Factor Interactions: 240.5

Four Factor Interaction Degrees
of Freedom: $\quad = \quad$ 16.

Mean Square: $\dfrac{240.5}{16} \quad = \quad$ 15.03

$$\text{Variance Ratio} = \frac{\text{Mean Square of Factor}}{\text{Mean Square of Four Factor Interactions}}$$

TAB'E XXVIII. X-RAY FLUORESCENT ANALYSIS OF DUPLEX SEALED ANODIC COATINGS

Treatment Combination	Ni Conc. ∝ Counts/sec.			Color Number As Sealed			Cr Conc. ∝ Counts/sec.		
	2024	7075	7178				2024	7075	7178
12 1216	84	108	92	5	7	7	184	264	280
12 1016	60	62	76	8	9	9	288	328	360
12 5216	424	352	448	6	5	6	200	168	248
12 5016	464	304	384	9	8	8	392	312	372
12 9216	816	640	720	3	4	4	252	196	224
12 9016	928	768	880	8	7	9	236	240	392
16 1216	92	116	88	5	8	5	214	222	202
16 1016	98	96	96	8	8	3	290	338	190
16 5216	480	448	532	6	6	6	222	250	274
16 5016	528	456	600	8	7	9	290	314	386
16 9216	1024	960	1296	3	2	5	134	130	158
16 9016	960	928	992	6	5	6	258	242	270
52 1216	120	116	146	5	7	8	10	13	20
52 1016	162	132	142	9	9	9	40	47	48
52 5216	496	464	464	5	4	5	16	15	24
52 5016	432	328	464	8	6	9	35	22	37
52 9216	1120	1024	1072	4	3	3	15	14	14
52 9016	768	768	976	6	6	5	14	16	18
56 1216	117	116	119	5	8	7	27	54	59
56 1016	160	150	160	8	9	9	91	108	133
56 5216	696	592	592	4	4	5	38	32	49
56 5016	612	600	624	8	6	7	68	76	78
56 9216	1728	1728	1824	4	4	6	38	41	50
56 9016	1344	1376	1344	6	4	6	56	49	41

1000

2000

1800

1600

X = 212°F
O = 180°F

1400

1200

Cr CONCENTRATION COUNT/SEC

Ni CONCENTRATION COUNTS/SEC

100

1000

800

600

200

10

100

100 120   200   400   600   1000

NICKEL ACETATE SEAL IMMERSION TIME IN SECONDS
1.25 W/O N$_i$ (C$_2$H$_3$O$_2$)
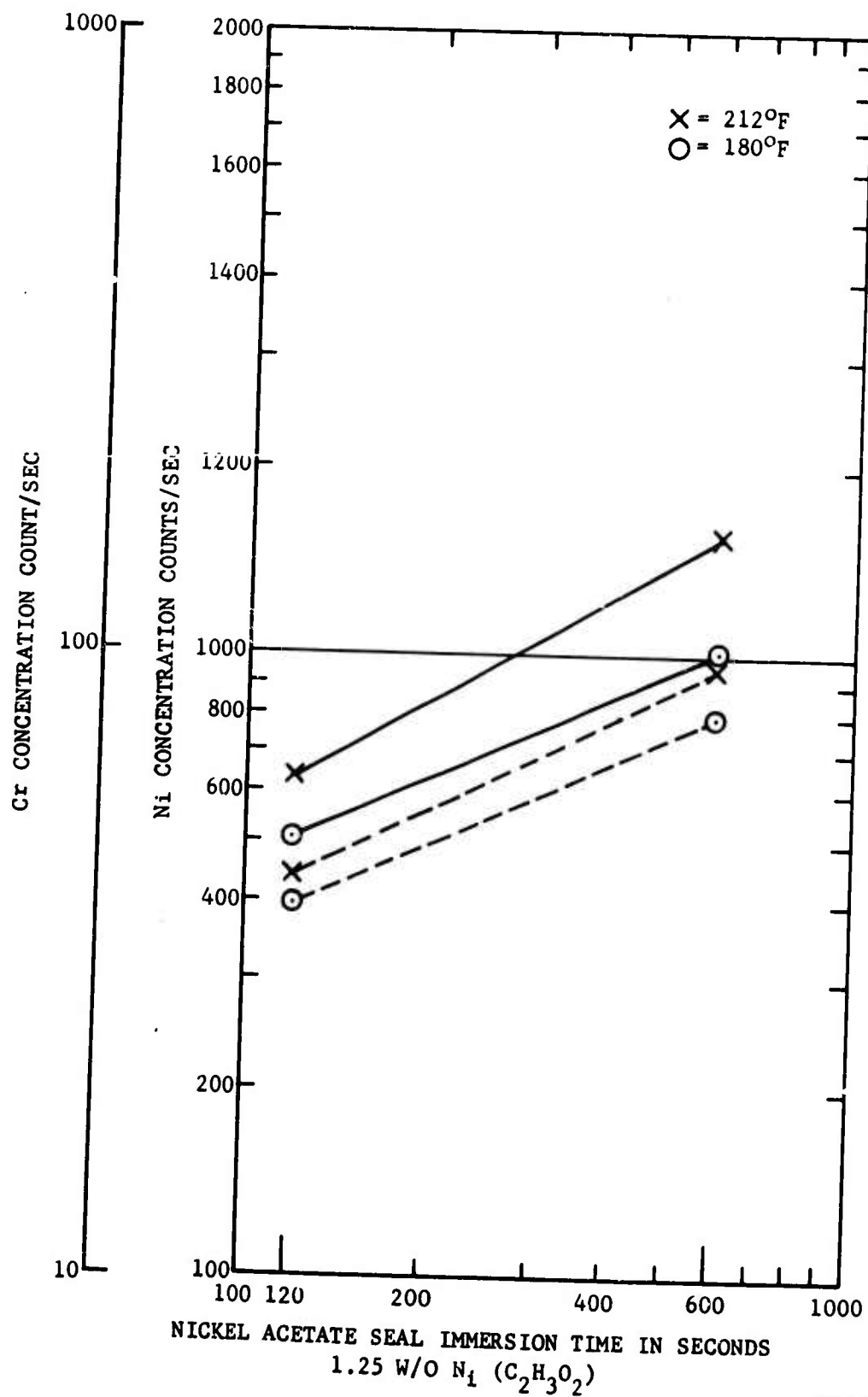
F09883 U

FIGURE 11.   CONCENTRATION OF THE SEALED FILMS VERSUS IMMERSION TIME

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As mentioned earlier, an attempt was made to use the rate of change of color intensity (chromate yellow) to anticipate corrosion performance. It is well known that chromate sealed samples tend to fade as exposure time increases. Since the chromate ion is an inhibitor of corrosion of the aluminum substrate, its loss through leaching action by salt fog could reduce the effectiveness of the anodic film.

Using 2024-T3 alloy, a series of color comparison samples was made up using various seal times in 5% $Na_2Cr_2O_7$ seal solutions on Type II anodized films. Seal times versus the various color numbers are listed in Table XXIX together with the X-ray analysis of chromium content.

The color numbers as sealed and after 10 days 5% NaCl fog exposure are given in Table XXX.

Comparing the data of Tables XXVIII and XXX, it is apparent that the color intensity and total chromium content are not related. This lack of correlation is most apparent in the 5XXXXX treatment combinations.

The reason for the lack of correlation between the color number and chromium concentration is not known. Two possibilities exist. The first is that chromium may be partially reduced to some lower valence state on chemisorption by the anodic film. The second possibility is electronic interaction of the chromium compound with divalent aluminum present in the anodic film. Since the visible spectra involves electronic transitions, any perturbation could modify the color intensity.

This finding suggests that the common shop practice of judging the quality of chromate sealed Type II anodized aluminum by its color may be invalid.

   f. <u>Coating Weight Analysis</u>. Since the coating weight is important in the corrosion resistance (MIL-A-8625B, paragraph 3.10.11) of aluminum alloys, the values were determined on all samples with the C_1C_6 treatment combination, and selected samples from C_1C_8, C_3C_6 and C_3C_8. The standard phosphoric acid/chromic acid mixture was used as described in MIL-A-8625B.

Selected typical values are summarized in Table XXXI. The listed coating weights are typical for the 30 minute anodizing time and are well above the specified minimum of 600 mg/ft.

TABLE XXIX. COLOR COMPARISON STANDARDS, 2024-T3, TYPE II, ANODIZED 30 MINUTES

Color Number	Seal Time 5% Na$_2$Cr$_2$O$_7$ @ 212°F	Comparative Cr Conc. Counts/sec.
0	Water Seal @ 212°F	0.0
1	0.5 sec.	9
2	1.0 sec.	12
3	30.0 sec.	16
4	2.0 min.	20
5	5.0 min.	25
6	10.0 min.	25
7	15.0 min.	36
8	30.0 min.	41
9	1.0 hr.	41
10	2.0 hr.	56

TABLE XXX. COMPARISON OF COLOR NUMBERS AS SEALED AND AFTER TEN DAYS' 5% NaCl FOG EXPOSURE.

Treatment Combination	Color Number As Sealed			Color Number After 10 Days' Salt Fog		
	2024	7075	7178	2024	7075	7178
12 1216	5	7	7	2	3	4
12 1016	8	9	9	4	7	6
12 5216	6	5	6	4	5	6
12 5016	9	8	8	5	7	3
12 9216	3	4	4	3	2	2
12 9016	8	7	9	6	5	6
16 1216	5	8	5	3	4	0
16 1016	8	8	3	2	4	0
16 5216	6	6	6	2	4	4
16 5016	8	7	9	5	5	6
16 9216	3	2	5	1	0	2
16 9016	7	4	6	2	3	3
52 1216	5	7	8	1	1	1
52 1016	9	9	9	3	6	6
52 5216	5	4	5	3	2	3
52 5016	8	6	9	4	5	6
52 9216	4	3	3	1	0	2
52 9016	6	6	5	1	3	2
56 1216	5	8	7	0	3	1
56 1016	8	9	9	3	6	7
56 5216	4	4	5	2	3	3
56 5016	8	6	7	3	3	4
56 9216	4	4	6	0	1	1
56 9016	6	4	6	3	2	3

TABLE XXXI.   COATING WEIGHT ANALYSIS - TREATMENT COMBINATION C_1C_6, 30 MINUTE ANODIZING TIME.

Treatment Combination	Coating Weight, Mg/ft^2		
	2024-T3	7075-T6	7178-T6
12 1216	1123	1756	1735
12 1016	1260	1627	1641
12 5215	1070	1325	1749
12 5016	1461	1584	972
12 9216	1648	1908	1468
12 9016	1620	1958	2109
16 1216	1065	1605	--
16 1016	1166	1404	--
16 5216	1231	1757	1540
16 5016	1166	1641	1742
16 9216	1216	1778	1641
16 9016	1245	1728	1663
52 1216	986	1519	1512
52 1016	1260	1814	1706
52 5216	1252	1828	1620
52 5016	1065	1497	1800
52 9216	1396	1929	1900
52 9016	1108	1886	1605
56 1216	1123	1584	1180
56 1016	1094	1649	1699
56 5216	1173	1418	1526
56 5016	1094	1440	1497
56 9216	1217	1526	1447
56 9016	1346	1893	1591

g. **Corrosion Evaluation of 7079-T6 Alloy.** Due to the late arrival and limited availability of 7079-T6 alloy sheet, only partial treatment combinations could be evaluated. At the time of sample preparation, it was necessary to "guess" the probable optimum treatment combination since conclusive results were not yet available from the other alloys. The treatment combination used and the number of 10-day corrosion exposure cycles to failure are summarized in Table XXXII.

As anticipated from the detailed analysis of the 2024, 7075 and 7178 alloys, the low temperature (180°F) $Ni(C_2H_3O_2)_2$ seal treatment combination showed the best corrosion resistance. Careful visual inspection of this group of 25 samples also showed that the low temperature $Ni(C_2H_3O_2)_2$ samples showed a minimum of color change, whereas the high temperature $Ni(C_2H_3O_2)_2$ faded completely. Additional samples have been anodized and duplex sealed using optimum treatment combinations for corrosion evaluation. Results of these data will be submitted as a supplement to this report after corrosion failure in 5% NaCl fog exposure.

h. **Corrosion Evaluation of Duplex Sealed 7075-T6 Alloy with Short Anodizing Times.** Because of the adverse effect of 30-minute anodizing times on the fatigue properties of aluminum alloys, shorter anodizing times and, hence, thinner anodic coatings would be desirable. Since duplex sealing increases the corrosion resistance at least one order of magnitude beyond the requirements o. MIL-A-8625b, sufficient corrosion protection may be possible with shorter anodizing times.

In this series of tests, it was also necessary to "guess" optimum process conditions because of the excessive time necessary to evaluate the main factorial design in 5% salt fog.

Standard 3" x 10" test coupons were anodized using the procedure described earlier except the anodizing time was reduced. The anodizing times used, seal treatment combinations and corrosion evaluation at the end of 3,360 hours (fourteen 10-day cycles) 5% NaCl fog exposure are given in Table XXXIII.

The corrosion evaluation of the samples given in Table XXXIII is based on the number of spots on the 3" x 10" samples that showed the typical white corrosion products. For example, sample 34-9616, with a 10-minute anodize time, showed three such spots, all of which were on the upward facing side. In the 20-minute column, two numbers are used. The first indicates the number of massive (white) corrosion spots which in all cases was zero, with the second number indicating the relative frequency of the very fine brown to black discoloration that often precedes massive attack.

Based on these data, and the fact that samples sealed at 180°F retain their color in salt spray, this series generally confirms the results obtained in the main factorial design.

TABLE XXXII.   TREATMENT COMBINATION AND CORROSION DATA FOR 7079-T6 ALUMINUM ALLOY

Treatment Combination	Number of 10-Day 5% NaCl Exposure Cycles to Failure
12 1016	Over 21
12 5616	Over 21
12 9016	Over 21
16 1616	Over 21
16 1016	Over 21
16 5616	18
16 9616	Over 21
16 9016	Over 21
32 5216	Over 21
32 5616	18
32 9216	Over 21
32 9016	7
34 5616	18
36 1216	7
36 1616	18
36 1016	Over 21
36 5016	Over 21
36 9216	Over 21
36 9616	Over 21
52 9016	Over 21
54 5616	7
56 1016	18
56 9216	Over 21
56 9616	Over 21
56 9016	Over 21

TABLE XXXIII. CORROSION EVALUATION OF SHORT TIME ANODIZED DUPLEX SEALED 7075-T6

	Anodizing Time in Minutes; 17% H_2SO_4 @ 12 amp/ft^2 @ 70°F			
	5	10	15	20
Seal Treatment Combination		Corrosion Evaluation		
3496-16	5	3	2	0/0*
3490-16	10	0	0	0/1-10
3696-16	14	3	10	0/10-20
5292-16	2	2	3	0/1-10
5290-16	15	5	0	0/1-10
5492-16	13	8	0	0/0
5496-16	10	4	1	0/0

*See Text.

The coating weights obtained versus anodizing time are given in Table XXXIV.

TABLE XXXIV. COATING WEIGHT VERSUS ANODIZING TIME

	Coating Weight - mg/ft^2			
Seal Treatment Combination	Anodizing Time			
	5'	10'	15'	20'
3496-16	597	893	1058	1440
3490-16	626	993	1228	1641
3696-16	662	871	1281	1541
5296-16	670	929	1123	1598
5290-16	648	943	1152	1469
5492-16	605	763	1080	1634
5496-16	655	964	1152	1541

Additional samples have been anodized and sealed under optimum process conditions. These samples are in salt spray and test rusults, when available, will be forwarded as an addendum to this report.

At 1680 hours (seven 10-day exposure cycles) none of the samples of this group had shown failure. Thus, it appears easily possible to achieve corrosion resistance substantially better than normally obtained with MIL-A-8625b, Type II coatings with reduced anodic film thicknesses.

3.3 DISCUSSION OF RESULTS AND CONCLUSIONS

3.3.1 OPTIMUM PROCESS CONDITIONS VERSUS CORROSION

The statistical analysis of the factorial design matrix shows conclusively that nickel acetate seal temperature of 200°F and 212°F are inferior to the 180°F treatment combination. X-ray fluorescent analysis shows that high nickel acetate seal temperatures drastically reduce the amount of chromium in the film. The chromium that is present is rapidly leached out of the coating under such seal conditions.

The reason for the unusual temperature sensitivity of the reactivity of $Na_2Cr_2O_7$ with nickel acetate treated anodic films is obscure. It appears that the 212°F $Ni(C_2H_3O_2)_2$ seal completely deactivates the anodic film and renders it incapable of chemisorbing or reacting with the dichromate ion. If the nickel acetate "plugged" all the pores and consequently prevented "pore plugging" by the dichromate, it would be logical to assume that the quantity of chromium present would be related to the nickel content of the film. This is clearly not the case either at 180°F or 212°F (see Table XXVII). This result strongly suggests that the "plugging theory" of sealing of anodic films is questionable.

The lack of correlation between color number and chromium concentration is also somewhat unexpected. In chromate sealed anodic films, the color intensity is approximately proportional to the chromate concentration. As shown in Table XXVII, the color intensity of duplex sealed coatings bears little relationship to the chromium content.

The infrared spectra analysis of anodic films by Dorsey[7] suggests that the sealing reaction may occur on a molecular scale with the Ni^{++} or $Cr_2O_7^=$ ion bridging the polymer-like Al-O net suggested. In duplex sealing, since both cations and anions are apparently involved in the process, it suggests that two different type sites may exist.

In many respects, the anodic film seems to behave somewhat like activated alumina used in catalysis. In a recent review[30] the infrared spectra work of Perri shows that the hydroxyl group exchanges hydrogen easily. The bonding in this case is largely ionic. This effect was noted by Dorsey using deuterated sulfuric acid for anodizing.

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The fact that gas is evolved during the initial stages of nickel acetate sealing suggests that the nickel II ion may be replacing part of the hydrogen present in the polymer-like tri-hydrate either (or both) in the barrier layer or porous layer. Such a reaction would tend to inhibit exchange and hence, may reduce the diffusion rate of corroding agents through the anodic film. The Ni II ion is also probably larger than H^+ and hence, would tend to "plug" the polymer net.

The unusual effect of the higher $Ni(C_2H_3O_2)_2$ seal temperature on the prevention of chromium adsorption or reaction is difficult to understand. A possibility exists that for some unknown reason, the acetate group reacts with the anodic film at the slightly higher temperature. Such a reaction is possible since the $Ni(C_2H_3O_2)_2$ is partially ionized and carbonylic acids of this type are known to react with aluminum to form aluminum soaps[31] Infrared or tracer techniques could resolve this problem.

Many perplexing questions have been raised concerning the mechanism of sealing of anodic films as a result of this study. Recent work by Dorsey[9] suggests that much that has been commonly accepted in this field should be more critically re-examined.

Based on statistical analysis of the results of 243 different sealing treatment combinations for each of the three alloys, 2024-T3, 7075-T6 and 7178-T6 after 5,000 hours exposure in 5% salt fog, the results conclusively show that the lowest nickel acetate seal temperature used, i.e., 180°F, gives superior corrosion resistance. The differences in performance at various seal solution concentrations is less definitive but suggests the use of the more dilute concentrations, namely, 1.25 w/o $Ni(C_2H_3O_2)_2$ and 4.12 w/o $Na_2Cr_2O_7$.

Treatment combination 129216 appears very near optimum. This process involves a ten-minute seal in $Ni(C_2H_3O_2)_2$ at 180°F followed by a two-minute seal in $Na_2Cr_2O_7$ at 180°F. Seal solution concentrations are 1.25 w/o and 4.12 w/o nickel acetate and sodium dichromate, respectively.

Anodizing times as short as five minutes gave very acceptable performances even though sealed at off-optimum conditions.

3.4 FATIGUE EVALUATION

Fatigue specimens of 2024-T3, 7075-T6, 7178-T6 and 7079-T6 aluminum alloys were machined to the configuration shown in Figure 12. Each sample was cleaned and anodized as described in Section 3.2.1 prior to sealing with various treatment combinations.

Fatigue tests were run on the Budd Fatigue Testing Machine, Model VSP-150. The maximum fiber stress on each alloy system was calibrated using SR-4 strain gages attached to the alloy specimen. The calibration curves of maximum fiber stress versus the deflection y_0 at the load point are given in Figure 13.

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THESE RADII SHALL BE TANGENT TO
ANGLE 10° - 18' AND SHALL NOT BE
UNDERCUT

R = 1/2   MINIMUM WIDTH 0.423 ± 0.002

3/8

SINE 1.788

10° - 18'

3/4

0.500
±
0.005

0.500
±
0.005

1 3/4

0.218 ± 0.005

0.375 ± 0.005

2 HOLES NO. 17 DRILL

0.250
±
0.005

1/2

SCALE DOUBLE SIZE

2.500 ± 0.005

2.750 ± 0.005
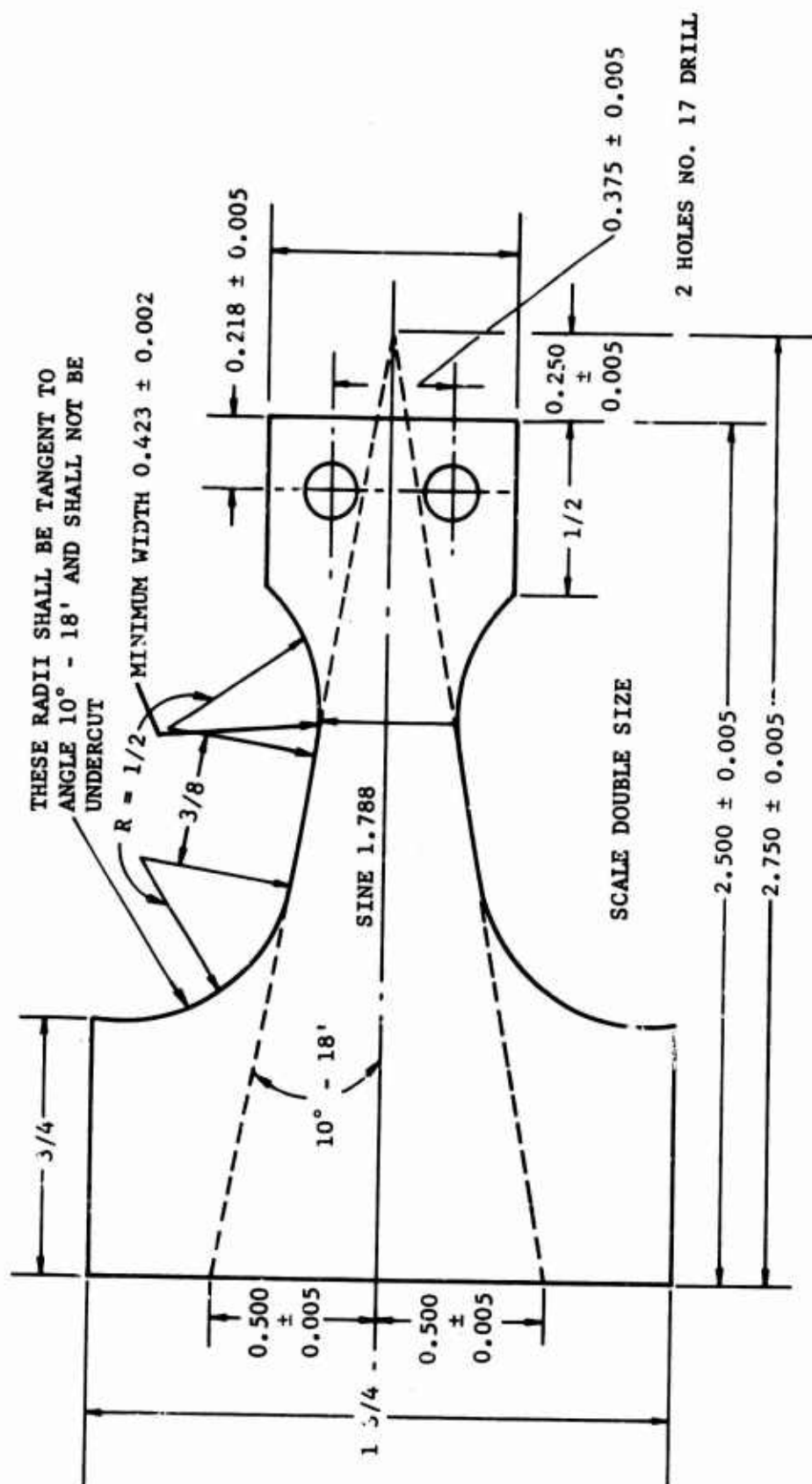
F09877 U

FIGURE 12.   SHEET FATIGUE SPECIMEN

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Where:
$\ell = 1.550''$
$h = 0.042''$
$Y_o =$ DEFLECTION IN INCHES OF LOADING POINT

$$\sigma_{MAX} = \frac{E \, Y_o \, h}{2\ell^2}$$

NOTE: DATA POINTS 7075 ALUMINUM AND STRESS CALCULATED FROM STRAIN GAGE MEASUREMENTS BY
$$\sigma_1 = \epsilon_1 E_1$$

MAX FIBER STRESS IN 10^3 PSI

DEFLECTION AT LOAD POINT, Y_o, IN INCHES
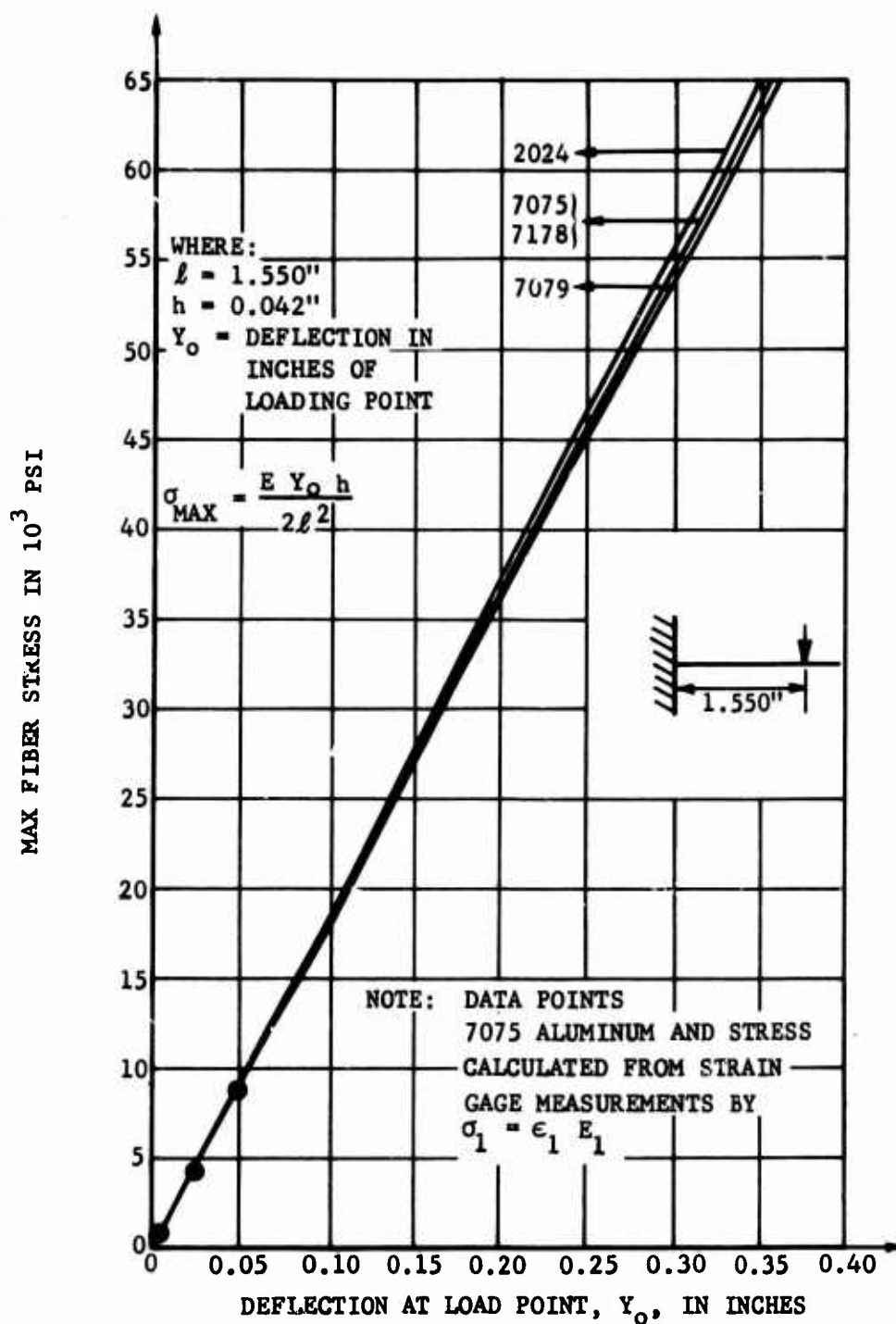
F09878 U

FIGURE 13.   STRESS DEFLECTION CURVES FOR VARIOUS ALUMINUM ALLOYS CANTILEVER BEAMS

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For comparison, fatigue tests were run on samples of the same alloy sheets used throughout the study in the bare condition and with MIL-A-8625b, Type II dichromate sealed samples. The values obtained are summarized in Figures 14 through 16.

Since corrosion test results on shorter anodizing times looked very promising, cursory fatigue life measurements were made on the 7075-T6 alloy versus anodizing time. These data are given in Figure 17.

The limited data available suggest that the fatigue life of the duplex sealed alloys are approximately equal to that of MIL-A-8625 type coatings. Substantially more data over a wider range of ultimate fiber stresses are needed to verify this point. In addition, complete fatigue data versus anodizing time with the optimum seal process is required. It appears entirely probable that anodizing times as short as ten minutes with duplex sealing could equal corrosion resistance performance of the conventional Type II MIL-A-8625 coatings.

3.5 PAINT ADHESIVE QUALITY OF DUPLEX SEALED HIGH STRENGTH ALUMINUM ALLOYS

The third objective of this program was to determine the paint adhesion quality of duplex sealed high strength aluminum alloys. Standard 3" x 10" test coupons were anodized and sealed as described in Section 3.2.2 for this evaluation. Primers and color coat were applied to the samples sealed as listed in Table XXXV.

The coating system consisted of a wash primer (MIL-C-8514A), zinc chromate primer MIL-P-7962A and a lacquer color coat (MIL-L-19537A) applied in accordance with the above specifications. After aging at room temperature for a minimum of 24 hours, all test panels were exposed to 100% relative humidity at 95°F for 14 days, using a modified Blue M Model CF-750H all stainless steel constant humidity chamber in accordance with the procedure outlined in Federal Test Method 141, Method 6201.

The Adhesion (Wet) Tape Test, Federal Test Method 141, Method 6301, was used to determine the adhesive quality of the coating system after temperature and humidity exposure. This method consists of the following steps:

(1) Scribe two parallel lines one inch apart through the coating to the metal substrate.

(2) Apply one inch strip of masking tape over the area between the lines with a 4½-pound roller as per the test method.

(3) Rapidly remove the tape with one quick motion.

The results of this test on the wash primer - primer - color coat system on the sealed anodized samples are summarized in Table XXXV.
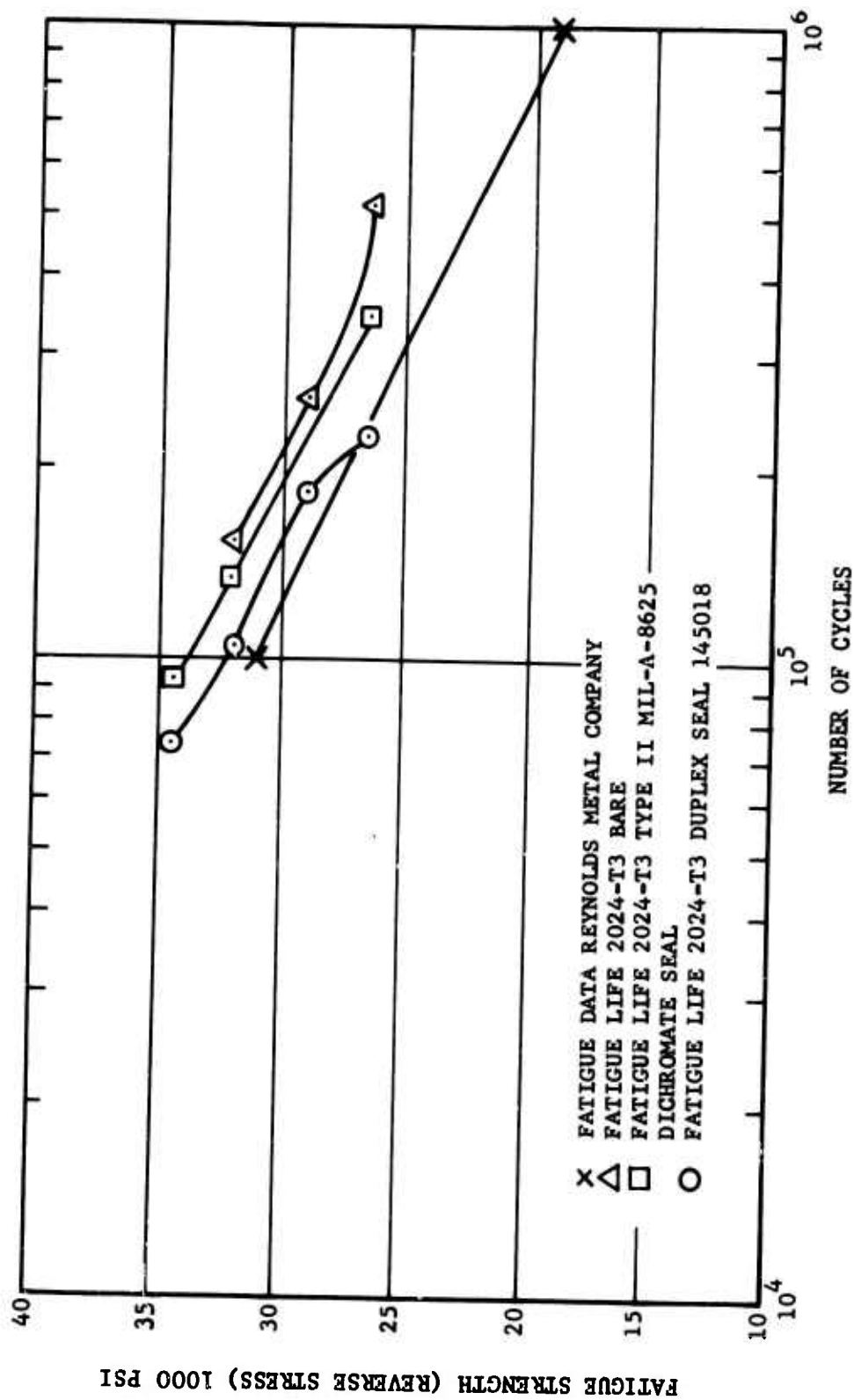
FIGURE 14. COMPARISON OF FATIGUE LIFE VERSUS ANODIZING SEAL PROCESS 2024-T3

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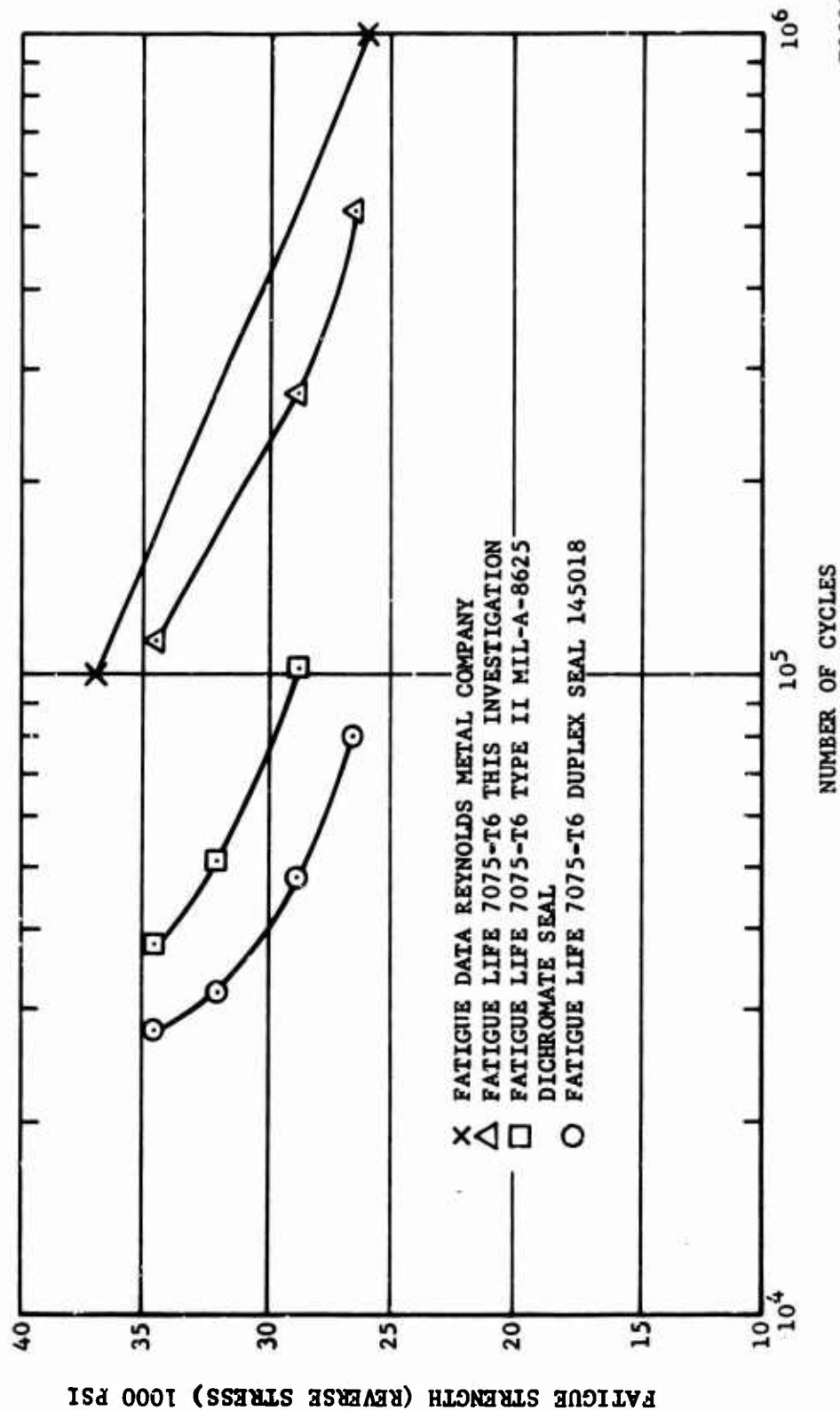
FIGURE 15. COMPARISON OF FATIGUE LIFE VERSUS ANODIZING SEAL PROCESS 7075-T6

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-75-
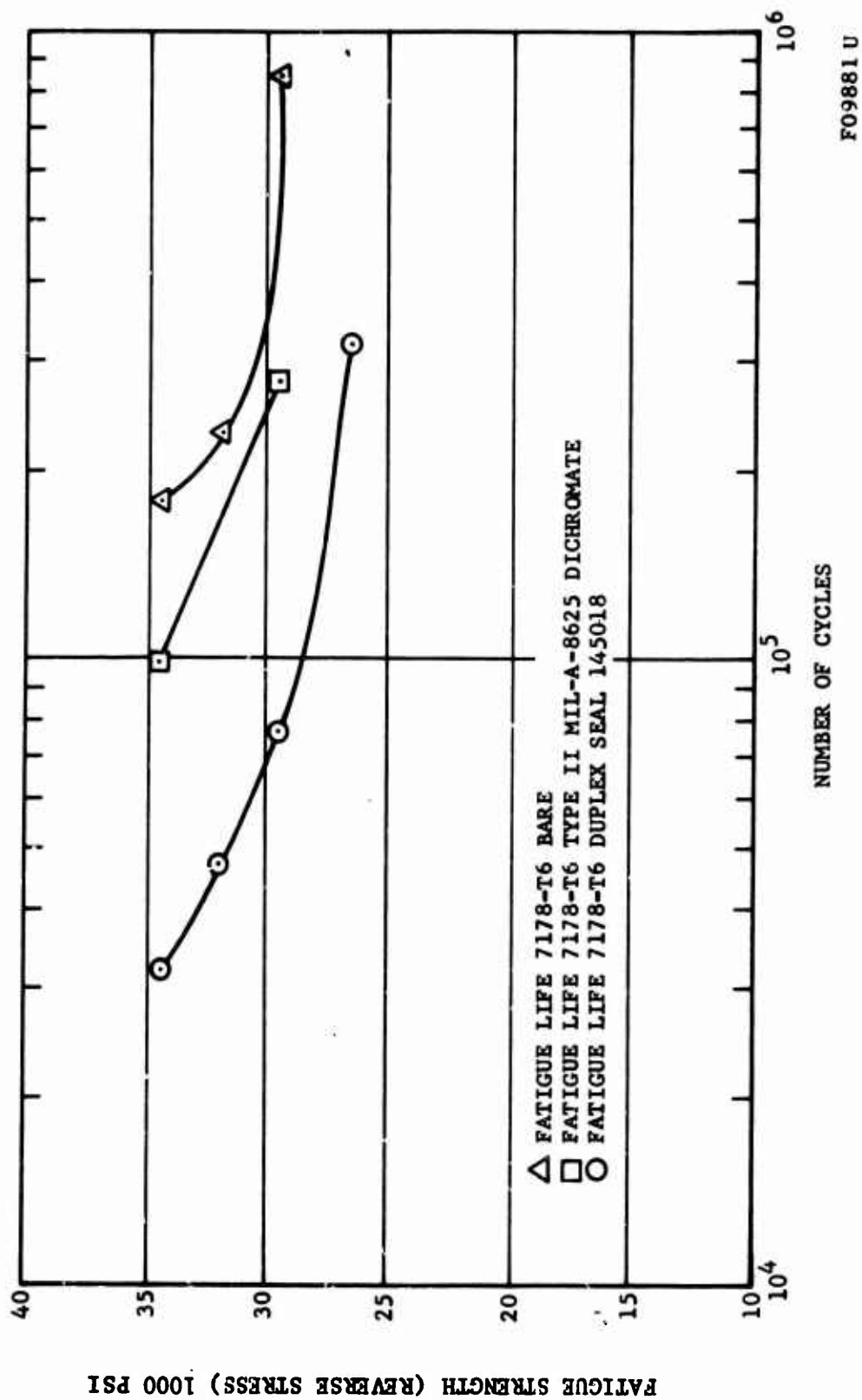
FIGURE 16. COMPARISON OF FATIGUE LIFE VERSUS ANODIZING SEAL PROCESS 7178-T6
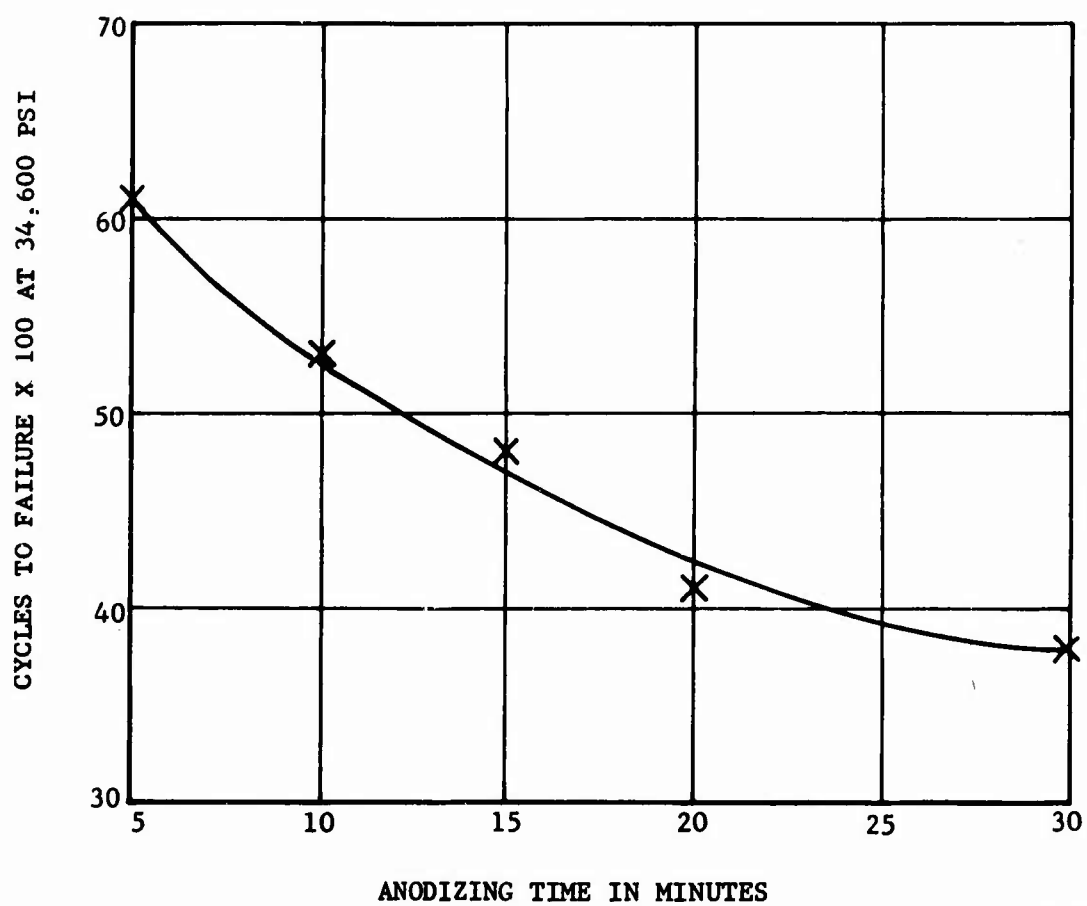
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FIGURE 17. FATIGUE LIFE VERSUS ANODIZING TIME FOR 7075-T6 ALLOY

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TABLE XXXV. ADHESION TAPE TEST

Seal Process	Percent of Color Coat Removed		
	2024-T3	7075-T6	7178-T6
5612 16	3	0	6
5616 16	23	3	0
5610 16	27	0	40
5652 16	88	0	41
5656 16	0	0	9
5650 16	0	2	0
5692 16	87	0	10
5696 16	1	12	56
5690 16	0	20	0
5612 38	0	87	100
5616 38	100	100	0
5610 38	100	0	0
5652 38	0	19	100
5656 38	100	0	0
5650 38	15	0	0
5692 38	0	0	3
5696 38	0	0	0
5690 38	0	0	1
5412 36	0	6	93
5616 36	0	2	2
5610 36	80	90	73
5652 36	0	20	80
5656 36	85	0	0
5650 36	99	26	0
5692 36	15	0	3
5696 36	0	0	94
5690 36	0	44	0

TABLE XXXV. ADHESION TAPE TEST
(Continued)

Seal	Percent of Color Coat Removed		
Process	2024-T3	7075-T6	7178-T6
5412 18	40	1	100
5616 18	2	3	2
5610 18	4	1	14
5652 18	1	5	12
5656 18	0	2	7
5650 18	42	52	9
5692 18	0	54	42
5696 18	18	2	6
5690 18	12	3	0

In the above series of tests, only the color coat was removed from the zinc chromate primer.

This series was repeated using only the wash primer - zinc chromate primer. In this group, 100% adhesion of the primer was observed under all seal conditions.

Based on these data, it appears that duplex sealed high strength aluminum alloys have excellent paint adhesion qualities.

In addition, samples as listed in Table XXXV were evaluated after 14 days exposure at 100% RH at 95°F using the Rondeau Scratch Tester.[32] This unit belongs to the type of tester wherein the load is linearly increased as the stylus progresses along the length of the scratch or point of applied load.

The total stylus excursion is 100mm. The results, given in Table XXXVI, are based on the percentage travel from the starting point to the point of break-through to the aluminum alloy substrate. The Rondeau Scratch Tester was used with the heavy spring, resulting in a load of 1200 grams at the end of the 100mm travel. This test gives some approximation, then, of the scratch resistance of the total coating system; i.e., paint/primer/ anodic film. In many instances, break-through did not occur under maximum load conditions.

TABLE XXXVI.   RONDEAU SCRATCH TEST RESULTS ON DUPLEX SEALED Al ALLOYS

Seal Condition	Percent of Stylus Travel Without Penetration of Coating to Base Metal		
	2024-T3	7075-T6	7178-T6
5612-16-2	47.5	60.0	65.0
5616-16-2	39.0	73.0	74.0
5610-16-2	47.5	75.5	84.0
5652-16-2	41.0	77.0	69.0
5656-16-2	34.0	63.0	81.0
5650-16-2	46.5	52.5	81.0
5692-16-2	49.0	70.0	89.0
5696-16-2	56.0	93.0	68.0
5690-16-2	61.5	70.0	77.5
5612-38-2	25.5	82.5	85.0
5616-38-2	62.0	100.0	90.0
5610-38-2	52.5	32.5	60.0
5652-38-2	87.5	100.0	100.0
5656-38-2	32.5	70.0	67.5
5650-38-2	85.0	97.5	95.0
5692-38-2	45.0	92.5	77.5
5696-38-2	70.0	100.0	100.0
5690-38-2	37.5	62.5	100.0
5612-36-2	47.5	50.0	55.0
5616-36-2	17.5	45.0	50.0
5610-36-2	30.0	37.5	42.5
5652-36-2	32.5	37.5	47.5
5656-36-2	27.5	32.5	47.5
5650-36-2	25.0	40.0	50.0
5692-36-2	--	25.0	45.0
5696-36-2	15.0	45.0	55.0
5690-36-2	37.5	45.0	45.0

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TABLE XXXVI. RONDEAU SCRATCH TEST RESULTS ON DUPLEX SEALED Al ALLOYS
(Continued)

Seal Condition	Percent of Stylus Travel Without Penetration of Coating to Base Metal		
	2024-T3	7075-T6	7178-T6
5612-18-2	67.5	87.5	100.0
5616-18-2	60.0	77.5	75.0
5610-18-2	47.5	72.5	75.0
5652-18-2	32.5	90.0	97.5
5656-18-2	42.5	80.0	80.0
5650-18-2	52.5	70.0	67.5
5692-18-2	42.5	80.0	95.0
5696-18-2	47.5	57.5	92.5
5690-18-2	37.5	70.0	82.5

SECTION IV

SUMMARY AND CONCLUSIONS

The sealing of sulfuric acid anodized high strength aluminum alloys with nickel acetate followed by sodium dichromate provides salt spray corrosion resistance substantially better than the conventional dichromate process.

The process parameters of this dual sealing procedure were investigated using factorial design experiments. Corrosion results were evaluated statistically using the Yates method.

This analysis showed that the most significant variable involved was the seal temperature of the nickel acetate. High seal temperatures, i.e., 200°F and 212°F, prevent the stable chemisorption of the chromate ion. While high nickel acetate seal temperatures result in intensely colored samples after chromate sealing, the total chromium content, by X-ray fluorescent analysis of the film, is extremely low. Likewise, the chromate ion is quickly leached during salt fog exposure. In contrast, the 180°F film, though only slightly colored, contains an order of magnitude more chromium. This chromium is tightly bound and even after 5,000 hours is still present in substantial amounts.

The optimum seal process conditions, based on this investigation, are:

> Seal in 1.25 w/o nickel acetate for ten minutes at
> 180°F, followed by a two minute seal in 4.12 w/o
> sodium dichromate at 180°F.

This treatment combination reduces the process time to one-fifth of that required using the MIL-A-8625 process.

Very promising corrosion resistance was achieved using anodizing times as short as five minutes with duplex sealing.

Contrary to common belief, the color intensity resulting from the dichromate ion is not indicative of the chromium content of the film. This is especially true in the duplex sealing process.

Based on limited fatigue data, the reduction in the fatigue life of duplex sealed high strength aluminum alloys is comparable to Type II coatings, MIL-A-8625.

The paint adhesive qualities of duplex sealed anodized aluminum alloys is very good. Not a single case of primer separation from the substrate was observed in the entire series of tests.

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13. ABSTRACT: Preliminary studies showed that outstanding corrosion resistance to humid N_2O_4 and salt fog could be achieved on sulfuric acid anodized 7075-T6 aluminum alloys when sealed first with nickel acetate followed by sodium dichromate. In this study, the nickel acetate-sodium dichromate sealing procedure, termed duplex sealing, was investigated in detail for 2024-T3, 7075-T6, 7178-T6 and 7079-T6 aluminum alloys to identify the treatment combinations giving optimum corrosion resistance. The process variables studied were seal solution immersion times, temperatures and concentrations. Factorial designed experiments were used, followed by statistical analyses of the corrosion resistance of the treatment combinations. The nickel acetate seal temperature was found to be the predominant variable affecting corrosion resistance. The lowest temperature, 180°F, resulted in the best corrosion resistance. Based on these studies, maximum corrosion resistance was achieved by sealing first in 1.25 w/o nickel acetate for ten minutes at 180°F followed by a two minute seal in 4.15 w/o sodium dichromate at 180°F. In duplex sealing, the chromium concentration in the sealed anodic film is not related to the chromate yellow color of the anodized alloy. High nickel acetate seal temperatures inhibit stable chemisorption or reaction of the chromate with the anodic film. Under such conditions, the chromium content is very low, even though the samples are intensely colored. Sulfuric acid anodizing times as short as five minutes, when duplex sealed, were resistant to 5% salt fog for times in excess of 1,000 hours. Based on limited fatigue data, duplex sealed sulfuric acid anodized high strength aluminum alloys are comparable to Type II, MIL-A-8625 process conditions. The paint adhesive qualities of duplex sealed high strength alloys is excellent. After 14 days exposure to 100% relative humidity at 95°F, 100% adhesion of the zinc chromate primer was observed on all samples.

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		ROLE	WT	ROLE	WT	ROLE	WT
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