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REPORT R-1524

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CORROSION OF WELDED ALUMINUM ALLOYS  
IN  
INHIBITED RED FUMING NITRIC ACID

By

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FA Project M154

January 1960

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RED FUMING NITRIC ACID

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January 1960

## OBJECT

To determine the resistance of welded aluminum alloys to corrosion by inhibited red fuming nitric acid

## SUMMARY

An investigation was conducted to determine the resistance of six welded aluminum alloys to corrosion by inhibited red fuming nitric acid (IRFNA) for 40, 100, 180, and 360 days at  $-30^{\circ}$ ,  $80^{\circ}$ ,  $114^{\circ}$ , and  $150^{\circ}$  F. Containers and weight-change specimens were fabricated by the gas tungsten-arc welding process from the base metal-filler metal combinations: 3003/1100, 2014/4043, 5052/5052, 1100/1100, 5154/5154, and 6061/4043. The corrosion resistance was determined by the change in weight of specimens suspended in the IRFNA and by the effect of the acid on the tensile strength of specimens machined from the walls of the containers. The influence of the water concentration of the acid on the corrosiveness of the acid was determined with the 3003/1100, 2014/4043, and 5052/5052 combinations.

In general, the corrosion of the welded alloy combinations exposed to IRFNA progressed with time except when exposed at  $-30^{\circ}$  F. No corrosion occurred at that temperature. The corrosion rates of all the welded combinations, except 5154/5154, were higher at  $80^{\circ}$  and  $114^{\circ}$  F than at  $150^{\circ}$  F. At the highest temperature ( $150^{\circ}$  F) the corrosion rates of the welded combinations, except 5154/5154, were retarded due to the formation of protective films.

The tensile strengths of the welds and base material were not adversely affected by contact with IRFNA for the duration of one year at the temperatures investigated.

The corrosion rates of the 3003/1100 and 5052/5052 combinations increased, whereas that of the 2014/4043 combination decreased as the water concentration of the IRFNA was increased to 7.5 percent. The 5052/5052 combination, however, exhibited the highest corrosion resistance of the three combinations investigated over the range of water concentrations from 3.5 to 7.5 percent.

AUTHORIZATION

WD 60304121-13-00002-18 and WD 80304120.1-1390018-01

## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
MATERIALS	2
Base and Filler Metals	2
Inhibited Red Fuming Nitric Acid (IRFNA)	4
Protective Clothing	4
METHODS	4
Container Design	5
Cleaning	5
Welding and Processing	6
Equipment	6
Longitudinal Welds	6
Girth Welds	6
Permanent Backing Rings	10
Radiographic Inspection of Longitudinal and Girth Welds	10
Heat Treatment of the Series B and F Containers	10
Welding of Top and Bottom Covers	11
Welding of Bung to Top Cover	11
Corrosion Specimens	11
Pressure Testing of Containers	11
Cleaning of Containers	12
Loading of Containers with IRFNA	12
Corrosion Specimens	14
Exposure of Experimental Containers	15
Pressure Measurements	15
Procedure after Exposure	16
Emptying	16
Sectioning of Containers	16
Sampling and Analysis of IRFNA	17
RESULTS AND DISCUSSION	17
Examination of Experimental Containers	17
Tensile Test Results	18
Control Containers	18
Exposed Containers	19

	<u>Page</u>
Analysis of IRFNA	23
Characterization of Sludge	28
Corrosion Specimens	29
Effect of Storage Temperature	29
Effect of Water Content at 80° F	34
Pressures	35
At -30° and 80° F	35
At 114° and 150° F	35
CONCLUSIONS	40
RECOMMENDATIONS	41
APPENDIX A - Protective Clothing List	42
APPENDIX B - Detail Photographs and Photomicrographs	43
APPENDIX C - Tensile Strength Data	65
APPENDIX D - Weight Change Data	71
REFERENCES	79
BIBLIOGRAPHY	81
Distribution	84

# CORROSION OF WELDED ALUMINUM ALLOYS IN INHIBITED RED FUMING NITRIC ACID

## INTRODUCTION

Redstone Arsenal is concerned with the design and fabrication of welded aluminum alloy tanks suitable for use with inhibited red fuming nitric acid (IRFNA), which is a liquid oxidizer in guided missiles. Welded tanks are used as: (1) storage tanks in which the acid is supplied by the manufacturer; (2) premeasured tanks in which the acid is measured and stored prior to transfer to the missile tank; and (3) missile tanks for fuels and oxidizers. Since IRFNA is stored in welded tanks, it is important to know the effect of storing the acid in such tanks on: (1) the mechanical properties of the tanks; (2) the chemical composition of the acid; and (3) the formation of sludge. Adverse effects on the mechanical properties of the welded tanks should be minimized, particularly if these could induce failure of the missile tanks. Further, the accumulation of sludge could conceivably inhibit proper flow of the oxidizer through orifice plates, thus leading to improper propulsion. A change of the chemical composition of the acid might result in a lowering of the effectiveness of the acid as the fuel oxidizer.

As the mission arsenal of the Ordnance Corps for nonferrous metallurgical research and development, Frankford Arsenal was requested by Redstone Arsenal to conduct a study of corrosion rates and the effects of IRFNA in contact with welded aluminum alloys. Information was needed on storage of the acid in welded aluminum alloy containers for periods up to one year. It was requested that corrosion tests be conducted at various temperature intervals between  $-30^{\circ}$  and  $160^{\circ}$  F and, also, that attention be given to the welding procedures and techniques.

## MATERIALS

### Base and Filler Metals

The aluminum alloys included in the experimental program were selected by mutual agreement between Redstone Arsenal and Frankford Arsenal. For the purpose of this report they were designated Series A through F; the base metals and their respective filler metals follow.

<u>Series</u>	<u>Base Metal</u>	<u>Filler Metal</u>
A	3003	1100
B	2014	4043
C	5052	5052
D	1100	1100
E	5154	5154
F	6061	4043

The chemical analyses of the base and filler metals of these alloys are given in Table I. The 1100 aluminum alloy base metal is a commercially pure aluminum and the lowest strength alloy in this series. The 3003 alloy is strengthened by the addition of 1 1/4 percent manganese. Alloys 5052 and 5154 are moderate strength, nonheat-treatable, and contain magnesium and chromium as the major alloying elements. The 2014 and 6061 are heat-treatable (precipitation hardenable) alloys; the 2014 is hardened primarily by the precipitation of a copper-aluminide phase ( $\text{CuAl}_2$ ) and the 6061 by the precipitation of a magnesium-silicide phase ( $\text{Mg}_2\text{Si}$ ). The filler metals are those commonly used in industrial practice with the respective base alloys. The 4043 alloy contains 5 percent silicon, which gives this alloy good fluidity and a low melting point when used as a filler metal in welding. Alloys 2014 and 6061 are not satisfactory filler metals since the welds have a pronounced tendency to crack.

The 1100, 3003, 5052, and 5154 alloy plates were received in the as-rolled condition. Hardness and tensile tests indicated that the tempers of these plates were between 1/4 and 1/2 hard. The 2014 plates were received in the T4 condition (solution heat-treated, followed by natural aging); the 6061 plates were received in the T6 condition (solution heat-treated, followed by artificial aging).

TABLE I. Chemical Analyses Representative of Aluminum Alloys

	Weight (%)											
	Mg	Si	Cu	Fe	Mn	Zn	Sn	Pb	Ni	Cr	Ti	Al*
<b>Base Metal</b>												
1100	<0.01	0.16	0.15	0.49	0.02	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	Rem
3003	<0.01	0.25	0.15	0.60	1.15	<0.05	<0.01	<0.01	<0.01	<0.01	<0.01	Rem
5052	2.60	0.10	<0.02	0.31	0.02	<0.05	<0.01	<0.01	<0.01	0.24	<0.01	Rem
5154	3.55	0.08	<0.05	0.22	0.01	<0.01	<0.05	<0.05	<0.01	0.22	0.10	Rem
2014	0.42	0.84	4.14	0.43	0.72	<0.1	0.01	0.01	0.01	0.03	0.03	Rem
6061	0.97	0.60	0.20	0.36	0.06	<0.05	<0.01	<0.01	<0.01	0.23	0.02	Rem
<b>Filler Metal</b>												
1100	<0.01	0.15	0.09	0.4	<0.01	ND**	ND	ND	<0.01	ND	ND	Rem
5052	2.39	0.2	0.08	0.2	0.03	0.03	ND	<0.01	ND	0.2	<0.01	Rem
5154	3.17	<0.1	<0.1	0.15	0.07	<0.05	<0.01	<0.01	<0.01	0.15	<0.01	Rem
4043	<0.05	4.98	0.01	0.2	0.01	ND	ND	ND	ND	ND	<0.01	Rem
<b>Backing Ring</b>												
1160	<0.005	<0.05	<0.03	0.01	ND	Rem						

\*Rem - Remainder

\*\*ND - None detected

## Inhibited Red Fuming Nitric Acid (IRFNA)

The IRFNA for this investigation was purchased as one lot and was certified as conforming to Specification MPD-138B and as having a water content of 2.14 to 2.19 percent. Analyses at this arsenal, however, showed that the IRFNA was not of a single lot and was not completely in accordance with the specification with regard to chemical composition. (Reference is made to "Results and Discussion" of this report for analyses details.) Approximately 1200 liters of IRFNA were shipped to Frankford Arsenal in 17 drums. The drums purchased for this purpose conformed to Proposed Military Specification MPD-115D.

### Protective Clothing

Special protective clothing (Appendix A) was used by personnel when the IRFNA was transferred into the experimental tanks and, at the completion of the environmental storage periods, when the tanks were emptied.

## METHODS

The selected aluminum alloys were cleaned and then fabricated into welded containers, 20 inches high and 8 inches in diameter (Figure B1, Appendix B).\* The girth and longitudinal welds of each container were radiographically inspected, and all containers were tested for leakage with compressed air. The container walls of the Series B and F containers were post weld heat-treated to obtain the maximum strength of these welded alloys. Ninety-six containers of the six series were half-filled with IRFNA in which the water concentration was approximately 3.5 percent. In addition, in 36 containers of the A, B, and C series, the IRFNA was modified with water and the effect of water concentration was investigated. Specimens of the base metal and weld were submerged in the IRFNA in each container for the purpose of measuring corrosion rates. The containers were stored at -30°, 80°, 114°, and 150° F for test periods of 40, 100, 180, and 360 days at each temperature. The vapor pressures

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\*All figures with the letter "B" before the number are presented in Appendix B.

of the IRFNA in each container were recorded throughout the exposure periods to detect sudden or excessive pressures.

A container of each series was opened after the completion of each exposure period and the corrosion specimens were removed. A sample of the acid was taken for analysis to obtain data on the decomposition of IRFNA. The containers were sectioned and examined, and specimens were removed for tensile tests and metallographic examination.

### Container Design

The container wall consisted of four rings joined by girth welds. Each ring was formed by rolling a 25 by 5 by 1/4 inch beveled plate and butt-welding the ends of the plate together. The top and bottom covers of each container were stamped from 1/4 inch thick plate of the same alloy as the plates used for the side wall. An extended threaded bung (2 1/4 inch OD and 1 1/4 inch ID) of 1100 aluminum alloy was provided on all containers. A small hook was made of the filler wire and welded inside each bung to support the corrosion specimen hanger.

### Cleaning

All aluminum alloys develop an oxide surface film upon exposure to air. Unless this film is removed immediately before welding, it will interfere with the deposition of the filler metal or remain in the weld as an inclusion. If any combustible materials (i. e., grease, oil, etc.) are in the path of the arc, they will burn and generate gases which may contaminate the shielding gas envelope. This contamination may also cause unsound welds. Therefore, prior to the welding of the aluminum alloy materials used in this study, the following chemical cleaning cycle was used.

1. Clean with 3% Aluminux (Diversey Corporation) solution for 3 to 5 minutes at 140° F.
2. Rinse with tap water.
3. Remove smut with 36% nitric acid.
4. Rinse with tap water.
5. Drain and dry, using compressed air.

During the subsequent welding operation every effort was made to prevent contamination of the metal surfaces.

## Welding and Processing

### Equipment

All welding was done by the gas tungsten-arc welding process with an 800-ampere, 60-cycle, ac, inert gas arc welder with an open circuit secondary voltage of 100 volts. A high-frequency pilot circuit was included in the machine to assist in starting the arc. This high-frequency circuit was automatically discontinued the instant the welding arc was established. Welding grade argon (99.6% pure) was used to shield the arc.

A turntable which contained a variable speed drive was used to rotate the rings as the girth welds were deposited. A variable speed filler metal feeder was used to feed the filler wire into the arc. The operator controlled the starting and stopping of the arc, the filler wire, and the turntable rotation.

### Longitudinal Welds

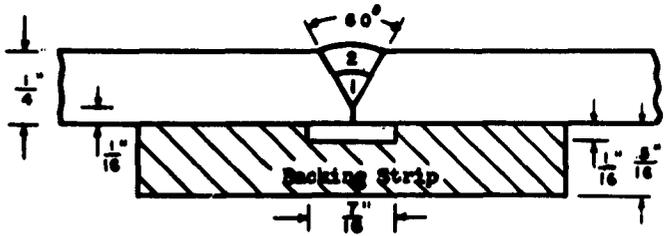
The design used to join the ends of each ring was 60° single V-groove butt joint with a 1/16 inch root face (Figure 1, Joint 1). The ends of the rolled plate were clamped to a stainless steel backing strip in such a manner as to allow no root opening. The backing strip was approximately 1 1/2 inch wide and was slightly curved to accommodate the curvature of the rolled plate. The welding was done manually in two passes. (The welding data of all the series are summarized in Table II.)

### Girth Welds

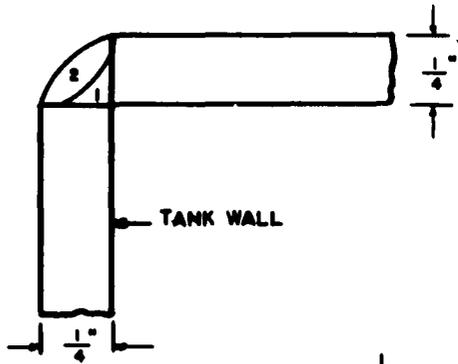
Preliminary experimental tests were conducted with Series D and E alloys to establish suitable procedures for making the girth welds. One- and two-pass welding techniques were investigated. Several rings, welded according to these techniques, were sectioned and machined to provide tensile test specimens. The test specimens from the containers welded with one pass failed in the heat-affected zone. Small cracks were noted in the welds of the fractured specimens from the Series D containers. The specimens from the containers (Series D and E) welded with two passes also failed in the heat-affected zone, but did not show any signs of cracks in the weld area. For this reason the girth welds of all containers were made with two passes.

The joint design of each girth weld was the same as that used for the longitudinal welds (Figure 1, Joint 1). A collapsible

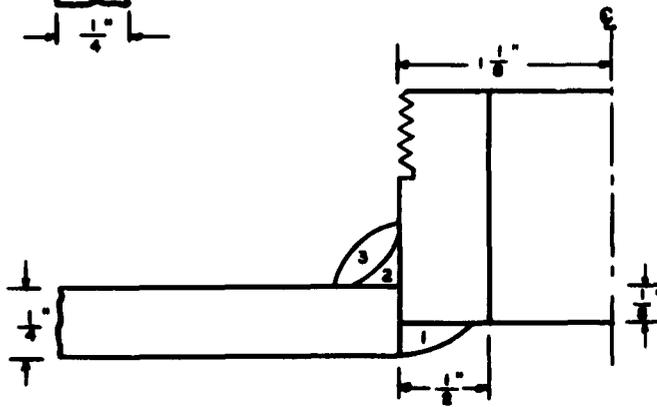
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Joint 1 -  
Longitudinal  
and girth welds



Joint 2 -  
Top and bottom  
covers welded  
to container  
walls



Joint 3 -  
Bung welded to  
top cover

Figure 1. Joint Design and Pass Sequence for Welded Aluminum Alloy Tanks

TABLE II. Welding Data

Argon shielding gas flow - 15 liters/min.  
 Tungsten electrode diameter - 3/16 in.  
 Filler rod diameter - 1/8 in.

Technique	Welds		Semi-automatic	Welds Joining	
	Longitudinal	Circh		Top & Bottom Covers to Container Wall	Bung to Top Cover
Arc length (in.)	Manual			Manual	Manual
1st pass	3/16	3/16		1/4	1/4
2d pass	7/16	7/16		1/4	1/4
3d pass	-	-		-	1/4
Welding speed (in./min)	NM*	11		NM	NM
	NM	9		NM	NM
	-	-		-	NM
Welding current (amp)	270 to 280	360 to 370		200 to 210	265 to 275
	235 to 245	360 to 370		200 to 210	265 to 275
	-	-		-	265 to 275
Series B, C, and F**	250 to 260	335 to 345		200 to 210	265 to 275
	210 to 220	335 to 345		200 to 210	265 to 275
	-	-		-	265 to 275

\*NM - not measured  
 \*\*Series

Series	Base	Filler
A	3003	1100
B	2014	4043
C	5052	5052
D	1100	1100
E	5154	5154
F	6061	4043

stainless steel backing ring was used to align the sections to be joined by a girth weld and it was removed after the girth weld was completed (Figure B2). The backing ring was 3 inches wide and contained a 1/16 by 1/2 inch groove. The sections were closed with temporary top and bottom covers and the assembly was purged with argon to prevent contamination of the underside of the weld. The tungsten electrode holder was locked in position so that the tungsten electrode tip was approximately 1/4 inch off center on the upside of the rotation (Figure 2).

Initially, the girth welds had a tendency to widen near the end of the weld pass. This increase in width was attributed to the inability of the relatively small container to dissipate the heat. This problem, however, would not be anticipated on the larger containers which are normally fabricated for missile application. A uniform weld contour was obtained by cooling the work as welding progressed. Refrigerated air was blown over the weld metal a few inches behind the arc area (Figure B2).

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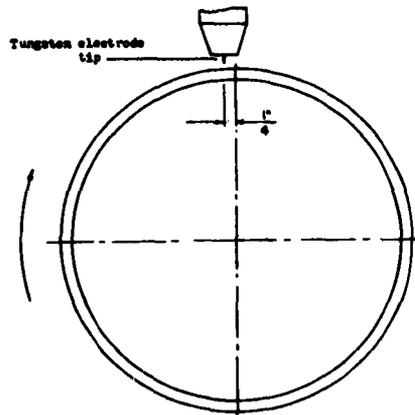


Figure 2. Tungsten Electrode Position in relation to Aluminum Alloy Container Wall

### Permanent Backing Rings

Redstone Arsenal suggested that one Series F container be fabricated, using permanent backing rings of 1160 aluminum alloy. This was done to determine if the presence of the backing rings would increase the tendency of the weldment to corrode when in contact with IRFNA. This interest stemmed from the fact that certain missile containers were being fabricated with permanent backing rings. These rings were rolled from high purity aluminum (99.6+%Al). The strips were 1/4 inch thick and approximately 1 1/4 inch wide. They were tack-welded (with 4043 filler metal) in position on the inside of the container wall before the girth welds were made.

### Radiographic Inspection of Longitudinal and Girth Welds

The longitudinal and girth welds of each container were subjected to 100 percent radiographic inspection after welding. Incomplete penetration, cracks, porosity, and tungsten inclusions were located in this way. The greatest problem was poor penetration of the girth weld at the junction of the longitudinal and girth welds. This was particularly true with the Series B containers. The poor penetration appeared to be due to the heat absorbed by the reinforcement of the longitudinal weld. Penetration was improved by decreasing the filler wire feed rate at the junction and resuming the feed rate after the junction was passed. Those areas showing poor penetration, cracks or large porosity, were gouged out and rewelded. A slight amount of fine, scattered porosity and tungsten inclusions were common, but were not expected to cause any difficulty.

### Heat Treatment of the Series B and F Containers

After the girth welds were completed, the container walls and the top and bottom covers of the B and F series were heat-treated to the T6 condition, using a conventional procedure. The purpose of the heat-treatment was to obtain the highest possible strength of these alloys. The thermal cycles used were:

1. For Series B
  - a. Solution heat-treat at 940° F for 3 hours in an air furnace.
  - b. Water quench.
  - c. Artificially age at 340° F for 18 hours in an air furnace.
  - d. Air cool.

## 2. For Series F

- a. Solution heat-treat at 970° F for 3 hours in an air furnace.
- b. Water quench.
- c. Artificially age at 350° F for 8 hours in an air furnace.
- d. Air cool.

### Welding of Top and Bottom Covers

The design used to attach the top and bottom covers to the container wall was a single-fillet corner joint (Figure 1, Joint 2). Each cover was tack-welded in position on the container wall and then manually welded with two passes as the container wall was rotated automatically.

### Welding of Bung to Top Cover

The bung was inserted in a hole in the cover to a depth of 1/8 inch and joined, as shown in Figure 1, Joint 3. Three manually-deposited weld passes, one on the inside and two on the outside, were used.

### Corrosion Specimens

Specimens for the determination of corrosion rates in terms of weight change were included in each container to which IRFNA was added. These specimens were 4 by 3/8 by 1/4 inches and had a hole at one end for attachment to the specimen hanger. Two specimens were of base metal, and two welded specimens represented the base-filler metal combination of the container. The welded specimens were made from the same materials and by the same welding technique as those used to form the container wall.

### Pressure Testing of Containers

The completed containers were tested under water with compressed air to insure their pressure tightness. It was originally intended to pressure-test all tanks at 125 psi, which is approximately double the maximum pressure expected with IRFNA in the experimental work. In the first few pressure tests the A and D Series containers sustained noticeable bulging in the lids at 125 psi, whereas the containers of the other series were not affected. The bulging was probably due to the low yield strength of the 3003 and 1100 alloys. Consequently, subsequent pressure tests were conducted at 80 psi for the A and D Series containers, and at 125 psi for all others.

## Cleaning of Containers

The completed containers and the corrosion specimens were cleaned before contact with IRFNA. The cleaning procedure was the same as that used prior to welding. An additional cleaning step was necessary with the Series B and F containers to remove black smut which deposited on the welds. Smut removal was accomplished using a solution consisting of approximately 36 percent nitric acid and 1/2 percent hydrofluoric acid.

## Loading of Containers with IRFNA

The bung cap on the IRFNA supply drum was loosened to permit the slow release of pressure before completely removing the cap. A bung cap with two orifices was fitted with two Teflon tubes. One tube (3/8 inch ID, 1/2 inch OD) was provided for acid delivery and the other (1/8 inch ID, 1/4 inch OD) for pressurizing the drum with helium. Both tubes were provided with glass stopcocks for controlling the flow of the IRFNA and preventing the backflow of nitrogen dioxide (NO<sub>2</sub>) fumes when the system was shut down.

This modified cap was screwed onto the supply drum and the delivery tube (stopcock closed) was lowered into the IRFNA supply drum just clear of the bottom. The other end of the delivery tube was lowered in the experimental container so as to almost touch the bottom. The pressurizing tube (stopcock closed) was connected in parallel with a mercury manometer and the valve (closed) of a pressure regulator on a helium cylinder. The main valve of the cylinder was opened slightly; then the regulator valve was opened so that the manometer indicated a positive pressure of 80 to 90mm. An electrical, level-indicating device (Figure 3) was placed in the experimental container at the predetermined loading level. Transfer of the IRFNA was controlled so that the level would be at the middle circumferential weld (approximately 8 liters) at the temperature at which the container would be exposed.

The actual filling operation was begun by opening the pressurizing tube stopcock. When the pressure became stabilized, the delivery tube stopcock was regulated to permit a desired rate of flow of IRFNA. When the IRFNA reached the desired level (indicated by the light of the level indicator), the delivery tube stopcock was immediately closed, the delivery tube was removed, and the experimental container was capped. Experimental container loadings were then continued in succession, simply by operating the delivery tube stopcock.

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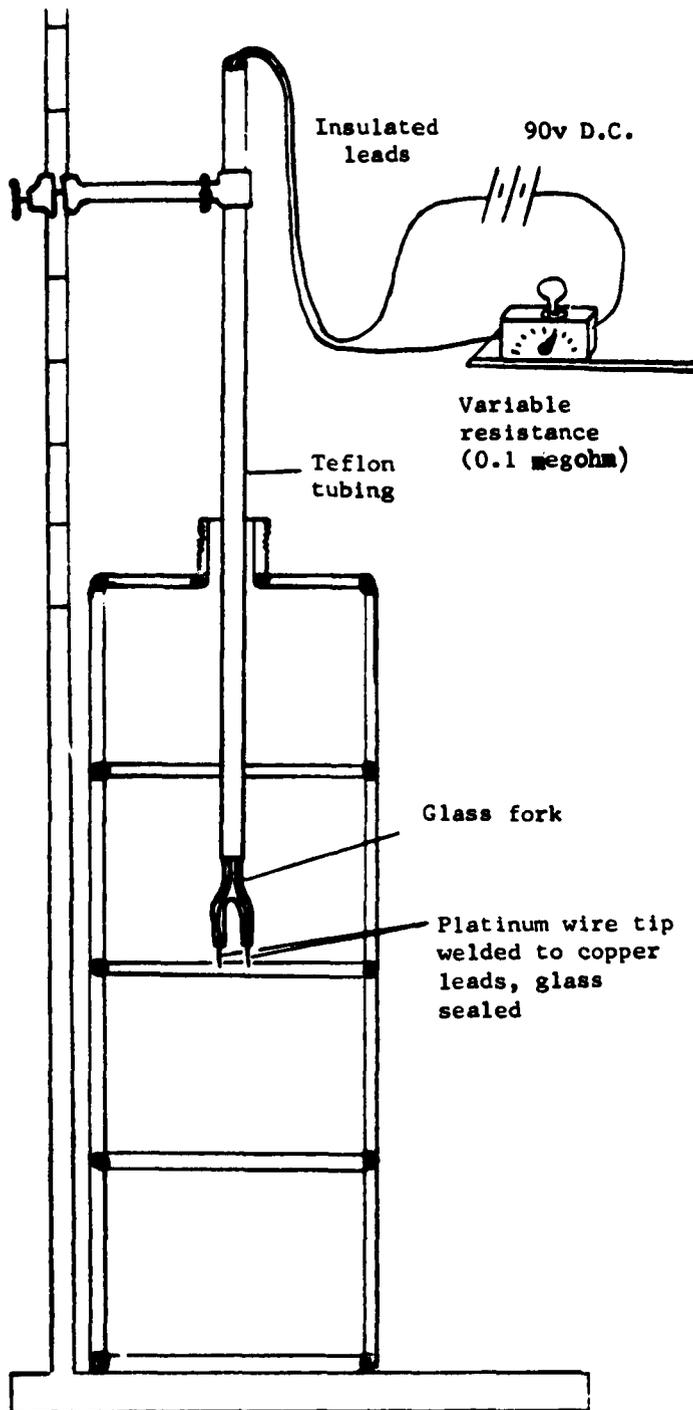


Figure 3. Cross section of experimental Container showing the Positioning of Electrical Level Indicator

The same procedure was followed when loading IRFNA modified by additions of water. A calculated amount of water was added to the predetermined amount of acid in the experimental container, under the surface of the IRFNA, near the bottom of the container. This was accomplished by using a separatory funnel to which a section of Teflon tubing was attached (loss of  $\text{NO}_2$  was negligible). The container was capped and then rolled and shaken to mix the water and IRFNA.

### Corrosion Specimens

The cleaned and dried specimens were weighed on an analytical balance and stored in desiccators until needed. For immersion in IRFNA, the specimens were attached to the hanger, as shown in Figure 4. Insulation was provided by Teflon rings. The specimens were then inserted through the bung hole of the container with slight tension outward on the specimen holder. This allowed them to hang separately after clearing the bung wall. The rack was lowered and fastened to a hook in the bung wall, submerging the corrosion specimens to about one-half the depth of the acid.

On completion of the exposure period, the specimens were removed from the acid and rinsed. The Teflon insulators were immediately removed and the specimens rinsed again, dried, weighed, and stored in desiccators for further examination.

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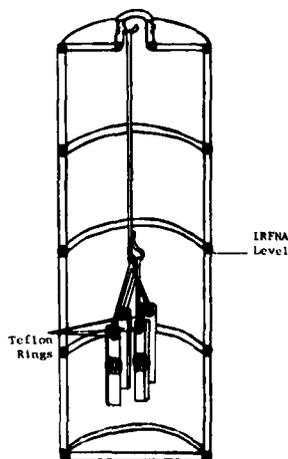


Figure 4. Cross section of experimental Container showing Positioning of Corrosion Specimens

## Exposure of Experimental Containers

After loading the experimental containers with IRFNA and inserting the corrosion specimens, the bung caps containing Teflon gaskets were screwed on and tightened with a wrench. The caps were tightened again after 24 hours' exposure since some plastic flow of the Teflon gaskets was expected, particularly at the higher temperatures. Bourdon pressure gages, made in accordance with Redstone Arsenal Drawing D 8026335, had been attached to each cap for the purpose of measuring the vapor pressure of the IRFNA during exposure. The gages were filled with Fluorolube FS oil, in accordance with the drawing, and sealed with Teflon or Kel F diaphragms. All the gages were calibrated against a standard gage after attachment to the bung cap.

One container of each series (A through F), containing IRFNA from the supply drums and having a water content of approximately 3 1/2 percent, was stored at each temperature for a given period. The temperatures were -30°, 80°, 114°, and 150° F and the periods were 40, 100, 180, and 360 days. Two additional containers of the age-hardened alloys (Series B and F) were stored without IRFNA at 150° F for 360 days to determine the effect of aging the containers of these series. The Series F container in which the permanent backing rings were welded was exposed with IRFNA to the same environmental condition as that of the aged containers.

Welded containers of Series A, B, and C, containing IRFNA which had been modified to have water concentrations of approximately 5, 6, and 7 1/2 percent, were exposed at 80° F for the four periods mentioned previously.

## Pressure Measurements

The internal pressures of the exposed containers, as indicated on the Bourdon gages, were read twice daily. Although the pressures became somewhat stabilized after several days' exposure, readings were continued throughout the exposure periods in order to detect excessive pressures.

## Procedure after Exposure

### Emptying

The containers were removed from the environmental storage cells at the conclusion of the test periods and were permitted to reach ambient temperatures before being opened. The bung caps were then loosened to lower the container pressure to that of the prevailing atmosphere. Immediately on opening, the corrosion specimens were removed from the acid and treated as previously described. The bung cap was replaced and tightened. The container was shaken to mix the acid and then was allowed to stand 24 hours to permit settling of any suspended matter. A sample of the acid was then taken for analysis. A Teflon rod was used to agitate the acid in the container and to dislodge any sludge which might have collected on the bottom. The container was tightly capped and thoroughly shaken to re-suspend loosened sludge. Following this step, a modified bung cap fitted with a Teflon drain tube (3/8 inch ID and 1/2 inch OD) and a Teflon air inlet tube (1/16 inch ID and 3/8 inch OD), each provided with a glass stopcock, were attached to the bung for emptying the container. (The air inlet tube almost reached the bottom of the container.) A glass filtering tube containing glass wool was attached to the drain tube. The container was inverted and the acid drained by gravity through the filter into a spent acid drum. The emptied container was thoroughly rinsed with tap water and allowed to drain.

### Sectioning of Containers

The containers were cut open, examined, and sectioned to provide specimens for tensile tests and metallographic studies.

Three tensile test specimens of the base metal and of the girth welds were machined from each container wall in the areas exposed to the vapor phase and to the liquid phase of the IRFNA. It was decided to withhold the testing of specimens from the areas of container walls exposed at the vapor-liquid interface pending the completion of the tensile test results obtained from the specimens of the vapor and liquid phases. If these results indicated that additional information might be gained, the interface specimens were to be tested. The tensile test specimens were machined to conform to Figure 5A of QQ-M-151a with the following exceptions:

1. The base plate specimens were 8 inches long and weld reinforcements, which were located in the grip ends, were ground flush with the base material.

2. The weld specimens were 7 inches long and the weld reinforcement located in the center of the 2 inch gage length was not ground flush.

### Sampling and Analysis of IRFNA

Samples of IRFNA from each of the supply drums, as received from the manufacturer, were taken about one day before transfer of the acid to the experimental containers. Samples of the water-modified acids were taken from each container immediately after mixing the water and acid. On completion of each storage period, samples of the acid were analyzed to determine the extent of decomposition of the acid. Approximately 250 ml of sample were taken for each analysis. This was accomplished with a glass syringe (10 inch by 1/2 inch diameter piston) attached by means of a ground glass joint to a 200-ml capacity glass pipette having a 15 inch by 1/8 inch ID tip.

## RESULTS AND DISCUSSION

### Examination of Experimental Containers

The visual examination of the internal surfaces of the containers revealed the presence of small cracks in the containers of the B and C series. These cracks were found in the fusion zones of the girth and bung welds of the Series B containers and in the welds of the Series C containers. Cracks were found in the areas of the containers exposed to the vapor as well as to the liquid phase of the IRFNA. The cracks were not noticed previously, nor were they visible in the radiographs which had been taken after welding. Similar cracks were found in the same locations on the external surfaces of these containers. Photomicrographs of typical cracks of the external and internal surfaces of the Series B containers are shown in Figures B3, B4, and B5, and of the Series C containers in Figures B6 and B7. A metallographic examination of the cracked areas revealed that the cracks on both surfaces of these containers were probably due to shrinkage cavities. There was no indication that chemical attack contributed to the formation of the cracks. However, the cracks on the internal surfaces appeared to have been enlarged due to the action of the cleaning solution and IRFNA.

Some discoloration was noted on virtually all the containers, as illustrated in Figure B8. The surfaces of the containers above the liquid level of the acid (i.e., the surfaces exposed to the vapor phase) were

gray. The surfaces exposed to the liquid phase varied from gray through orange, and some were iridescent. Within individual containers the discoloration was generally uniform on the welds and on the base metal surfaces. There seemed to be no relationship between the color and exposure time, exposure temperature, or water content of the acid. None of the containers showed "knifeline" corrosion in the heat-affected zone of the base alloy. The condition of the A, D, E, and F series containers was virtually unaffected except for the deposition of film. The container with the permanent backing rings was sectioned and visually examined. No crevice corrosion was observed between the backing rings and the container wall.

## Tensile Test Results

### Control Containers

A control container, one not exposed to IRFNA, was used for comparison in the evaluation of the corrosion resistance of each alloy. Specimens were machined from these containers and were tested to establish the tensile properties of the base materials and weld joints. The tensile strengths and the estimated standard deviations are given in Appendix C (Tables C-I through C-VI). In general, the average tensile strengths of the base material specimens agreed with the accepted values for each of the alloys.

All the control weld specimens from the Series A, C, D, and E (not heat treated) containers fractured in the heat-affected zone and the strengths of these specimens were found to be in accord with the typical reported values for the annealed alloys.

Approximately 80 percent of the control weld specimens of the Series F containers fractured in the base metal adjacent to the weld. The remainder failed through the fusion zone or the weld metal. The strengths of the fractured weld specimens were found to be close to the strength of the base material.

The control weld specimens of the Series B containers broke, partially through the fusion zone and partially through the weld metal. The tensile strengths were erratic, as indicated by the large value of the estimated standard deviation.

The average ultimate tensile strength of the weld specimens from the Series B control container was 51,900 psi (Table C-II),

whereas the strength of the base plate specimen was 71,100 psi. It is believed that the low strength of the control weld specimens could be attributed to intergranular melting of the base material adjacent to the weld. In addition, the solution heat-treatment to which these containers were subjected after welding was inadequate to allow complete solution of the  $\text{CuAl}_2$  phase.

### Exposed Containers

Three tensile specimens of the base metal and of the girth welds were taken from each of the areas exposed to the vapor and liquid phases. However, only those specimens from containers exposed for 40, 180, and 360 days at 80°, 114°, and 150° F were tested. It was decided to withhold testing of specimens from containers exposed for 100 days until the testing of specimens from containers exposed for 180 days was completed. If the specimens from the containers exposed for 180 days differed significantly from the specimens of containers exposed for 40 days, then the specimens from containers exposed for 100 days were to be tested. Since the tensile strengths of the specimens from the containers exposed for 40 and 180 days were not significantly different, the specimens from the containers exposed for 100 days were not tested. It was decided that no specimens from containers stored at -30° F for all periods would be tensile tested. This decision was made because no change was observed to occur in the corrosion specimens stored at this temperature.

Series A (3003 base-1100 filler) Containers: In general, the tensile strengths of the base plate specimens from the exposed Series A containers were not significantly different from the average strength of the base plate specimens from the control containers.

All the weld specimens failed in the heat-affected zones. The strengths of the exposed weld specimens were approximately equal to the average strengths of the control weld specimens except for nine weld specimens from containers numbered A5, \* A20, and A27 (Table C-I). There seemed to be no correlation between the low tensile strengths of the weld specimens from these three containers and the parameters: exposure time, temperature, and water content of the IRFNA. A visual examination revealed that the original temper of the base materials of these weld specimens was different from that of the base materials in the other weld specimens. The tensile strength of welded nonheatable alloys is a function of original temper, energy input, and filler metal composition.<sup>(1)\*\*</sup> Since the containers of this

\*Letters denote the series and figures indicate container numbers.

\*\*Superscripts pertain to References listed at the end of this report.

series were welded by the same technique (i.e., welding current, filler composition, etc.), it follows that the differences in original temper might contribute to the different tensile strengths.

Series B (2014 base-4043 filler) Containers: The average ultimate tensile strength of the base plate specimens from the control container was 71,100 psi (Table C-II). However, the average ultimate tensile strength of the base plate specimens from the exposed containers seemed to fall into two groups - the 70,000 to 73,000 psi range and the 66,000 to 67,000 psi range. A visual examination of the fractured tensile specimens offered no explanation for the different tensile strengths.

Fractured weld tensile test specimens from a representative container of each group (B20 of the 70,000 to 73,000 psi group and B16 of the 66,000 to 67,000 psi group) were then subjected to metallographic examination. A fractured weld specimen from the Series B control container was included for comparison purposes. Metallographic sections were removed from a grip end (base metal unaffected by welding heat) and from the weld region of each specimen. These sections were mounted, polished, etched, and compared (Figures B9, B10, and B11). It was found that the contrast of the grain structure in the grip end and in the area adjacent to the weld was the same for each specimen. This similarity indicated that the specimens and, therefore, the containers were heat-treated after welding. However, the comparison revealed that the contrast of the grain structure was different in the same location on the three specimens. The B16 specimen exhibited less contrast than the control specimen and the B20 specimen, thereby indicating different post weld heat-treatment procedures. The appearance of the B16 specimen (Figure B10) is typical of an overaged condition, i.e., the loss of grain contrast was due to precipitation of the second phase in the matrix.

Diamond pyramid hardness values (15 Kg load) were taken at approximately 1/8-inch intervals along the longitudinal axis of the three metallographic specimens (Figure 5). The results of the hardness tests agree with those of the metallographic examination. Post weld heat-treatment of each specimen was indicated by the similar hardness pattern of the base material in the grip end and in the area adjacent to the weld. It is evident from the hardness values, however, that the three specimens were not heat-treated in the same manner after welding. This condition, therefore, would account for the low tensile strength of the specimens from containers representative of the B16 specimen.

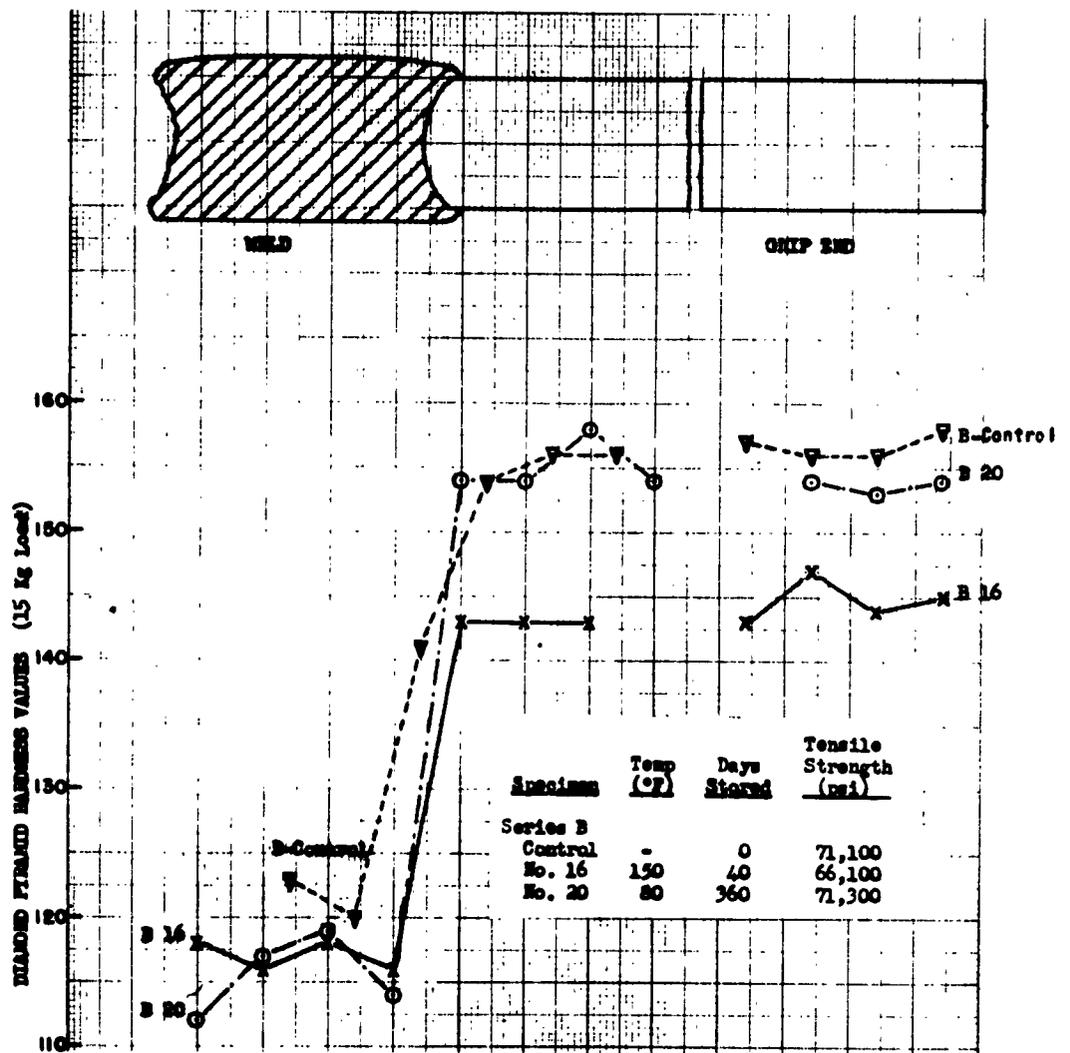


Figure 5. Diamond Pyramid Hardness Values of fractured Tensile Test Specimens from exposed Series B (2014 base metal-4043 filler metal) Containers

The tensile strength of the base metal specimens from the aged container of Series B (stored without IRFNA at 150° F for 360 days) was not significantly different from the strength of similar specimens from the control container. It follows, therefore, that the base materials of all the other Series B containers did not undergo appreciable aging as a result of being stored at the various environmental test conditions.

A comparison of the tensile strengths of the control and exposed weld specimens disclosed that, in the main, the strengths of the exposed specimens had increased regardless of exposure time, temperature, and water content of the IRFNA. Since the strength of the weld specimens from the aged container also increased, the results indicated that the increase was due to aging of the weld regions during the exposure tests.

Series C (5052 base-5052 filler) Containers: The results of the tensile tests which were conducted on the base metal and weld specimens of the Series C containers, after exposure to IRFNA, are presented in Table C-III. These results indicate that the strengths of the specimens were not significantly affected by exposure to IRFNA.

Series D (1100 base-1100 filler) Containers: The tensile test results (Table C-IV) indicated no change in the tensile strengths of the base plate and weld specimens after exposure to IRFNA.

Series E (5154 base-5154 filler) Containers: The average tensile strengths of the specimens from the exposed Series E containers are listed in Table C-V. The results indicated that the tensile strengths of these containers were not significantly affected after exposure to IRFNA.

Series F (6061 base-4043 filler) Containers: The base metal specimens exhibited a small increase in tensile strength (Table C-VI). The exposure conditions and water content of the IRFNA apparently did not influence the strength of these specimens. It is believed that aging contributed to the increase in strength exhibited by the specimens exposed to IRFNA, since the aged container also exhibited higher strength after being stored without acid for one year.

There was no significant change in the tensile strength of the exposed weld specimens (Table C-VI) and the aged weld specimens when compared to the control weld specimens. It was concluded, therefore, that if any aging did occur during the environmental exposure tests, this aging process did not affect the strength of the exposed weld specimens.

### Analysis of IRFNA

The proposed specification, MPD-138B, (2) requires that technical IRFNA consist of:

Nitrogen dioxide (NO <sub>2</sub> )	14.0 ± 1.0 percent
Water (H <sub>2</sub> O)	2.5 ± 0.5 percent
Nitric acid (HNO <sub>3</sub> )	81.3 to 84.5 percent
Hydrofluoric acid (HF)	0.6 ± 0.1 percent
Total solids (as nitrates)	0.1 percent max
Specific gravity	1.556 to 1.570 (20°/20° C)
Melting point	-51° C (-60° F)

The IRFNA ordered for this investigation was to conform to the specification except that the water content was to be between 2 and 2.5 percent by weight. The IRFNA received was certified as meeting the requirements of the specification and as having a water content of 2.14 to 2.19 percent, and was indicated to be of one lot, but analyses (Table III) performed at this arsenal in accordance with the procedure of Specification MPD-138B revealed that the entire lot did not comply with the specification, at least in regard to one of the acid constituents. The acid in supply drum 1 was found to contain 21.74 percent NO<sub>2</sub> and 75.54 percent HNO<sub>3</sub>; the acid in the other drums (2 through 17) conformed to the specification for NO<sub>2</sub> and HNO<sub>3</sub>, but the water ranged from 3.06 to 3.65 percent. Evidently the acids in drum 1 and in drums 2 through 17 represented different lots. However, it was decided to use the acid which had been received, since reordering would have imposed a long delay in the commencement of the corrosion study.

Analyses of the acids are given in Tables III and IV. These represent results for unmodified acid, as received, after storage (Table III) and water-modified acid before and after storage (Table IV).

An examination of the tabulated results revealed some differences which were inconsistent with expected directional changes of certain acid constituents and which were, apparently, attributable to the inherent shortcomings of the analytical method. For example, acid constituents will change with: (1) the progress of corrosion of the aluminum alloy containers; (2) thermal decomposition of IRFNA; and (3) the formation of the fluoride film on the metal surfaces in contact with IRFNA. The NO<sub>2</sub> and H<sub>2</sub>O concentrations should increase as the HNO<sub>3</sub> and HF concentrations decrease. (3, 4, 5) The results presented in Table III indicate that such directional changing of the IRFNA constituents was not uniformly evident for acids stored in the experimental aluminum containers.

TABLE III. IRFNA Composition as Modified by Storage at Various Temperatures

ACID DRUM NO.	CONTAINER		WEIGHT (%)											
	SERIES	NO.	NO <sub>2</sub>				HNO <sub>3</sub>				HF			
AS RECEIVED; NO STORAGE														
1			21.74				75.54					0.36		
2			14.38				81.43					0.68		
3			14.32				81.32					0.70		
4			14.16				81.74					0.59		
5			14.38				81.48					0.63		
6			14.02				81.92					0.63		
7			14.45				81.54					0.60		
8			14.35				81.78					0.59		
9			14.45				81.92					0.55		
10			14.47				81.92					0.54		
11			14.52				81.84					0.47		
12			14.48				81.80					0.58		
13			14.54				81.40					0.61		
14			14.38				81.82					0.62		
15			14.47				81.35					0.67		
16			14.40				81.48					0.64		
17			14.38				81.57					0.65		
AFTER STORAGE AT TEMPERATURES (°F) OF														
			-30	80	114	150	-30	80	114	150	-30	80	114	150
40 DAYS' STORAGE														
1	A	4,8,12,16	22.06	21.96	22.01	21.95	75.29	75.26	75.18	75.38	0.36	0.32	0.33	0.30
	B	4,8,12,16	22.06	22.17	22.51	22.43	74.97	75.05	74.62	74.89	0.47	0.34	0.29	0.30
11	D	1,5,9,13	14.62	14.67	14.86	14.74	81.45	81.53	80.80	81.24	0.62	0.56	0.60	0.67
	E	1,5,9,13	14.57	14.40	14.74	14.76	81.30	81.89	81.20	80.85	0.65	0.57	0.61	0.66
12	F	1,5,9,13	14.44	14.40	14.61	14.63	81.24	81.48	81.35	80.69	0.73	0.66	0.62	0.69
100 DAYS' STORAGE														
13	A	6	-	13.74	-	-	-	82.87	-	-	-	0.49	-	-
	B	6	-	13.78	-	-	-	82.70	-	-	-	0.54	-	-
14	A	2	14.15	-	-	-	82.14	-	-	-	0.61	-	-	-
	B	2	13.45	-	-	-	82.84	-	-	-	0.60	-	-	-
	C	2,6,10	13.63	13.89	14.21	-	82.53	82.18	81.89	-	0.64	0.59	0.57	-
	D	2,6	13.12	13.77	-	-	83.40	82.84	-	-	0.61	0.52	-	-
	E	2	13.66	-	-	-	82.40	-	-	-	0.59	-	-	-
	F	2	13.99	-	-	-	82.74	-	-	-	0.60	-	-	-
15	E	6	-	14.21	-	-	-	82.13	-	-	-	0.51	-	-
	F	6	-	13.66	-	-	-	82.73	-	-	-	0.49	-	-
16	A	10	-	-	14.49	-	-	-	81.39	-	-	-	0.63	-
	B	10	-	-	14.55	-	-	-	81.25	-	-	-	0.63	-
	D	10	-	-	14.18	-	-	-	82.05	-	-	-	0.57	-
	E	10	-	-	14.41	-	-	-	81.58	-	-	-	0.65	-
17	A	14	-	-	-	14.05	-	-	-	82.30	-	-	-	0.57
	B	14	-	-	-	13.93	-	-	-	82.35	-	-	-	0.56
	C	14	-	-	-	14.25	-	-	-	81.93	-	-	-	0.61
	D	14	-	-	-	14.06	-	-	-	82.29	-	-	-	0.56
	E	14	-	-	-	14.19	-	-	-	82.20	-	-	-	0.58
	F	10,14	-	-	14.18	14.26	-	-	82.05	81.79	-	-	0.61	0.63
180 DAYS' STORAGE														
5	A	3,7,11,15	14.37	14.39	14.58	14.47	81.49	81.92	81.65	81.35	0.70	0.48	0.53	0.55
	B	3	14.43	-	-	-	82.09	-	-	-	0.47	-	-	-
6	B	7,11,15	-	14.37	14.78	14.43	-	82.06	81.58	81.80	-	0.44	0.51	0.53
	C	3,7,11,15	14.40	14.21	14.35	14.23	82.41	82.03	81.67	82.20	0.55	0.52	0.53	0.51
	D	3	14.18	-	-	-	82.17	-	-	-	0.58	-	-	-
7	D	7,11,15	-	14.39	14.66	14.65	-	81.56	81.53	82.76	-	0.52	0.52	0.57
	E	3,7,11,15	14.52	14.61	14.02	14.59	81.47	81.46	82.15	81.69	0.57	0.54	0.51	0.50
	F	3	14.10	-	-	-	82.20	-	-	-	0.60	-	-	-
8	F	7,11,15	-	14.40	14.15	14.12	-	81.65	81.93	81.80	-	0.53	0.50	0.51
380 DAYS' STORAGE														
2	C	4,8,12	13.72	13.80	14.11	-	82.41	82.36	82.01	-	0.56	0.64	0.54	-
	D	4,8,12,16	13.63	14.24	13.96	14.92	82.85	82.17	82.34	81.16	0.49	0.47	0.53	0.52
3	C	16	-	-	-	13.94	-	-	-	82.07	-	-	-	0.60
	E	4,8,12,16	13.53	13.99	14.27	13.96	82.49	82.84	81.85	82.17	0.63	0.51	0.57	0.59
	F	4,8,12,16	13.90	13.77	14.25	14.12	82.34	82.47	81.78	82.11	0.51	0.50	0.63	0.54
9	A	1,5,9,13	13.96	13.92	14.40	14.49	82.45	82.55	81.94	81.54	0.54	0.59	0.46	0.55
10	B	1,5,9,13	13.96	14.00	14.03	14.58	82.51	82.41	82.47	81.53	0.56	0.53	0.56	0.50
	C	1,5,9,13	14.50	14.51	14.74	14.98	81.72	81.57	81.35	81.03	0.55	0.57	0.57	0.59

TABLE III. INFNA Composition as Modified by Storage at Various Temperatures (Cont'd)

ACID DRUM NO.	CONTAINER		WEIGHT (%)				SPECIFIC GRAVITY							
	SERIES	NO.	H <sub>2</sub> O		SOLIDS									
AS RECEIVED; NO STORAGE														
1			2.34			0.02				1.588				
2			3.48			0.02				1.558				
3			3.65			0.01				1.559				
4			3.80			0.01				1.558				
5			3.80			0.01				1.559				
6			3.42			0.01				1.558				
7			3.40			0.01				1.558				
8			3.27			0.01				1.558				
9			3.07			0.01				1.564				
10			3.06			0.01				1.564				
11			3.15			0.02				1.565				
12			3.42			0.02				1.565				
13			3.44			0.01				1.566				
14			3.28			0.01				1.569				
15			3.50			0.01				1.570				
16			3.42			0.02				1.570				
17			3.38			0.02				1.570				
AFTER STORAGE AT TEMPERATURES (°F) OF														
			-30	80	114	150	-30	80	114	150				
40 DAYS' STORAGE														
1	A	4,8,12,16	2.27	2.20	2.46	2.41	0.02	0.02	0.02	0.01	1.600	1.600	1.600	1.600
	B	4,8,12,16	2.62	2.42	2.55	2.37	0.01	0.02	0.03	0.03	1.600	1.601	1.601	1.600
11	D	1,5,9,13	3.26	3.22	3.62	3.34	0.03	0.02	0.02	0.01	1.578	1.577	1.574	1.575
	E	1,5,9,13	3.46	3.19	3.44	3.71	0.02	0.01	0.01	0.01	1.572	1.572	1.572	1.572
12	F	1,5,9,13	3.58	3.44	3.38	3.81	0.01	0.01	0.03	0.02	1.572	1.572	1.572	1.572
100 DAYS' STORAGE														
13	A	6	-	2.89	-	-	-	0.01	-	-	-	1.583	-	-
	B	6	-	2.96	-	-	-	0.01	-	-	-	1.584	-	-
14	A	2	3.10	-	-	-	0.003	-	-	-	1.583	-	-	-
	B	2	3.09	-	-	-	0.02	-	-	-	1.583	-	-	-
	C	2,6,10	3.19	3.34	3.32	-	0.01	0.03	0.01	-	1.583	1.584	1.587	-
	D	2,6	2.87	2.87	-	-	0.003	0.003	-	-	1.583	1.585	-	-
	E	2	3.34	-	-	-	0.01	-	-	-	1.583	-	-	-
	F	2	3.08	-	-	-	0.01	-	-	-	1.580	-	-	-
15	F	6	-	3.13	-	-	-	0.02	-	-	-	1.584	-	-
	F	6	-	2.89	-	-	-	0.03	-	-	-	1.584	-	-
16	A	10	-	-	3.48	-	-	-	0.01	-	-	-	1.587	-
	B	10	-	-	3.55	-	-	-	0.01	-	-	-	1.587	-
	D	10	-	-	3.15	-	-	-	0.02	-	-	-	1.587	-
	E	10	-	-	3.35	-	-	-	0.01	-	-	-	1.587	-
17	A	14	-	-	-	3.07	-	-	-	0.01	-	-	-	1.587
	B	14	-	-	-	3.12	-	-	-	0.01	-	-	-	1.588
	C	14	-	-	-	3.20	-	-	-	0.01	-	-	-	1.588
	D	14	-	-	-	3.06	-	-	-	0.01	-	-	-	1.588
	E	14	-	-	-	3.02	-	-	-	0.01	-	-	-	1.588
	F	10,14	-	-	3.14	3.31	-	-	0.01	0.01	-	-	1.587	1.588
180 DAYS' STORAGE														
5	A	3,7,11,15	3.44	3.20	3.22	3.62	0.04	0.01	0.01	0.01	1.578	1.581	1.581	1.584
	B	3	3.00	-	-	-	0.01	-	-	-	1.579	-	-	-
6	B	7,11,15	-	3.12	3.12	3.23	-	0.01	0.01	0.01	-	1.581	1.581	1.583
	C	3,7,11,15	3.07	3.22	3.43	3.05	0.01	0.02	0.02	0.01	1.579	1.581	1.583	1.583
	D	3	3.08	-	-	-	0.02	-	-	-	1.579	-	-	-
7	D	7,11,15	-	3.32	3.28	4.00	-	0.01	0.01	0.01	-	1.581	1.583	1.585
	E	3,7,11,15	3.43	3.38	3.31	3.21	0.01	0.01	0.01	0.01	1.580	1.581	1.583	1.581
	F	3	3.09	-	-	-	0.01	-	-	-	1.580	-	-	-
8	F	7,11,15	-	3.21	3.40	3.43	-	0.01	0.02	0.02	-	1.581	1.582	1.583
360 DAYS' STORAGE														
2	C	4,8,12	3.30	3.19	3.32	-	0.01	0.01	0.02	-	1.587	1.581	1.590	-
	D	4,8,12,16	3.01	3.11	3.18	3.40	0.01	0.01	0.02	0.008	1.586	1.588	1.590	1.581
3	C	16	-	-	-	3.38	-	-	-	0.01	-	-	-	1.590
	E	4,8,12,16	3.34	3.05	3.33	3.03	0.01	0.01	0.01	0.01	1.586	1.589	1.590	1.591
	F	4,8,12,16	3.24	3.24	3.33	3.22	0.01	0.02	0.01	0.01	1.587	1.589	1.590	1.591
9	A	1,5,9,13	3.03	2.85	3.39	3.41	0.01	0.01	0.01	0.02	1.583	1.583	1.595	1.594
10	B	1,5,9,13	2.96	3.07	2.94	3.38	0.01	0.01	0.01	0.01	1.584	1.584	1.588	1.585
	C	1,5,9,13	3.21	3.32	3.32	3.39	0.02	0.03	0.02	0.01	1.575	1.577	1.577	1.577

TABLE IV. Analyses of Water-modified IRFNA Before and After Storage

Acid Drum No.	Container Series No.		Days Stored	Before Storage					After Storage						
				Weight (%)					Sp Gr	Weight (%)					Sp Gr
				NO <sub>2</sub>	HNO <sub>3</sub>	HF	H <sub>2</sub> O	Solids		NO <sub>2</sub>	HNO <sub>3</sub>	HF	H <sub>2</sub> O	Solids	
4	A	20	360	14.15	81.18	0.70	3.96	0.01	1.561	13.98	80.64	0.56	4.70	0.02	1.557
		24		14.04	80.10	0.69	5.16	0.01	1.555	13.79	79.72	0.49	5.98	0.02	1.578
	B	20		14.36	81.04	0.69	3.90	0.01	1.560	13.84	81.11	0.57	4.46	0.02	1.585
		24		14.08	80.10	0.69	5.16	0.01	1.555	13.40	79.32	0.57	6.68	0.03	1.572
	C	20		14.26	80.91	0.68	4.14	0.01	1.561	13.67	81.33	0.61	4.37	0.02	1.585
		24		14.04	80.10	0.69	5.16	0.01	1.555	13.68	79.84	0.55	5.91	0.02	1.578
5	A	28	360	14.05	78.91	0.65	6.38	0.01	1.550	13.57	78.76	0.41	7.25	0.01	1.571
	B	28		14.05	78.91	0.65	6.38	0.01	1.550	13.32	78.92	0.53	7.22	0.01	1.570
	C	28		14.05	79.00	0.65	6.29	0.01	1.551	13.51	78.67	0.55	7.26	0.01	1.570
8	A	19	180	14.14	80.30	0.63	4.88	0.05	1.559	14.92	79.04	0.63	5.39	0.02	1.574
		23		13.95	78.86	0.63	6.52	0.04	1.554	14.46	78.22	0.55	6.76	0.01	1.567
		27		13.80	78.09	0.63	7.45	0.03	1.548	14.55	76.96	0.57	7.91	0.01	1.571
	B	19		14.16	80.29	0.63	4.88	0.04	1.563	14.43	79.71	0.61	5.24	0.01	1.577
		23		13.95	78.96	0.66	6.40	0.03	1.556	14.21	78.49	0.58	6.70	0.02	1.567
9	B	27	180	13.61	77.41	0.66	8.31	0.01	1.543	14.37	76.11	0.66	8.85	0.01	1.556
		19		13.92	79.63	0.66	5.75	0.04	1.557	14.55	78.55	0.58	6.31	0.01	1.569
	C	23		13.67	78.50	0.66	7.16	0.01	1.545	14.89	76.76	0.60	7.73	0.02	1.562
		27		13.65	77.41	0.67	8.25	0.01	1.551	14.53	76.02	0.62	8.82	0.01	1.556
12	A	17	40	14.14	79.86	0.61	5.27	0.02	1.557	14.16	79.59	0.59	5.65	0.01	1.563
		21		13.94	78.84	0.57	6.62	0.03	1.550	13.88	78.77	0.53	6.81	0.01	1.557
		25		13.73	77.71	0.62	7.92	0.02	1.544	13.86	77.90	0.46	7.78	0.01	1.547
13	B	17	40	14.24	80.52	0.64	4.58	0.02	1.563	14.02	80.50	0.55	4.92	0.01	1.568
		21		14.01	79.85	0.62	5.71	0.01	1.564	14.10	79.54	0.55	5.80	0.01	1.559
		25		13.88	78.32	0.65	7.08	0.03	1.549	13.82	78.72	0.51	6.94	0.01	1.553
	C	17		14.23	80.71	0.64	4.41	0.01	1.562	14.10	80.90	0.57	4.42	0.01	1.568
		21		13.98	79.23	0.61	6.07	0.01	1.555	14.06	79.76	0.54	5.66	0.01	1.557
		25		13.87	78.48	0.62	7.02	0.01	1.549	13.76	79.01	0.53	6.67	0.01	1.554
15	A	18	100	14.03	80.70	0.61	4.76	0.002	1.572	13.21	82.05	0.53	4.20	0.01	1.576
		22		14.06	79.51	0.62	5.91	0.003	1.564	13.28	80.35	0.49	5.86	0.02	1.560
		26		13.69	78.59	0.63	7.18	0.001	1.559	13.37	79.30	0.41	6.90	0.02	1.563
	B	18		14.25	80.48	0.60	4.67	0.005	1.572	13.70	81.40	0.52	4.37	0.01	1.576
		22		13.91	80.18	0.61	5.38	0.01	1.565	13.67	80.03	0.47	5.81	0.02	1.568
		26		13.79	78.70	0.55	6.92	0.04	1.559	13.19	79.33	0.51	6.96	0.01	1.563
16	C	18	100	14.27	80.48	0.59	4.66	0.002	1.573	13.32	81.96	0.50	4.20	0.02	1.576
		22		13.94	80.10	0.58	5.67	0.01	1.565	13.67	80.03	0.47	5.81	0.02	1.568
		26		13.81	78.70	0.60	6.89	0.01	1.559	13.19	79.33	0.51	6.96	0.01	1.563

The analytical method does not permit the detection of small changes in chemical composition which apparently occur in the IRFNA on contact with aluminum alloys. The specification allows  $\pm 0.2$  percent variation for total acidity, which could result in almost  $\pm 0.2$  percent variation in water content since water is determined by difference. Although independently determined, the HF assay by specification is allowed a precision of  $\pm 0.3$  percent. It is understandable, therefore, that differences which exist between analyses of the same acid sampled from different experimental containers do not necessarily signify that these are the result of chemical reaction between the IRFNA and the alloy.

Further support of the theory of inadequacy of the analytical method to reveal fine differences resulting from interaction of the acid and aluminum alloy containers can be readily demonstrated by the analyses of IRFNA from supply drum 1 before and after storage at  $-30^{\circ}$  F. The acid from this drum showed an increase in the  $\text{NO}_2$  content from 21.74 to 22.06 percent and a decrease in  $\text{HNO}_3$  content from 75.54 to 75.29 percent. However, after storing the corrosion specimens at  $-30^{\circ}$  F, no corrosion or film formation was present (see results under Corrosion Specimens, p 29). Therefore, the IRFNA constituents should have remained unchanged.

Analyses of water-modified acids before and after storage (Table IV) also showed that the analytical results were not consistent with known chemical changes.

Additions of calculated amounts of water to IRFNA were made for the purpose of determining the corrosive effects of water-modified IRFNA on the aluminum alloy containers. Three modifications of the acid with water in increasing increments of approximately  $1\frac{1}{4}$  percent were intended so that the water contents of the IRFNA would be approximately 4.75, 6.00, and 7.25 percent. The additions were made on the basis of water content of the unmodified acids from certain supply drums (Table III). It will be noted in Table IV that the water analyses do not show uniform increases from the original water contents shown in Table III. The  $\pm 0.2$  percent difference in water content, which could be introduced because of the specified permissible acid variation, was apparently carried through the determination of the unmodified and modified acid. This could account for as much as  $\pm 0.4$  percent water content variation in individual cases.

Some consideration was given to the conductimetric<sup>(6)</sup> and infrared<sup>(7)</sup> methods for determining water content in fuming nitric acid.

\*Letters denote the series and figures indicate container numbers.

Reproducibility and acceptable accuracy of water determinations in red fuming nitric acid were claimed for the conductimetric method if the  $\text{NO}_2$  content did not exceed 4.02 percent. This imposed limitation precluded the use of the method in this work. The infrared absorption method was indicated as especially useful in determining water content of red fuming nitric acid containing salt. Superiority of the infrared method over the MPD-138B method for the acids employed in this investigation could not be ascertained. No results were available for water determinations in inhibited fuming nitric acid in which the conductimetric and the infrared methods had been used. It was not known whether HF would interfere in either or both of the methods. Consequently, the MPD-138B method was relied on.

An examination of Table IV reveals that the results which should occur with stored acids were reversed with respect to the directional change of the  $\text{NO}_2$  and  $\text{HNO}_3$  constituents. Listed under drums 4, 5, and 15, for example, the stored acids show decreases in  $\text{NO}_2$  and, in some cases, increases of  $\text{HNO}_3$ , but the HF contents generally decrease and  $\text{H}_2\text{O}$  contents generally increase, as both should. Certain irregularities can be seen between analyses of unmodified acid (Table III) and water-modified acids (Table IV). Modified acids from drums 4, 5, 8, 9, and 12 are shown to have higher HF contents after water additions. Water contents of containers A20\*, B20, and C20, under drum 4, are indicated to be approximately 0.5 percent higher than the parent acid although water was added to increase the water content of the acid to approximately 4.75 percent.

It must be recognized that the analytical method cannot be depended upon to indicate the actual changes which occur in IRFNA as a result of storage in the aluminum alloy containers. Therefore, the corrosive effect of IRFNA on the containers cannot be resolved by the analytical method of Specification MPD-138B. The corrosion specimens, however, have provided more information concerning the attack on aluminum alloys by IRFNA (see Corrosion Specimens, p 29).

#### Characterization of Sludge

A very small quantity of sludge was formed in each of the containers. The quantity collected on the glass wool filter after any one container was emptied was estimated as one half gram or less. In removing the sludge from the filter for analysis it was virtually impossible to avoid contamination with the glass wool. Consequently, a true chemical identification of the collected material was not obtained.

\*Letters denote the series and figures indicate container numbers.

The sludge was soft and gelatinous, a consistency which would allow it to be forced through plate orifices.

### Corrosion Specimens

The corrosion specimens of the base metals and welds which had been stored in unmodified and water-modified IRFNA yielded useful information. Some anomalies relative to the effects of temperature, water content of the IRFNA, and duration of storage, on corrosion were uncovered. For any one set of conditions involving alloy, temperature, water content, and storage time, the results for the base metal and weld specimens follow somewhat the same trend (Tables V and VI, and Figures D1 through D8, Appendix D).

#### Effect of Storage Temperature

At  $-30^{\circ}$  F, no corrosion occurred with any of the alloy series during the one-year period. Differences in the results between base metal and welded specimens were negligible (Figure D1). Although weight increases of a few  $\text{mg}/\text{dm}^2$  were noted, film formation on the specimen surfaces could not be detected visually; the surfaces were bright and clean and, apparently, unchanged.

It was found, from the data obtained in the  $80^{\circ}$  and  $114^{\circ}$  F tests, that more corrosion occurred at one or both of these temperatures with the Series A, B, C, D, and F than at  $-30^{\circ}$  and  $150^{\circ}$  F. Series C and E alloys were comparable in corrosion and were least corroded among all the alloys stored at  $80^{\circ}$  F; Series E and F were least corroded of all the alloys at  $114^{\circ}$  F.

The irregularities in the weight changes (i.e., inconsistencies with the indicated trend) of both the base metal and weld specimens (Figures D2 and D3) warrant clarification. According to other investigators, (4, 8) such scatterings might be caused by irregular formation of the fluoride oxide film on the metal surfaces, and its removal<sup>(4)</sup> (which apparently accompanies and alters the corrosion process). The following values are approximate average rate changes of the base metal and the weld specimens at the specific temperatures.

TABLE V. Weight Change of Corrosion Specimens Stored in Unmodified IRFNA

Series	Days Stored	Weight Change (mg/dm <sup>2</sup> ) after Storage at							
		-30° F		80° F		114° F		150° F	
		BM*	W*	BM	W	BM	W	BM	W
A	40	1	-1	-2	0	-16	-25	21	-42
	100	1	2	-14	-38	-1	-13	18	-14
	180	2	4	-46	-64	-35	-51	10	-4
	360	1	3	-106	-55	-30	-126	19	23
B	40	0	1	-2	1	-26	1	21	40
	100	1	2	-40	-51	-4	-8	-3	26
	180	1	4	-89	-74	-33	-30	6	32
	360	1	6	-74	-109	-48	-33	4	29
C	40	-1	0	0	1	-3	-2	4	-15
	100	1	2	-1	-1	4	3	-4	-11
	180	2	3	-4	-3	-13	-5	22	27
	360	1	8	-15	-8	-25	-50	-2	29
D	40	0	0	-6	-9	-3	3	5	22
	100	0	2	-21	-20	-24	-24	-13	-12
	180	2	3	-3	-23	-27	-27	15	27
	360	1	4	-65	-52	-84	-68	-36	-22
E	40	0	0	-2	1	-3	3	-60	20
	100	1	0	1	7	-41	-145	-34	0
	180	1	5	-5	-1	-11	8	29	-13
	360	1	1	-14	-7	-28	4	-90	-40
F	40	1	1	-15	-22	-14	-11	17	24
	100	1	2	-35	-33	-4	3	21	29
	180	4	4	-43	-48	8	-1	9	20
	360	2	3	-68	-53	6	11	20	30
	360	-	-	-	-	-	-	9**	19**

\*BM - Base metal specimens

W - Weld specimens

\*\*Tank contained 1160 aluminum alloy permanent backing rings.

NOTE: The listed values are the average of two specimens. The positive values represent gain in weight, whereas the negative values represent loss in weight.

TABLE VI. Weight Change of Corrosion Specimens Stored in Modified IRFNA at 80° F

Series	Days Stored	Weight Change (mg/dm <sup>2</sup> ) of IRFNA with Water Content of											
		3.5%		5%		6%		7.5%					
		BM*	W*	BM	W	BM	W	BM	W	BM	W		
A	40	-2	-1	-35	-25	-45	-48	-74	-32				
	100	-14	-38	-39	-35	-68	-62	-107	-57				
	180	-46	-64	-85	-77	-110	-94	-156	-112				
	360	-106	-55	-119	-85	-176	-102	-317	-85				
B	40	-2	1	-37	-35	-49	-52	-40	-41				
	100	-41	-52	-51	-47	-42	-37	-33	-28				
	180	-89	-75	-63	-76	-16	-3	-14	-4				
	360	-78	-108	-71	-78	-76	-59	-48	-43				
C	40	0	1	-5	-3	-5	-3	-13	-10				
	100	-1	-1	-7	-3	-21	-16	-26	-19				
	180	-4	-3	-27	-20	-14	-13	-1	-1				
	360	-15	-8	-41	-40	-53	-43	-53	-43				

\*BM - Base metal specimens

W - Weld specimens

NOTE: The listed values are the average of two specimens. The positive values represent gain in weight, whereas the negative values represent loss in weight.

Series	Rate (mg/dm <sup>2</sup> /yr) of		
	Loss in Weight at		Gain in Weight at
	80° F	114° F	
A*	80	80	-
B	90	40	-
C	12	35	-
D	60	75	-
E	10	12	-
F	60	-	9

\*Corrosion increased with storage time, and the rates were about the same at both temperatures.

Results obtained with the aluminum alloys of Series A, B, C, D, and F in contact with IRFNA at 150° F were not entirely unusual or unexpected. The alloys were markedly corrosion resistant under this set of conditions. Keeler et al<sup>(9)</sup> noted that corrosion resistance of aluminum alloys in HF inhibited red and white fuming nitric acids was higher at 160° F than at 130° F. Series A, B, C, and F were found to gain weight over the one-year storage period; the gains were approximately 21, 17, 14, and 25 mg/dm<sup>2</sup>/yr, respectively (Table V). Series D showed a loss at 150° F of almost 30 gm/dm<sup>2</sup>/yr, but this was about half the loss which resulted with this alloy at 80° and 114° F. The weight gains and, in one case, the comparatively lower corrosion rate for the above alloys at 150° F were ascribed to the protective fluoride-oxide film which had formed on the surfaces of the aluminum alloys. The films were visibly evident on the specimens which had gained weight. Apparently, the 150° F temperature was more favorable for producing protective films than 80° or 114° F. In previously reported information, the general opinion was that corrosion progresses with increasing temperature.<sup>(4, 10)</sup> The Series E alloy was found to behave in this way, i.e., more corrosion occurred at 150° F than at -30°, 80°, or 114° F.

It is evident that the formation of protective film at 150° F involves the consumption of some of the metal. Table V indicates that certain alloy specimens lost weight in the shorter periods of storage, but eventually gained weight and exceeded the original weight of the specimen. In an effort to determine how much metal, if any, had been consumed at 150° F, all the specimens were subjected to a treatment to remove the protective film and to ascertain the weight of the bare specimens. This was accomplished by immersing the specimens in a phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)-chromic acid (H<sub>2</sub>CrO<sub>4</sub>) solution heated to 190° F.

Weights of the specimens were determined before and after each interval of treatment. (Each specimen was immersed for 5 minutes, followed by successive one-minute immersions, flushed with tap water after each removal, dried, and reweighed). Typical base plate specimen weights obtained after cleaning are plotted in Figure D5. These weights are compared to weights of the base plate specimens before and after storage in IRFNA at 150° F. A plot of the weights for a typical specimen of each of Series A, B, D, and F, obtained after treatment, shows a discontinuity. Film removal is represented principally by that portion of the plot to the left of the discontinuity point. Presumably, some metal is dissolved during this period but this is of minor extent. The portion of the plot to the right of the discontinuity, which crosses the base (before storage weight) line, represents principally the rate of metal dissolution after removal of most of the protective film. In the case of Series C, a less abrupt discontinuity is evident, but removal of the film apparently did not occur in ten minutes of treatment and the plot to the right of the discontinuity does not cross the base line. The two portions of the plot for Series C depict two different rates of combined film and metal removal. It is evident, therefore, that the film which developed on the Series C metal during the 150° F storage was more resistant to the chemical action of the treating solution. It is recognized that the treatment did not permit a direct determination of the corrosion rate from the alloy specimens stored at 150° F, but the information produced thereby indicated that

1. The protective film was formed at or near the inception of storage in IRFNA at 150° F.
2. The weight of the protective film is greater than the difference in the weights of the specimen before and after storage in IRFNA at 150° F.
3. A close approximation of the corrosion rate can be made from the derived, approximate weight of the protective film, represented by the difference in the weights of the specimen before and after storage in IRFNA at 150° F.

If the composition of the fluoride-oxide protective film can be accepted as  $2AlF_3 \cdot Al_2O_3$ , or  $Al_2F_6 \cdot Al_2O_3$ , the weight of combined aluminum is 40 percent. From this, the weight of metal consumed to form the protective film can be readily determined in the cases where weight gains occur. If the average weight gains for the Series A, B, C, and F alloys are 21, 17, 14, and 25 mg/dm<sup>2</sup>/yr, respectively, the approximate average film weights are 35, 29, 23, and 42 mg/dm<sup>2</sup>/yr, respectively. This, then, represents a consumption of aluminum for the mentioned alloys of approximately 14, 12, 9, and 17 mg/dm<sup>2</sup>/yr, respectively.

The corrosion rate for the Series D alloy (150° F storage) is not readily ascertained from the available information. This alloy showed an average loss of 30 mg/dm<sup>2</sup>/yr, although a film was produced at 150° F. Corrosion of this alloy at 150° F was at a lower rate than at either 80° or 114° F.

These data indicate that, at best, a thin but not too protective film was formed at 150° F on the Series E alloy. Consequently, the average weight loss obtained with this alloy at 150° F, i.e., 65 mg/dm<sup>2</sup>/yr, is indicated as the corrosion rate.

The specimens stored at 80° and 114° F were noted to be iridescent or darkened. Therefore, it was decided to subject these specimens to the cleaning treatment (three minutes' immersion followed by successive one-minute immersions). This was done to ascertain whether removal of the films would alter the corrosion data obtained and to determine the relative amount of protection these films afforded. Results of typical specimens are plotted in Figures D6 and D7 from which it was deduced that (1) the dissolving action of the treating solution on the metal was immediate, (2) the film which afforded some protection in IRFNA was very thin, and (3) the weight of the film could not significantly alter the corrosion data.

#### Effect of Water Content at 80° F

Increasing the water content of IRFNA over the range of approximately 3.5 to 7.5 percent and prolonging the storage time had definite effects on the corrosion of Series A, B, and C alloys at 80° F. The results are presented in Table VI and plotted in Figure D8.

Markedly accelerated corrosion of the Series A alloys occurred as the water content was increased. At each water level, corrosion also increased with time of storage. A less marked increase of corrosion was found with the Series C alloys. Both higher water content and longer storage time contributed to the increase, but the combined effects of these factors was greater with the Series A alloys. Contrary effects were found with the Series B alloy. In general, increasing the water content above the 3.5 to 7.5 percent range lessened the corrosion of the Series B alloys.

## Pressures

### At -30° and 80° F

The pressures in containers stored at -30° and 80° F were insufficient to cause gage responses. Therefore, the readings for these containers were not collected. Pressures within containers stored at -30° F were expected to be negative with respect to the prevailing atmospheric pressures, hence they would not be indicated by the gages. However, the containers were equipped with gages as a safety precaution to indicate pressures which might have developed from unforeseen chemical reactions.

### At 114° and 150° F

Pressure profiles for experimental containers which contained IRFNA at 114° and 150° F are shown in Figure 6. The bands represent the pressure fluctuations (indicated as four stages) obtained with the experimental containers of all the alloys, i.e., the range of pressures encountered both within a series and among the series.

Pressure equilibria within the experimental containers stored at 114° and 150° F were reached within six to ten days. If the temperature was kept within  $\pm 2^\circ$  F, the pressures remained constant over long periods. The IRFNA from supply drum 1, with 21.78 percent NO<sub>2</sub>, developed pressures up to 52 psig in the experimental containers stored at 150° F and 24 psig maximum at 114° F (Figure 6, Stage 1). The IRFNA containing approximately 14 percent NO<sub>2</sub> developed 39 to 44 psig at 150° F and 14 to 18 psig at 114° F at equilibrium (Stage 1).

When the storage had continued for approximately 140 days, the temperatures in the 114° and 150° F storage cells were inadvertently increased to 120° and 160° F, respectively. Consequently, pressure rises occurred in the containers being stored (Stage 2). The pressures in the containers rose to 62 psig at 160° F and 23 psig at 120° F. When the temperature change had been detected (first indicated by the pressure rise), the cell heater controls were readjusted to bring the temperature in the cells back to the original temperatures, i.e., 114° and 150° F. Since the 160° and 120° F temperatures persisted only for 2 to 3 days, equilibrium pressures had not been attained at these temperatures. The inadvertent temperature change and the return to original temperature conditions are illustrated by Stage 2 in Figure 6.

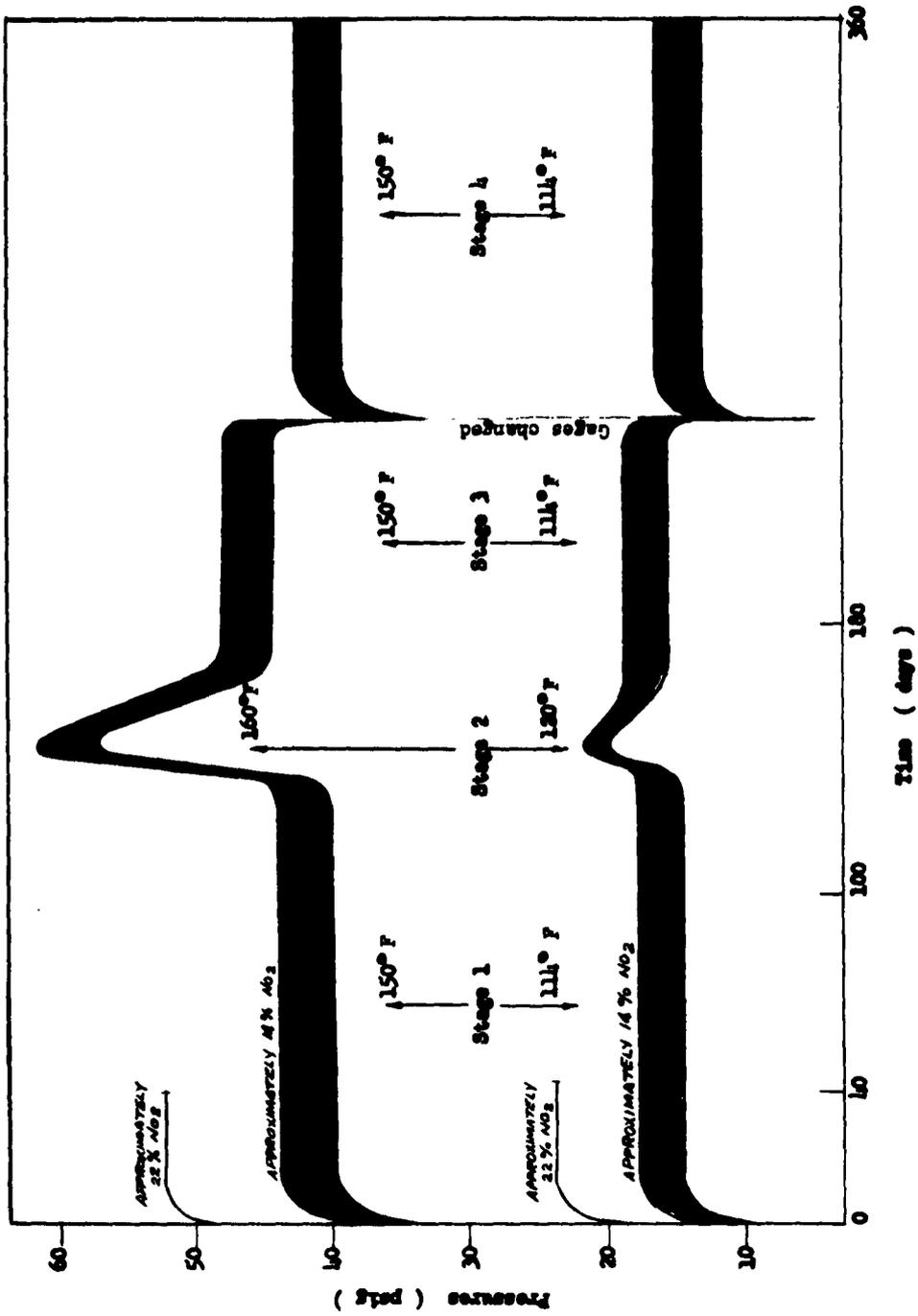


Figure 6. Profiles of Pressures of IRFNA for all Series of experimental Containers

When equilibrium had again been reached at 114° and 150° F (Stage 3), the pressures in each of the containers were somewhat higher than the pressure attained previously (Stage 1). The differences between the Stage 1 and Stage 2 pressures were greater at 150° than at 114° F.

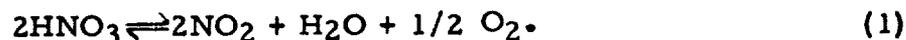
It was not known whether the higher pressures of Stage 3, relative to Stage 1, were the result of further decomposition of IRFNA occurring at the higher temperatures (Stage 2), or the result of additional corrosion or gage malfunctioning. It was decided, therefore, to replace the gages on some of the containers in order to ascertain the reliability of these gages in indicating equilibrium pressures.

One container each of Series A, B, and C, stored at 150° F, was removed from storage and cooled overnight to ambient temperature. The gages on these containers were replaced with newly calibrated gages. The gages which had been removed were examined and recalibrated and were found to agree with the original calibration. An oily film was found on the outside of the diaphragm and on recessed surfaces of the gage coupler; a gas bubble, approximately 1/8 inch in diameter, was noted in the oil behind the diaphragm of each gage; a film of green corrosion product (copper nitrate) was noted around the visible end of the gage tube. The Fluorolube FS oil was tested, using water-moistened indicator paper, and found to be acid. This reaction indicated that the NO<sub>2</sub> had permeated the diaphragm. The containers were put back into the 150° F storage cell. When equilibrium pressure was again achieved, the pressure was found to be slightly lower (Stage 4) than the equilibrium pressure at Stage 1. Similar but comparatively less pronounced pressure changes occurred when gage replacements were made on several containers stored at 114° F. The gages were less affected, i.e., gas bubbles were smaller and green corrosion film was less pronounced; also, oil seepage was detected in these gages. As a result of these findings it was decided to replace all gages on containers which were in storage for one year at 114° and 150° F. All containers on which gages were replaced gave slightly lower pressures at Stage 4 than at Stage 3.

Explanations are advanced for the differences in the pressure equilibria, namely Stages 1, 2, 3, and 4. In connection with this it is perhaps fitting to review the principal reactions which contribute to the pressures exerted by IRFNA in closed systems.

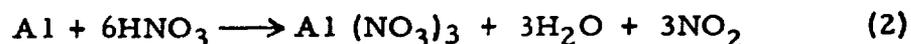
First, the dissolved NO<sub>2</sub>, HNO<sub>3</sub>, HF, and residual H<sub>2</sub>O exert their respective partial vapor pressures at the temperature to which the system is subjected. The greatest pressure from these is

exerted by the dissolved  $\text{NO}_2$ . For the purposes of this discussion, the pressures exerted by  $\text{NO}_2$ ,  $\text{HF}$ , and  $\text{H}_2\text{O}$  can be considered reversible with temperature, i.e., these constituents will redissolve in the IRFNA on cooling. In general, on the other hand, the  $\text{HNO}_3$  will undergo thermal decomposition according to the reaction:<sup>(3, 4, 5)</sup>



The bulk of the gases produced in equation (1) was shown by Fontana<sup>(10)</sup> to come from the decomposition of liquid  $\text{HNO}_3$ . Fontana also showed that equation (1) is reversible under critical pressures, e.g., about 230 psig at 77° F, with the ratio of volume of gas to total volume of sample,  $V_g/V = 0.533$ . It is evident that the magnitude of pressures required for reversibility was not attained in this work; consequently, oxygen produced in the thermal decomposition of IRFNA is a factor to be considered, since it is relatively insoluble in IRFNA at ambient temperature.<sup>(5, 10)</sup>

The second principal reaction which can contribute to the decomposition of IRFNA is that involving the corrosion of the aluminum alloys:



Presumably, with IRFNA this reaction will vary in rate of initiation and progression, depending on the temperatures involved and the effectiveness of the protection afforded by the fluoride-oxide film which forms on the alloy surfaces by the action of the inhibitor ( $\text{HF}$ ).

These reactions will be considered with reference to the pressure profiles in Figure 6, representing the pressures developed in the experimental containers.

Stage 1 is indicative of pressures developed by reactions (1) and (2). Reaction (2) should be more pronounced in the early phases of this stage until sufficient protective film is deposited to retard or stop the reaction.

Stage 2 represents the approach to an equilibrium condition at higher temperatures (120° and 160° F). It is assumed that reactions (1) and (2) are both involved. Presumably, reaction (2) is of lesser importance in this stage than in Stage 1, as deduced from the low corrosion rates of specimens stored in IRFNA at 150° F.

Stage 3, it will be noted, is a higher pressure level than Stage 1, although the temperatures were the same as that of Stage 1 (114° and 150° F). The increase of temperature in Stage 2 (120° and 160° F) resulted in further thermal decomposition of IRFNA. Since oxygen is relatively insoluble in IRFNA and since the total pressures were below the critical range, oxygen produced during Stage 2 may account for the higher level of Stage 3, as compared to Stage 1. This explanation could very likely be substantiated if more were known concerning the activation and rate of decomposition of IRFNA under the Vg/V ratio and temperature conditions involved in these experiments.

On cooling the containers to ambient temperature for the removal of the gages, the bulk of the NO<sub>2</sub>, H<sub>2</sub>O, and other vapors which are soluble in IRFNA were redissolved in the liquid IRFNA. Presumably, only a small amount of oxygen which had been generated at the higher temperature could have redissolved, since oxygen is relatively insoluble in IRFNA. Therefore, when the containers had been opened in order to replace the gages, some of the oxygen escaped from the system. It was found that when the containers had been replaced in storage at 114° and 150° F and equilibrium had been reached at these temperatures, the pressures attained in Stage 4 (Figure 6) were slightly lower than those attained initially in Stage 1.

Considering that the NO<sub>2</sub> and H<sub>2</sub>O concentrations were unchanged in the chemical system and that the Vg/V was unaltered, the slightly lower equilibrium pressure in Stage 4 would seem to be due to the small reduction in the O<sub>2</sub> concentration in the system (resulting from opening the containers). But Kay et al<sup>(12)</sup> demonstrated that removal of O<sub>2</sub> from a system involving pure, concentrated nitric acid causes very little disturbance of the equilibrium pressure at a given Vg/V, whereas the effect of changes in NO<sub>2</sub> and H<sub>2</sub>O are marked. Therefore, the reason for the slightly lower equilibrium pressure in Stage 4 is not clear. This phenomenon occurred with all experimental containers on which gages had been replaced and which had been stored for 360 days. It would be desirable to study the phenomenon under more precisely controlled conditions.

## CONCLUSIONS

The following conclusions resulted from this study:

1. None of the welded alloy combinations studied corroded at  $-30^{\circ}$  F. The corrosion rates of all the series except E were higher at  $80^{\circ}$  and  $114^{\circ}$  F than at  $150^{\circ}$  F. At the latter temperature the corrosion rates of all the series except E were markedly retarded due to the formation of protective films.

2. The corrosion rates of the Series A and Series C alloys increased as the water content of the IRFNA increased. The corrosion rate of the Series B alloy diminished, however, with increasing water content up to 7.5 percent. Of these three series, the C alloys exhibited the highest corrosion resistance over the range of water contents from 3.5 to 7.5 percent.

3. In general, the corrosion rates of aluminum alloys exposed to IRFNA at a particular storage temperature progressed with time. At  $150^{\circ}$  F, however, the corrosion rates seemed to diminish with time up to a period of one year.

4. In general, the tensile strengths of the welds and base metals of the containers were not adversely affected by contact with IRFNA for one year at the temperatures investigated.

5. Except for the formation of protective films, there was no visible corrosion on the container resulting from IRFNA after the completion of a one-year exposure period.

6. The chemical analytical method of Specification MPD-138B does not permit the detection of precise results with small changes in the chemical composition of IRFNA.

7. Based on results obtained with the Series F container, the use of permanent backing rings in contact with IRFNA did not introduce any crevice corrosion problem.

## RECOMMENDATIONS

It is recommended that

1. Welded containers of 5052 base-5052 filler metal be used for the storage of IRFNA at temperatures up to 150° F. If the temperature does not exceed 114° F, the 5154 base-5154 filler metal combination is equally suitable.

2. The 5052 base-5052 filler metal containers be used in the event that IRFNA having a water content up to 7.5 percent is to be stored at 80° F. (Specification MPD-138B specifies a water content up to  $2.5 \pm 0.5$  percent.)

3. Further investigation be made to develop a more reliable chemical analytical procedure for IRFNA which should permit the detection of minute changes of the IRFNA constituents resulting from: (a) the thermal decomposition of the acid, and (b) the chemical interaction of the acid with the container metals.

## APPENDIX A

### PROTECTIVE CLOTHING FOR PERSONNEL

<u>Nomenclature</u>	<u>Stock No.</u>
Suit, Protective, Acid and Fuel Resistant	8415-272-3005*
Suit, Protective, Acid and Fuel Resistant	8415-272-3009*
Gloves, Protective, Acid and Fuel Resistant	8415-264-3598*
Hood, Protective, Acid and Fuel Resistant	8415-276-7624*
Boots, Rubber	DF8430-147-1023 and DF8430-299-0340**

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\*National Stock Catalog number

\*\*Quartermaster stock numbers

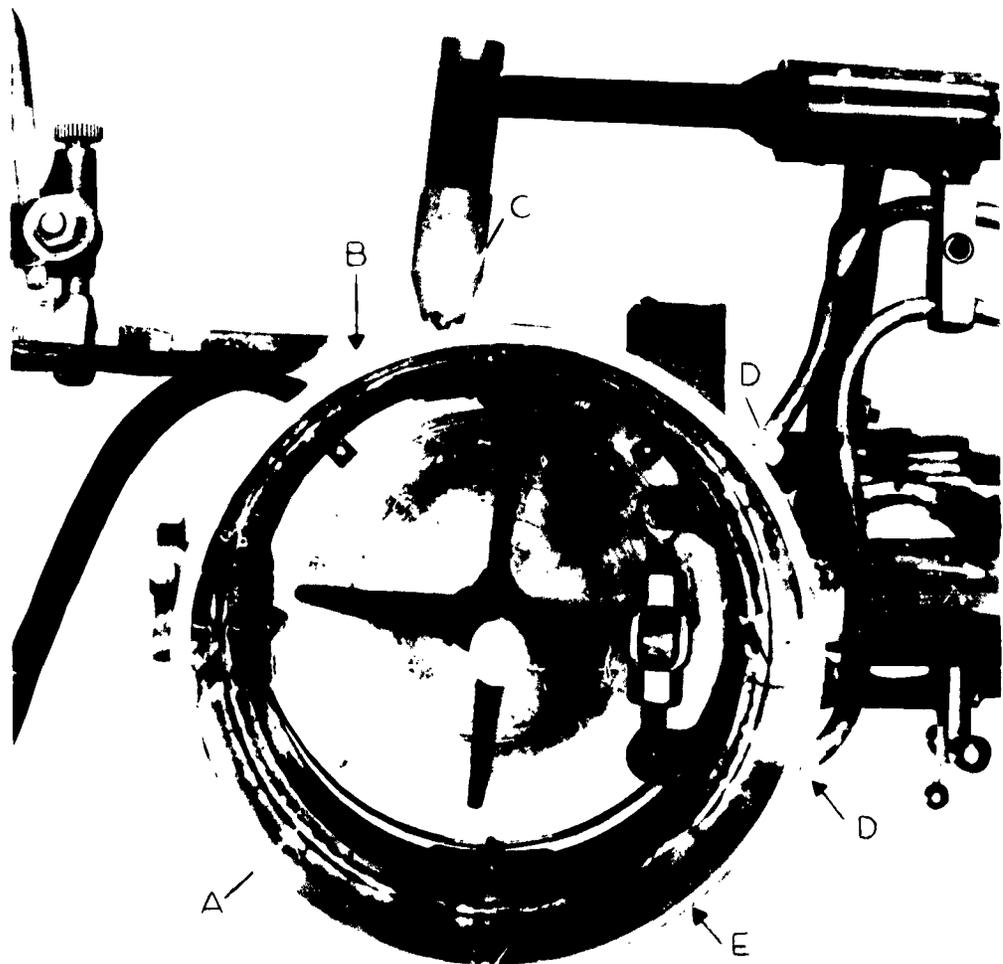
APPENDIX B

DETAIL PHOTOGRAPHS AND PHOTOMICROGRAPHS

36.231.S1006/ORD.60  
R-1524



Figure B1. Experimental welded Aluminum Alloy  
Container with pressure gage



- |                            |                             |
|----------------------------|-----------------------------|
| A - Removable backing ring | C - Tungsten electrode tip  |
| B - Filler wire            | D - Source of cold air jets |
| E - Aluminum alloy rings   |                             |

Figure B2. System for joining Aluminum Alloy Rings  
to Girth Welds to form Container Wall

36.231.S1008/ORD.60  
R-1524

Unexposed surface

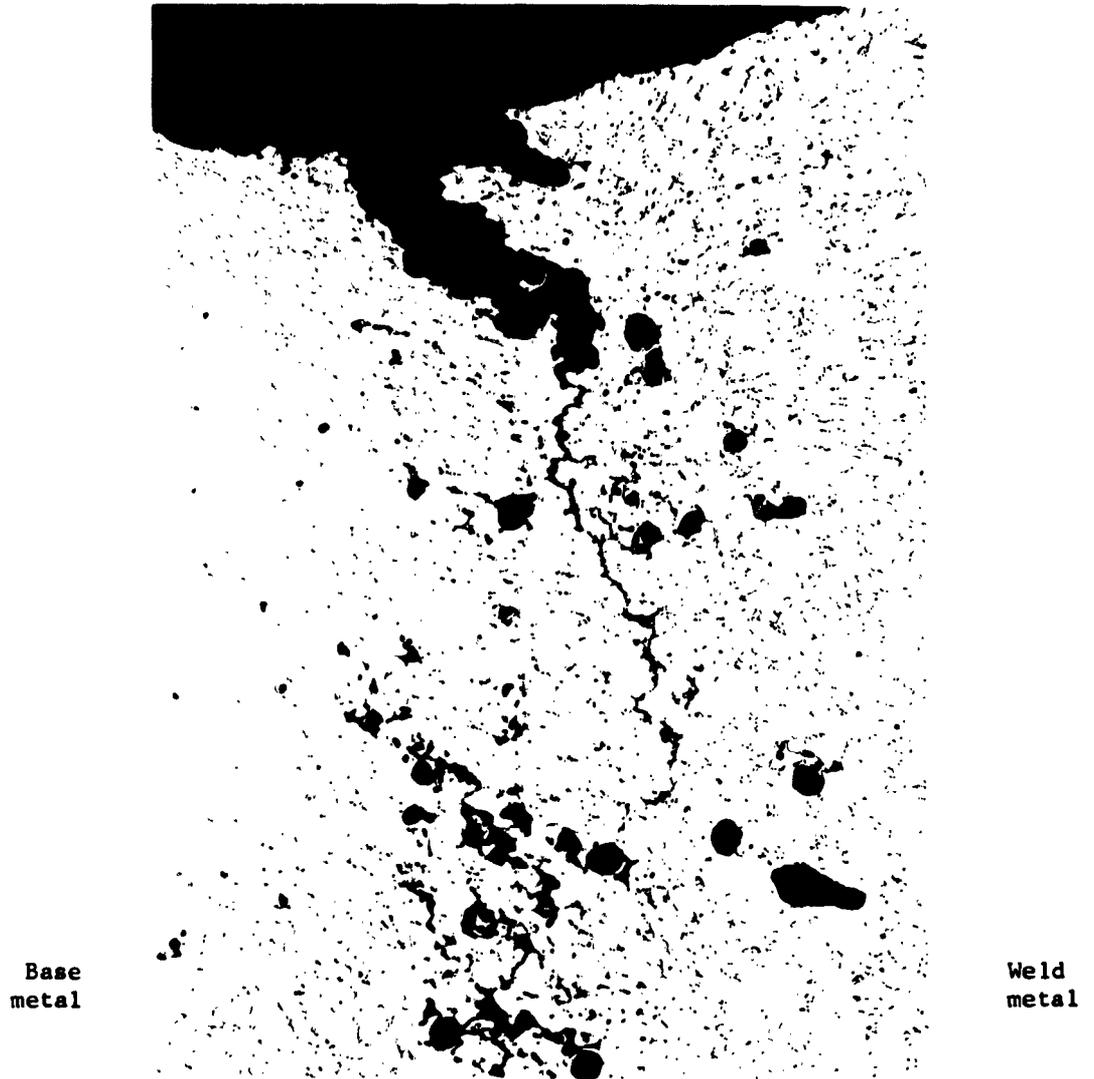
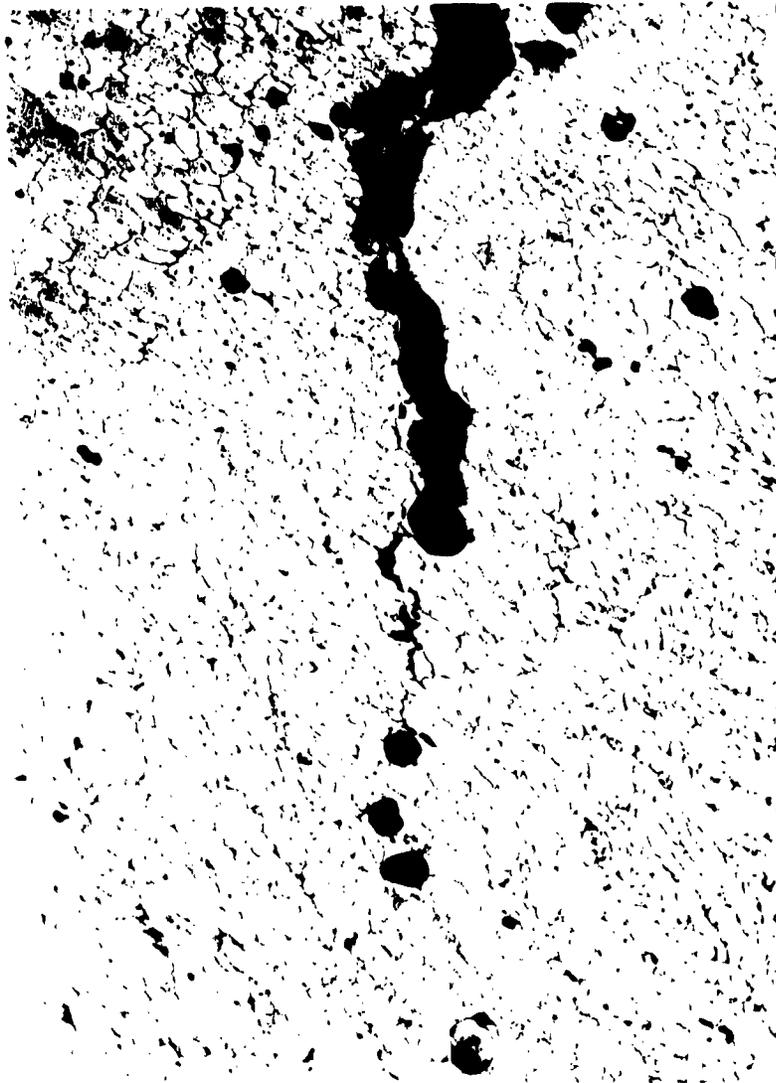


Figure B3. Cracked Fusion Zone Area on unexposed surface of a Transverse Weld Specimen from a Series B (2014 base metal-4043 filler metal) Container

Etchant: 3% HF  
Mag: 100X

Exposed surface

Base  
metal



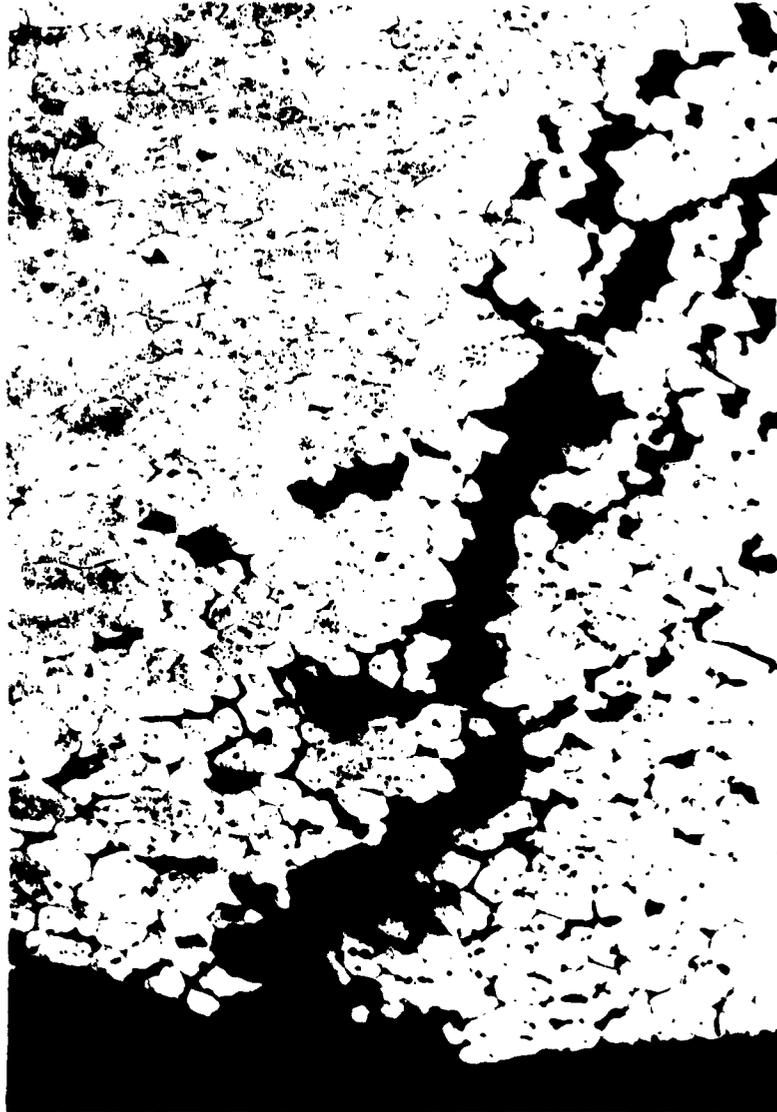
Weld  
metal

Figure B4. Cracked Fusion Zone Area adjacent to  
Girth Weld on unexposed side of Series B  
(2014 base metal-4043 filler metal)  
Container No. 16

Etchant: 3% HF  
Mag: 100X

36.231.S1010/ORD.60  
R-1524

Base  
metal



Weld  
metal

Exposed surface

Figure B5. Cracked Fusion Zone Area adjacent to  
Bung Weld on exposed side of Series B  
(2014 base metal-4043 filler metal)  
Container No. 15

Etchant: 3% HF  
Mag: 200X

36.231.S1011/ORD.60  
R-1524



Figure B6. Cracks at junction of Longitudinal  
and Girth Welds of Series C  
(5052 base metal-5052 filler metal)  
Container No. 9

No etchant  
Mag: 3.5X

36.231.S1012/ORD.60  
R-1524

Surface exposed to IRFNA



Figure B7. Cross section view of cracked  
Longitudinal Weld in Series C  
(5052 base metal-5052 filler metal)  
Container No. 9

Etchant: 3% HF  
Mag: 50X

36.231.S1013/ORD.60  
R-1524

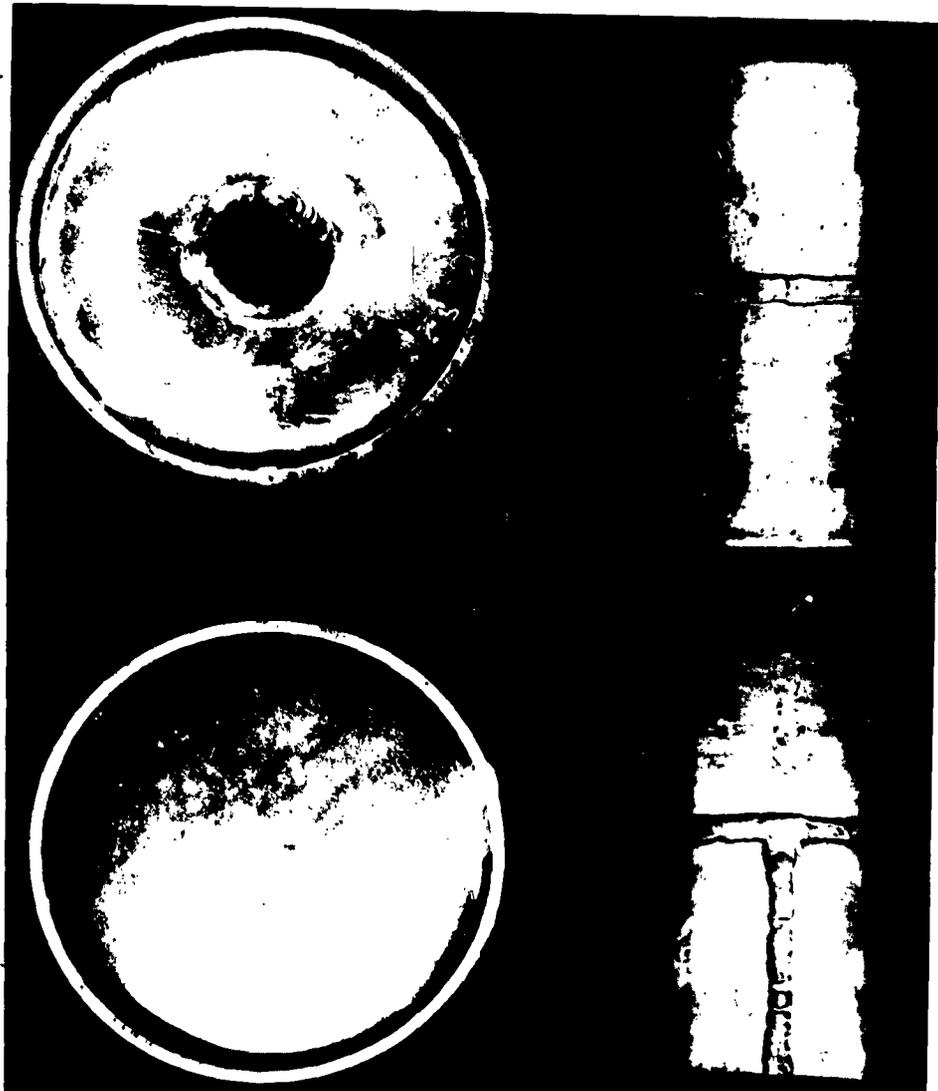
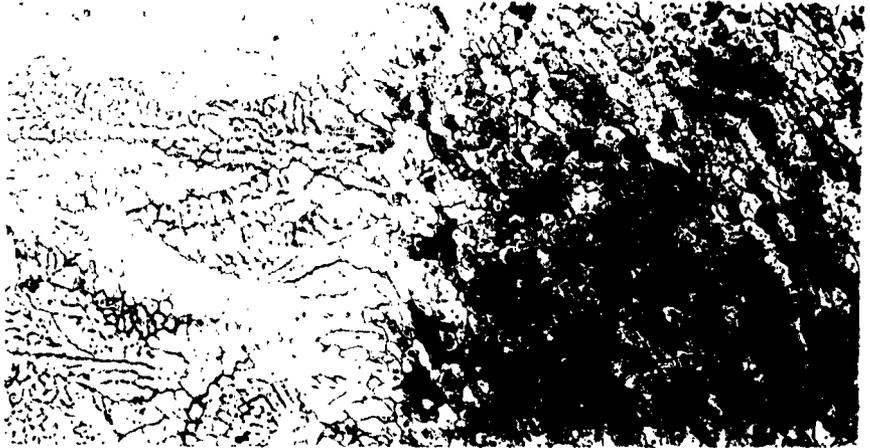


Figure B8. Internal appearance of Series E  
(5154 base metal-5154 filler metal) Container  
after exposure to IRFNA (2.2% water)  
for 40 days at 80° F

Weld metal-  
base metal  
interface



Weld metal

Base metal

Base metal  
adjacent to  
weld region



Base metal  
in grip end

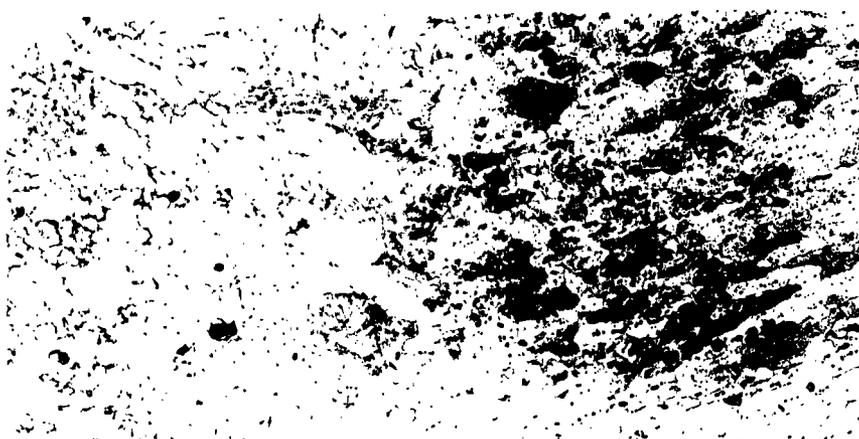


Figure B9. Photomicrographs of fractured Transverse Weld Specimen from Series B (2014 base metal-4043 filler metal) Control Container

Etchant: Keller's  
Mag: 100X

36.231.S1015/ORD.60  
R-1524

Weld metal-  
base metal  
interface



Weld metal

Base metal

Base metal  
adjacent to  
weld region

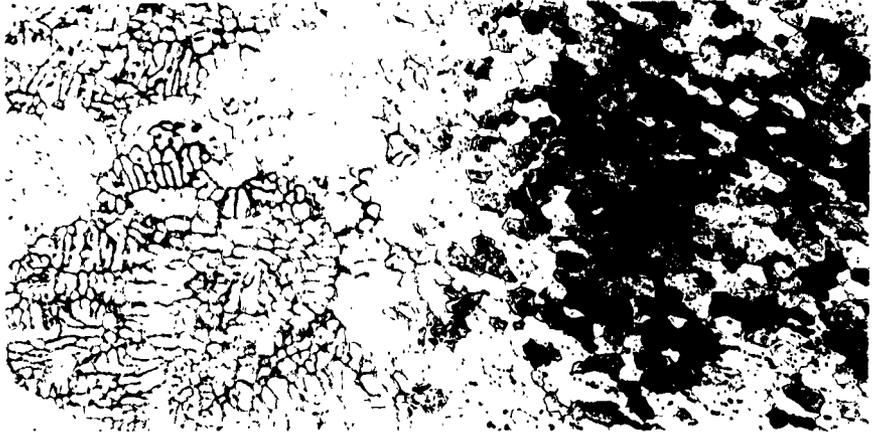


Base metal  
in grip end



Figure B10. Photomicrographs of fractured transverse weld  
Specimen from Series B (2014 base metal-4043 filler metal)  
Container No. 16, exposed to IRFNA for 40 days at 160° F  
Etchant: Keller's  
Mag: 100X

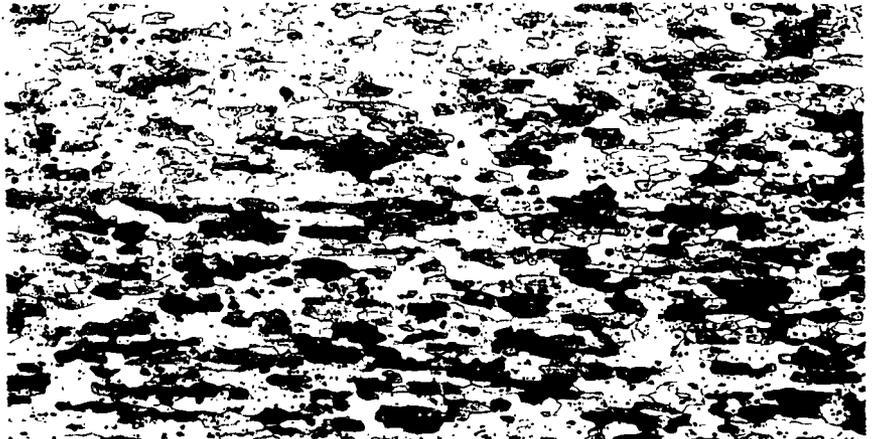
Weld metal-  
base metal  
interface



Weld metal

Base metal

Base metal  
adjacent to  
weld region



Base metal  
in grip end



Figure B11. Photomicrographs of fractured Transverse Weld Specimen from Series B (2014 base metal-4043 filler metal) Container No. 20, exposed to IRFNA for 360 days at 80° F  
Etchant: Keller's  
Mag: 100X







TABLE C-IV. Average Ultimate Tensile Strength of Specimens of Series J  
(1100 base-1100 filler) Containers after Exposure to IRFNA

Container No.	H <sub>2</sub> O Conc in IRFNA (wt %)	Days Exposed	Temp (°F)	Avg* Ultimate Tensile Strength (psi) of Test Specimens														
				Control			Container Specimens			Base Alloy			Weld					
				Ø **	Weld	Ø **	Vapor Phase	Ø **	Liquid Phase	Ø **	Vapor Phase	Ø **	Liquid Phase	Ø **	Vapor Phase			
Control	None	0	-	18,600 <sup>a</sup>	300	12,700 <sup>b</sup>	100											
5	2.2	40	80					NTC	-	NTC	-	12,900	100	12,300	100			
9			114					NTC	-	NTC	-	12,900	100	12,800	300			
13			150					NTC	-	NTC	-	12,800	200	13,000	200			
8	3.5	360	80					19,700	2200	18,800	700	13,200	300	13,000	200			
12			114					17,400 <sup>d</sup>	-	17,200 <sup>d</sup>	-	12,000	300	12,400	300			
15	3.4		150					17,900	100	18,400	300	12,400	300	12,600	100			

\*The listed values are the average of 3 specimens, except as noted below.

a - Average of 12 specimens

b - Average of 16 specimens

c - None tested

d - Average of 2 specimens.

\*\*Estimated standard deviation

TABLE C-V. Average Ultimate Tensile Strength of Specimens of Series E  
(5154 base-5154 filler) Containers after Exposure to IRFNA

Container No.	H <sub>2</sub> O Conc in IRFNA (wt %)	Days Exposed	Temp (°F)	Avg* Ultimate Tensile Strength (psi) of																
				Control					Test Specimens											
				Container Specimens		Base Alloy		Liquid Phase		Vapor Phase		Weld								
Base Alloy	Weld	Weld	σ**	σ**	σ**	σ**	σ**	σ**	σ**	σ**	σ**									
Control	None	0	-	43,000 <sup>a</sup>	600	34,600 <sup>b</sup>	300													
5	2.2	40	80			43,300	100	43,700	100	35,300	200	33,400	3300							
9		114	114			44,100	300	43,500	200	35,400 <sup>c</sup>	300	35,100	200							
13		150	150			44,000	0	44,100	500	35,200	200	35,400	400							
7	3.4	180	80			NTd	-	NTd	-	35,200	100	35,700	100							
11		114	114			43,200	300	42,900	200	34,900	200	34,900	200							
15		150	150			44,900	300	44,100	200	35,500	200	35,500	0							
8	3.6	360	80			44,500	200	44,300	600	34,900 <sup>c</sup>	500	35,100	600							
12		114	114			43,500	400	43,800	500	35,200	200	35,100	400							
16		150	150			44,600 <sup>e</sup>	-	44,500	300	36,000	200	34,800	200							

\*The listed values are the average of 3 specimens, except as noted below.

a - Average of 11 specimens  
b - Average of 17 specimens

d - None tested  
e - Average of 2 specimens

\*\*Estimated standard deviation.

TABLE C-VI. Average Ultimate Tensile Strength of Specimens of Series F  
(6061 base-4043 filler) Containers after Exposure to IRFNA

Container No.	H <sub>2</sub> O Conc in IRFNA (wt %)	Days Exposed	Temp (°F)	Avg* Ultimate Tensile Strength (psi) of											
				Control				Test Specimens				Weld			
				Base Alloy	Weld	σ**	σ**	Vapor Phase	σ**	σ**	σ**	σ**	Vapor Phase	σ**	σ**
Control	None	0	150	44,800 <sup>a</sup>	300	45,200 <sup>b</sup>	400	45,600	100	45,600	100	46,500 <sup>d</sup>	100	46,200 <sup>a</sup>	400
		360	150	45,700 <sup>c</sup>	200	44,900 <sup>c</sup>	1000	45,600	100	45,600	200	45,800 <sup>d</sup>	600	46,700 <sup>e</sup>	400
5	2.4	40	80					45,600	100	45,700	100	46,500 <sup>d</sup>	100	46,200 <sup>a</sup>	400
9			114					46,000	200	46,200	200	46,700	200	46,700 <sup>e</sup>	400
13			150					45,600	100	45,600	200	45,800 <sup>d</sup>	600	46,100 <sup>e</sup>	200
7	3.3	180	80					NT <sup>f</sup>	-	NT <sup>f</sup>	-	43,300 <sup>e</sup>	900	45,000 <sup>d</sup>	2400
11			114					46,300	100	46,600	100	46,600	0	47,200 <sup>d</sup>	300
15			150					46,400	100	46,400	200	47,000	300	46,000 <sup>d</sup>	2900
8	3.6	360	80					45,400	100	45,600	100	45,900	200	46,100	100
12			114					45,000	400	45,300	100	45,200 <sup>d</sup>	600	45,600 <sup>e</sup>	-
16			150					45,800	200	45,600	200	45,500 <sup>d</sup>	300	45,400 <sup>e</sup>	-
Backing ring	3.5		150					46,400	100	46,700	100	NT <sup>f</sup>	-	45,600 <sup>e</sup>	-

\*The listed values are the average of 3 specimens, except as noted below.

a - Average of 12 specimens

b - Average of 18 specimens

c - Average of 6 specimens

d - One specimen failed through the weld-heat affected zone.

e - Two specimens failed through the weld-heat affected zone.

f - None tested

g - Average of 2 specimens

h - This container was exposed to IRFNA with permanent backing rings which were removed from the specimens before the tensile tests.

\*\*Estimated standard deviation

APPENDIX D  
WEIGHT CHANGE DATA

36.231.S0998/ORD.60  
R-1524

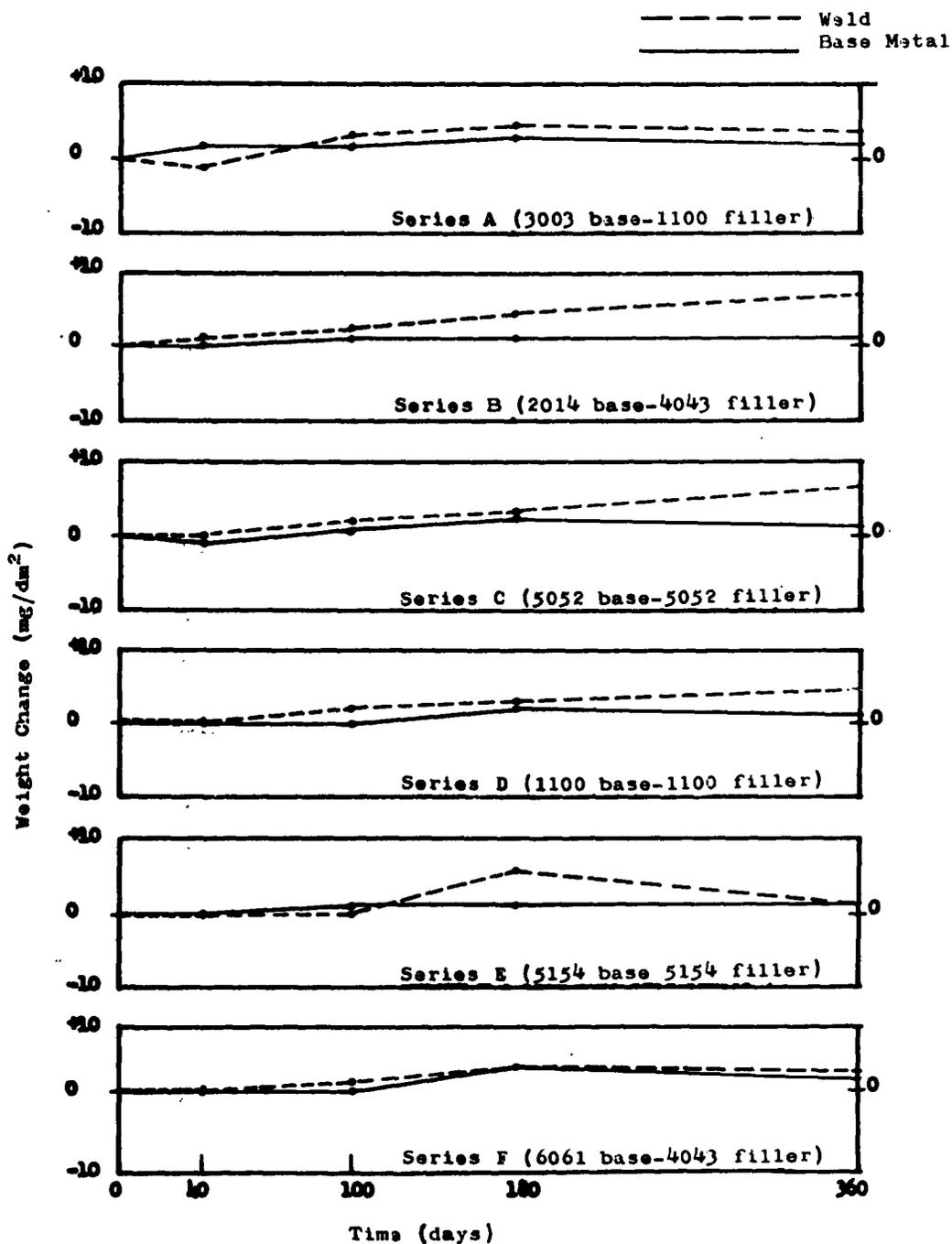


Figure D1. Weight Change of Corrosion Specimens suspended in Unmodified IRFNA at -30° F

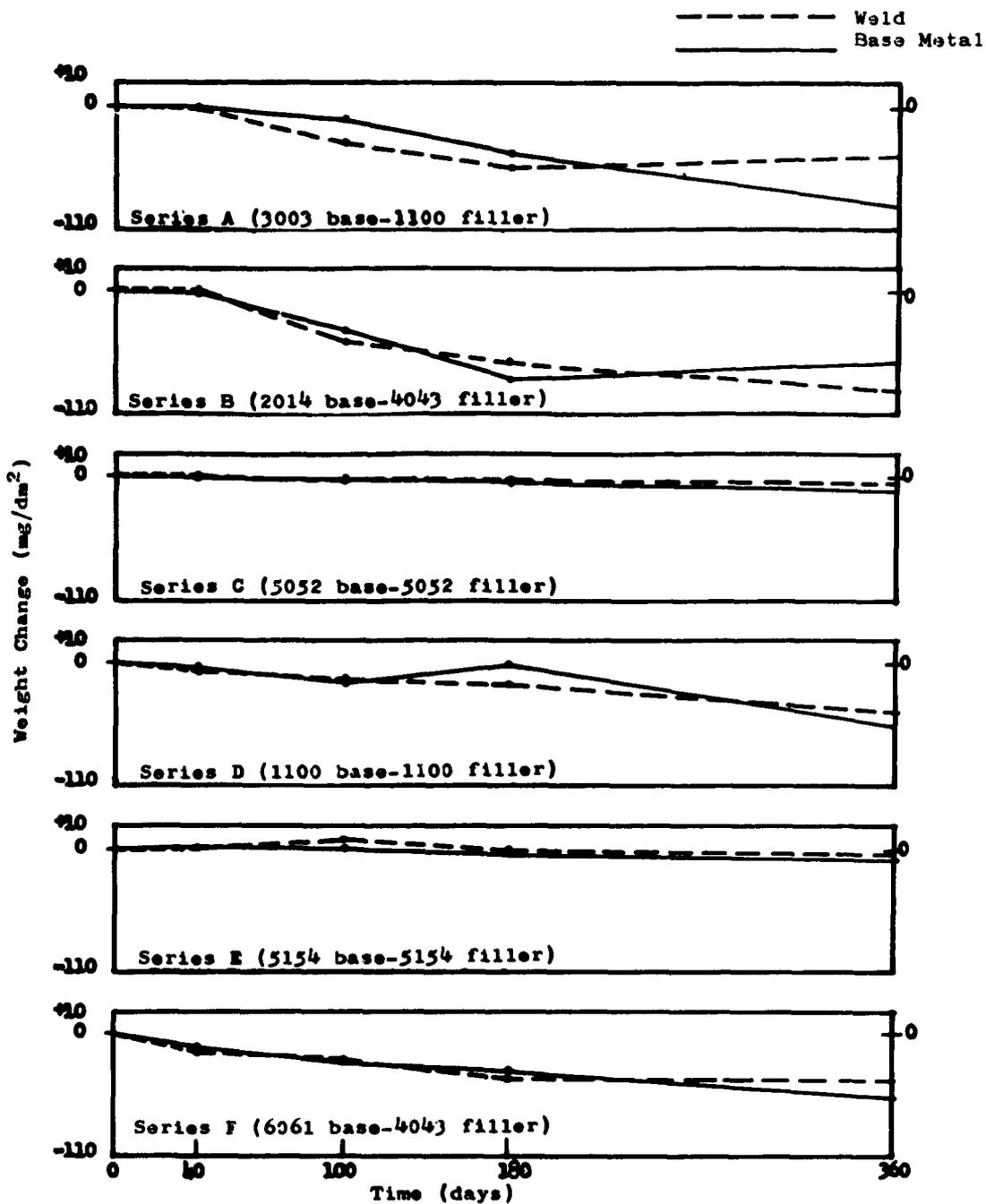


Figure D2. Weight Change of Corrosion Specimens suspended in Unmodified IRFNA at 80° F

36.231.S1000/ORD.60  
R-1524

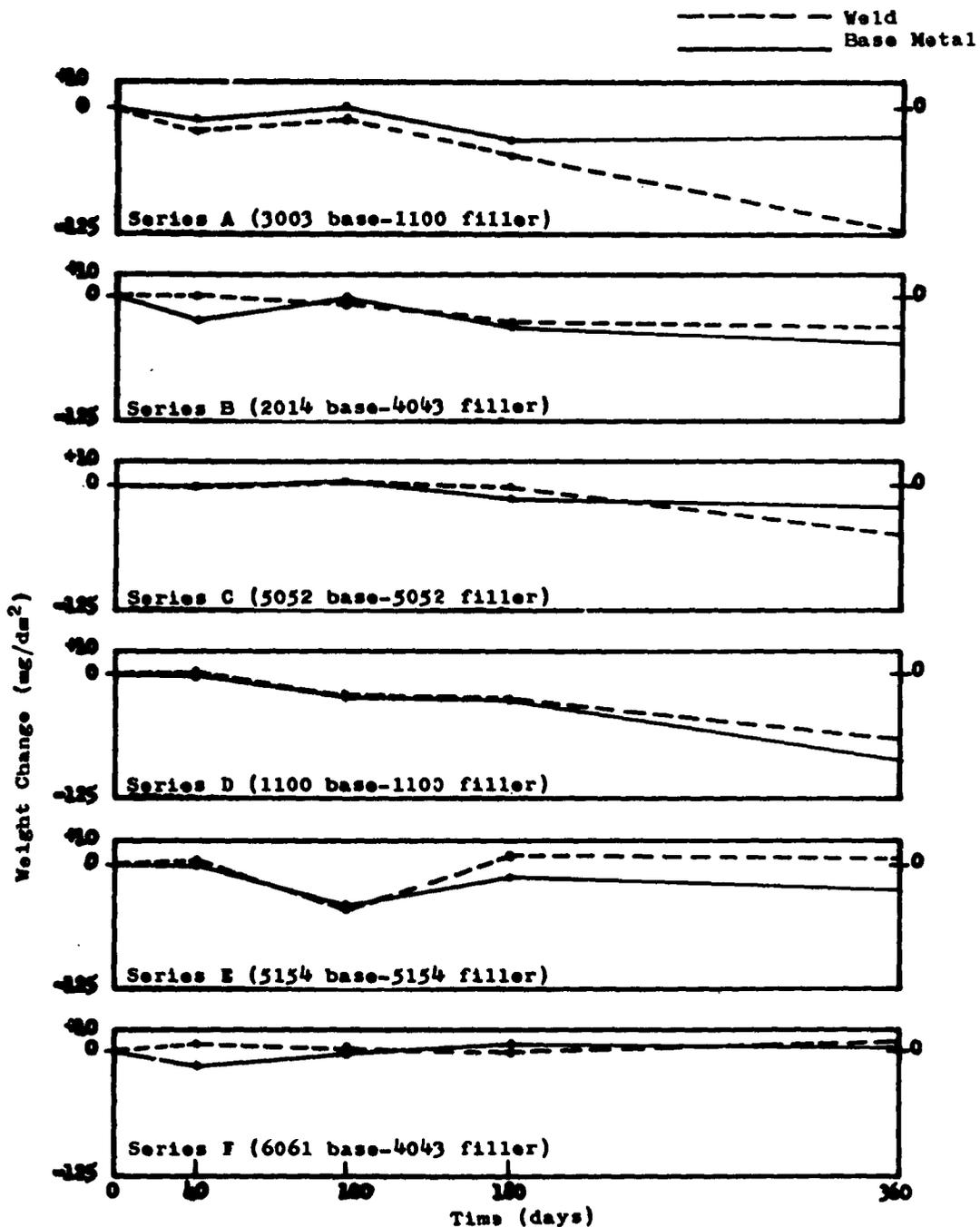


Figure D3. Weight Change of Corrosion Specimens suspended in Unmodified IRFNA at 114° F

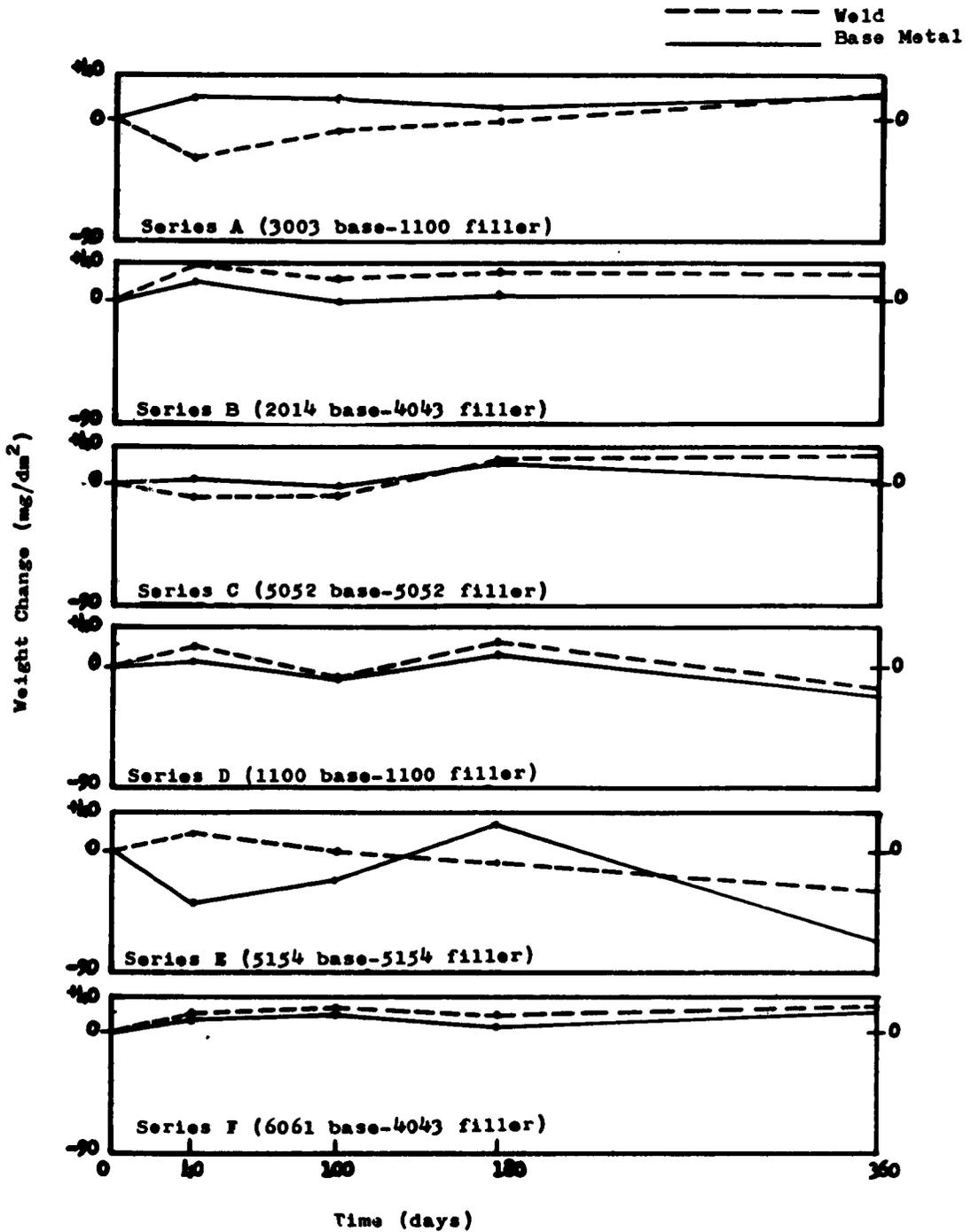


Figure D4. Weight Change of Corrosion Specimens suspended in Unmodified IRFMA at 150° F

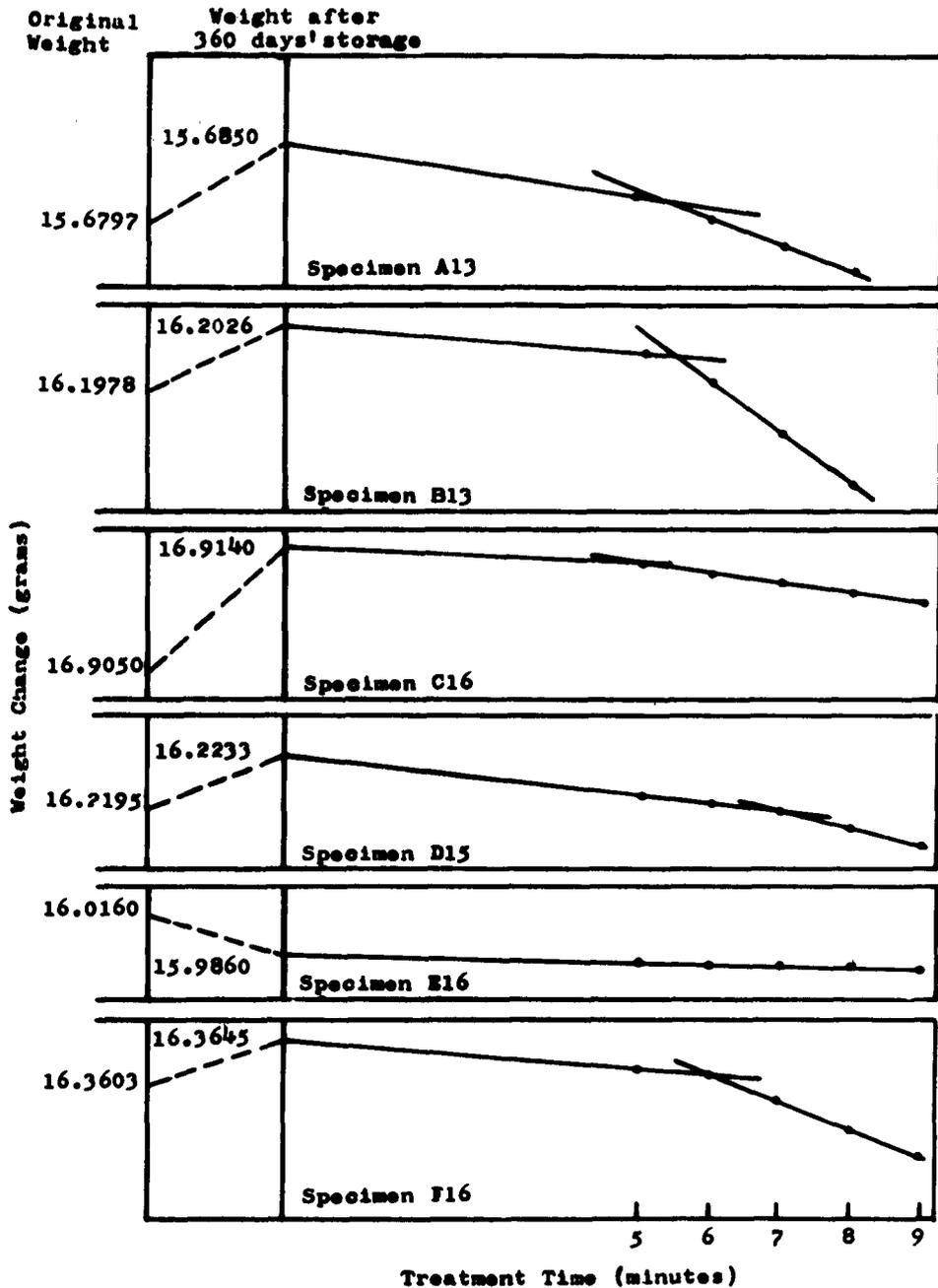


Figure D5. Weight Change of Corrosion Specimens treated with Phosphoric-Chromic Acid Solution after storage for one year at 150° F

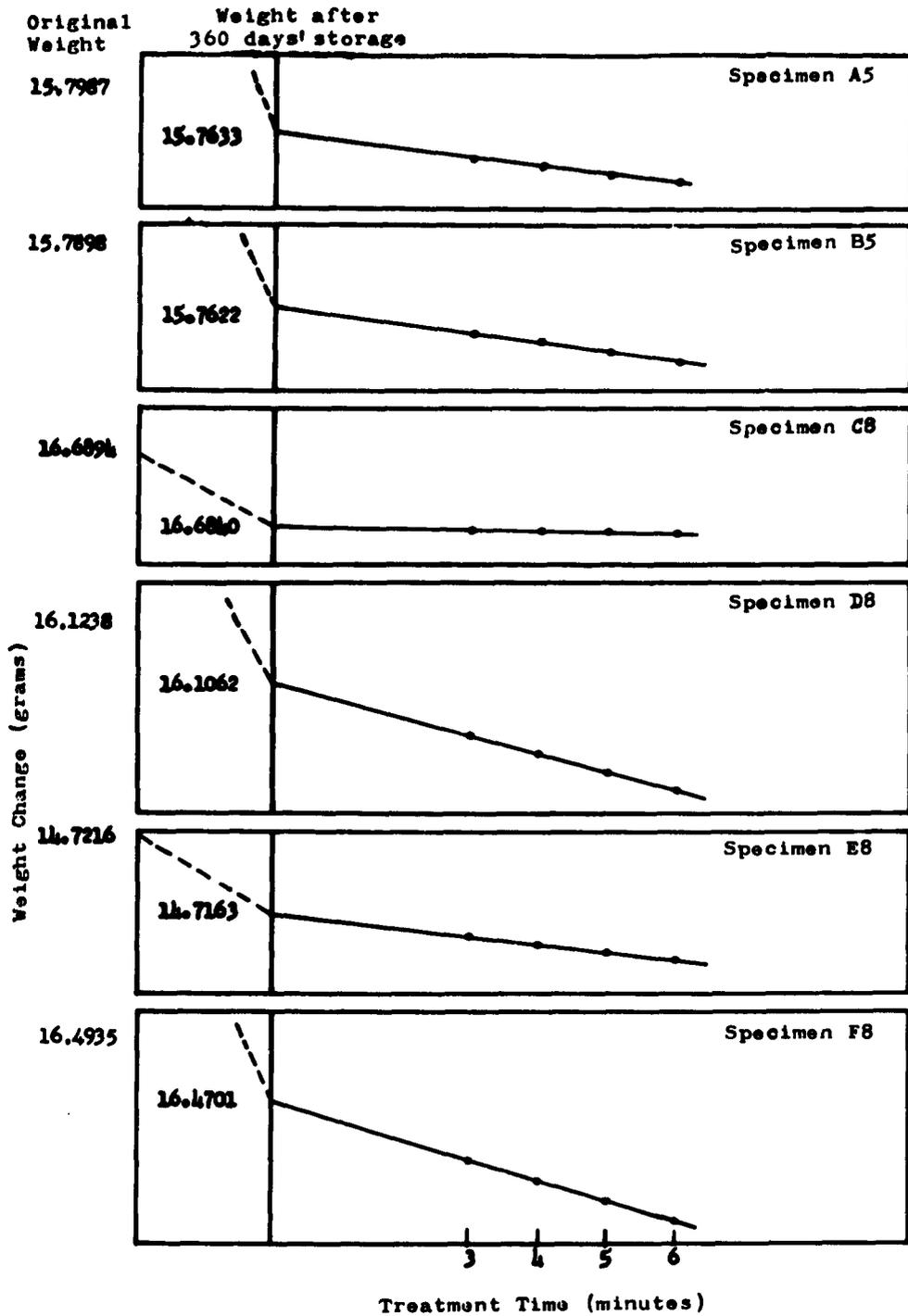


Figure D6. Weight Change of Corrosion Specimens treated with Phosphoric-Chromic Acid Solution after storage for one year at 80° F

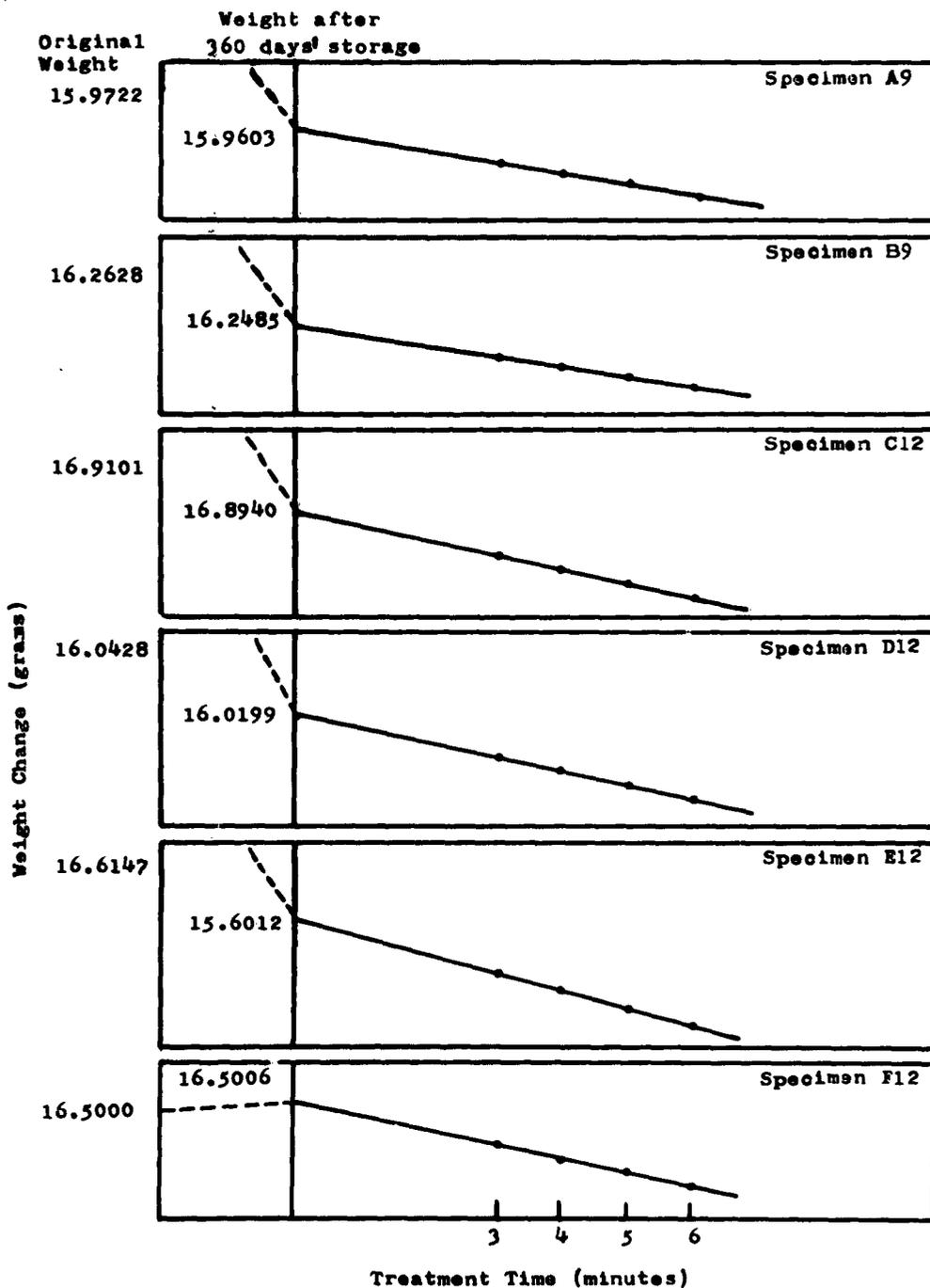


Figure D7. Weight Change of Corrosion Specimens treated with Phosphoric-Chromic Acid Solution after storage for one year at 114° F

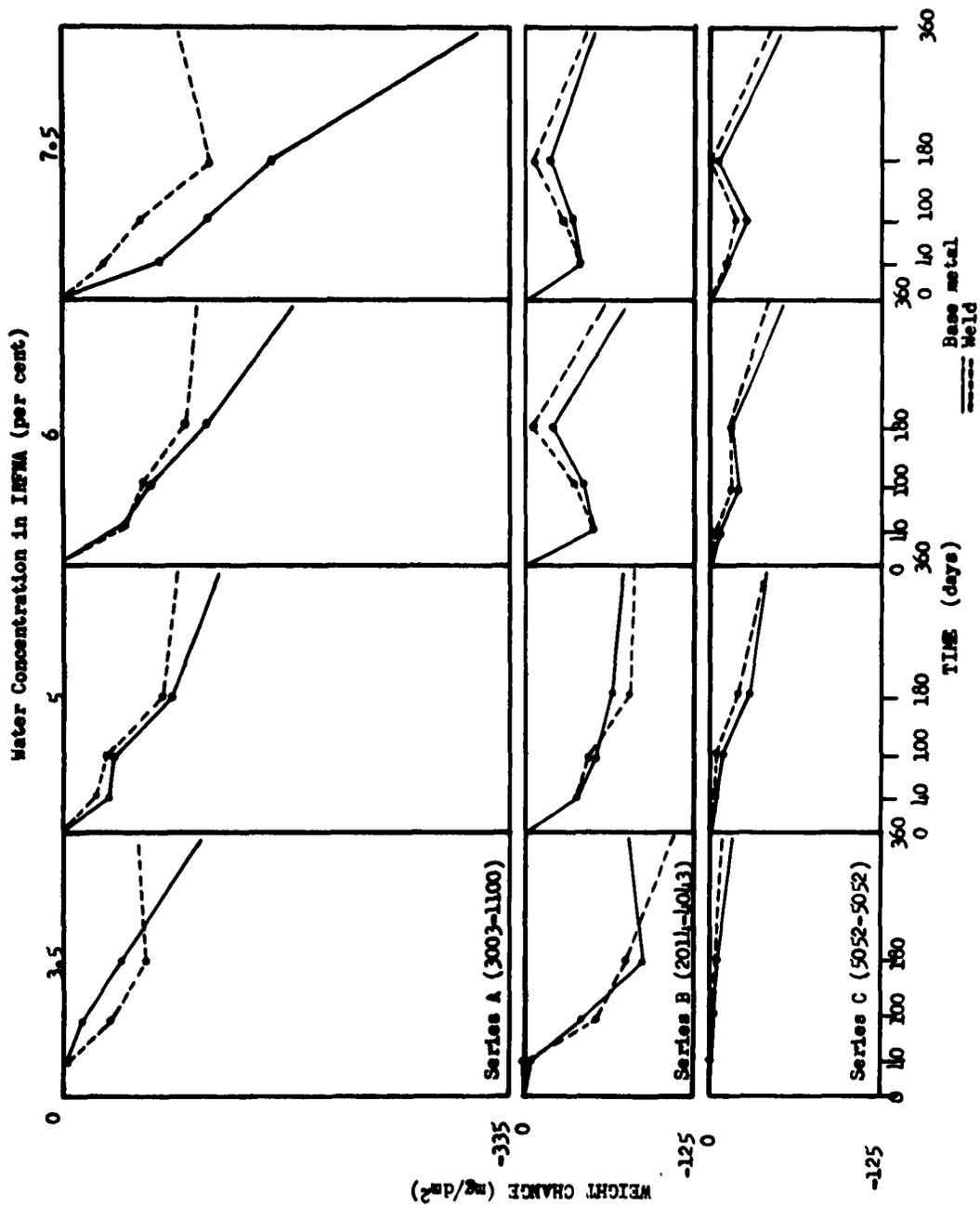


Figure D8. Weight Change of Corrosion Specimens suspended in IRFNA having different water contents, at 80° F

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