UNCLASSIFIED

AD NUMBER

AD875081

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; May 1970. Other requests shall be referred to Air Force Rocket Propulsion Lab., Attn: RPOR/STINFO, Edwards AFB, CA 93523.

AUTHORITY

Air Force Rocket Propulsion Lab ltr dtd 29 Sep 1971

THIS PAGE IS UNCLASSIFIED

AD875081

AFRPL-TR-70-43

LONG-TERM STORABILITY OF PROPELLANT TANKAGE AND COMPONENTS

INTERIM REPORT #1

R. B. MEARS, 1st LIEUTENANT, USAF

MAY 1970

AD No. ____
DDC FILE COPY

D D C
OCT 6 1970

THIS DOCUMENT IS SUBJECT TO SPECIAL EXPORT CONTROLS AND EACH TRANSMITTAL TO FOREIGN GOVERNMENTS OR FOREIGN NATIONALS MAY BE MADE ONLY WITH PRIOR APPROVAL OF AFRPL (RPOR/STINFO) EDWARDS, CALIFORNIA 93523

215

NOTICES

When U. S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

AFRPL-TR-70-43

LONG-TERM STORABILITY OF PROPELLANT TANKAGE AND COMPONENTS

INTERIM REPORT #1

R. B. MEARS, 1ST LIEUTENANT, USAF

TECHNICAL REPORT AFRPL-TR-70-43

May 1970

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL (RPOR/STINFO), Edwards, California 93523.

AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTORATE OF LABORATORIES
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
EDWARDS, CALIFORNIA

FOREWORD

This report covers the testing of liquid rocket propellant tankage and propulsion subsystems to evaluate their long-term storage characteristics. The testing is being conducted by the Air Force Rocket Propulsion Laboratory, Edwards, California, under project number 305805FRJ. The testing is being conducted in test area 1-40. The project engineer is Lt Richard B. Mears, and the time period covered by this report is from March 1969 through February 1970. This report supplements AFRPL-TR-69-82, Long Term Storability of Propellant Tankage and Components.

This report has been reviewed and approved.

DONALD H. CLEGG, Capt, USAF
Chief, Propulsion Subsystems Branch

ABSTRACT

Air Force weapons systems require long-term maintenance-free storage, preferably under uncontrolled environmental conditions. Liquid propulsion system components must be capable of satisfactory operation after years of exposure to highly reactive propellants while retaining the propellant without leakage under severe ambient conditions of temperature and relative humidity. Oxidizer leakage caused by improper component design and severe ambient storage conditions has presented serious operational problems.

The Air Force Rocket Propulsion Laboratory (AFRPL) has initiated a program to investigate the storability of liquid system components and tankage under extreme conditions of relative humidity and temperature. A variety of system components and tankage materials are being evaluated for long-term storability with storable liquid rocket fuels and oxidizers. Storage conditions are 85°F temperature and 85 percent relative humidity for oxidizer systems and +65 to +165°F temperature for fuel systems. The propellants under test are N_2O_4, ClF_5, N_2H_4, and MHF-5. Tankage materials under test are various alloys of aluminum, steel, and titanium.

The results of almost 3 years of testing on a representative number of tankage materials have indicated that leakage of propellant can occur as a result of improper weld joint design, inadequate quality control in fabrication and inadequate acceptance leakage testing. Factors which can contribute to the development of oxidizer leakage are a high ambient relative humidity (>30 percent) and stress corrosion cracking susceptibility of the tank material in combination with the propellant and trace quantities of foreign compounds/elements in the propellant.

TABLE OF CONTENTS

ILLUSTRATIONS

TABLES

SECTION I

INTRODUCTION

Experience with liquid propellant rocket feed systems has shown that leakage of oxidizers can occur and constitute a difficult problem under certain environmental conditions. In propellant tankage, leakage has been observed in or adjacent to weldments, and more specifically in weldments in which a double heat cycle has occurred, either by repeated welding to effect a repair or by intersecting weldments. It has been shown experimentally (Reference 1) in the case of N_2O_4, that when a vapor leak occurs the result is drastically influenced by the relative humidity of the atmosphere surrounding the tanks. If the relative humidity is on the order of 30 percent or lower, the nitric oxide vapor, which is the leaking fluid, dissipates into the atmosphere and does nothing to aggravate the leakage. If the relative humidity is in the order of 40 percent or greater, however, it does not dissipate, but rather hydrolyzes, forming dilute nitric acid on the exterior surface in the immediate vicinity of the leak (Figure 1). The action of the nitric acid is to enlarge the original leakage path, working inward toward the source of the leak. Eventually, a small, or even minute vapor leak can become a large liquid leak, if it is allowed to proceed. Although a similar detailed experimental program has not been performed with the storable fluorinated oxidizers such as ClF_3 and ClF_5, an analagous process would be expected with hydrogen fluoride as the hydrolysis product.

In the past, the selection of materials for systems applications has been based on conventional fluid compatibility testing to determine discoloration, pitting, weight loss or gain, notch sensitivity and stress corrosion cracking susceptibility as well as potential degrading effects on the propellant. Even after this thorough analysis and selection process, the material or the processing used in the propellant tankage may not function properly for extended periods or may develop leaks during its storage life. The use of conventional compatibility criteria, while certainly an essential part of the material selection process, has not served to screen out materials or processes which are not suitable for extended storage of liquid propellants when fabricated into system tankage. The major limitation on interpreting long-term storability effects in realistically severe environmental conditions of storage or service life is the inability of conventional compatibility criteria to predict leakage. The possible exception is the identifying of susceptibility to stress corrosion cracking. In liquid propellant tankage, this susceptibility usually leads to catastrophic rupture of a tank rather than leakage, since few, if any, flight-weight tanks have a "leak before burst capability". Small, undetected pin holes or microcracks could be formed by an attack of the propellant on grain boundary precipitates and inclusions, but would not be detected by weight gain or loss calculations and would probably go undetected. The possibility of such defects forming is greater in the limited-weldability materials where there is a tendency for microcracking. The size and methods of producing test specimens used in compatibility work eliminates many of the manufacturing and quality control problems associated with production systems. Smooth, polished samples, welded or unwelded, are not comparable to fabricated tankage material. The 2014 T-6 aluminum alloy is compatible with nitrogen tetroxide (N_2O_4 MIL-P-26639B), however, experience has shown that N_2O_4 leakage can occur with this 2014 T-6 material, usually in the heat-affected weld zone, in a humid environment (>30 percent). Long periods of storage may affect the functional performance and system reliability of prepackaged liquid propulsion systems. There are many areas to consider in providing data to supplement coupon compatibility testing. Storage conditions must be selected that are representative of system operational conditions. Such factors as humidity and temperature play an important role. A detailed propellant analysis before and after testing is required to evaluate the effects of storage on the propellant. The cleanliness levels of test articles must be known for reasons of safety, but equally important, to evaluate the processes which were used to effect this level. Materials and chemicals used for cleaning may have an effect on the system life. In the same manner, manufacturing processes and quality control standards may impose many unforeseen conditions which vary from one manufacturer to another. Throughout the fabrication of a test article (i.e., during welding, X-ray dye penetrant inspection and test), all data should be available to result in a meaningful post-failure analysis in the event that leakage occurs. Metal preparation prior to welding may make the difference between a satisfactory or unsatisfactory weld with regard to its ability to contain propellant without leakage. Helium leak testing of systems and the technique of leak testing are very important since small leakage which cannot be detected by X-ray or dye penetrant inspection can lead to propellant leakage under adverse environmental conditions. These variables must be known and controlled in a meaningful storability program.

The long term storage of fuels present a different problem. Hydrazine fuels are inherently unstable and decompose at elevated temperatures. This decomposition is catalyzed by impurities in tankage materials, and therefore tanks must be prepassivated or must be allowed to self-passivate when loaded with propellant. Completely fabricated tanks must be loaded with propellant and tested to determine which tankage materials will passivate and will therefore be capable of storing the propellant for an extended time with a negligible pressure rise.

SECTION II

PROGRAM STRUCTURE

The Air Force Rocket Propulsion Laboratory (AFRPL) initiated a program entitled "Packaged System Storability" to supplement laboratory compatibility work. This program deals with evaluation and demonstration of long-term (5 to 10 years) storage of tankage, components and integrated propulsion feed systems with present and advanced propellants. Materials under investigation include aluminum, steel, and titanium alloys. Test systems include tankage, integrated systems, consisting of tankage and feed system components, and complete feed systems including tankage, components, expulsion devices, and gas pressurization systems.

Due to the large number of tanks and systems being tested, the program structure has been reorganized from that which was reported in the first progress report (Reference 2).

The test systems are divided into three groups. The tanks discussed are those which have been added since the first progress report (Reference 2).

Group I - Small Container Testing

This group consists of all tanks which were in the original Phase I. Tanks added: Arde cylinders: small cylindrical containers, developed by Arde, Inc. as high pressure CO_2 cylinders of AISI 301, cryogenically stretchformed stainless steel. These cylinders are used to evaluate the storability of N_2H_4 with this material, in both the aged and unaged condition. (Figure 2)

Group II - Representative Tanks

This group consists of all tanks which were in the original Phase III, Fifteen Gallon Tanks, and Phase IV, Existing Tanks.

Tanks added: Thirty-five 10 gallon tanks of various steels, titanium, and aluminum, procured from Martin-Marietta Company, are being tested with N_2H_4. Six tanks of 6Al-4V Titanium and six tanks of 2021 T8X* Aluminum, fabricated by General Dynamics/Convair are also being tested (three of each material) with N_2H_4. The same number of tanks of the same materials are also being tested with N_2O_4. (Figures 3 and 4)

Group III - Expulsion and Feed Systems

This group consists of tanks which were in the original Phase II, Integrated Systems, and Phase V, Prepackaged Feed Systems.

Systems added: Six tanks of AISI 301 cryogenically stretch-formed stainless steel, with AISI 304 stainless steel diaphragms (annealed), were installed in test with ClF_5, N_2O_4, and N_2H_4. These tanks/diaphragms were fabricated by Arde, Incorporated. (Figure 5)

*T8X solution heat treated, formed, welded and artificially aged.

SECTION III

TEST FACILITIES

Storage testing of fuels is conducted in a test building equipped to provide a constant controlled temperature and uncontrolled relative humidity. The controlled temperature can be varied between +65°F and +165°F. The storage test building is insulated by a spray-in-place foam (polyurethane). Temperature conditioning is maintained by a heating and refrigeration system. Safety provision in the storage building consists of a FIREX-type water deluge system and large water drain piping. (Figure 6)

The oxidizer facility is reported in Reference 2.

SECTION IV

PROCEDURES

The addition of N_2H_4 testing, where decomposition of the fuel is the failure mode criteria, has required a means of determining the pressure inside each individual test article. All tanks loaded with fuels are monitored by daily recording the pressure indicated by pressure gages installed on each tank. (Figure 7)

The procedure for fuel systems loading is similar to that used in loading N_2O_4 (Reference 2) with the exception that an air-driven pump is used to transfer the propellant instead of pressurized nitrogen gas.

SECTION V

DISCUSSION OF RESULTS (APRIL 1969 - NOVEMBER 1969)

During this period a total of twelve tanks were analyzed for cause of failure. These analyses were accomplished by the Martin-Marietta Company under contract to the AFRPL, and by the AFRPL Chemical Laboratory. The reports are presented in Appendix I and Appendix II of this report.

On 14 August 1969 twelve Phase II integrated systems were loaded with ClF_5. Approximately two weeks later the environment in the oxidizer storage facility was maintained at 85°F and 85 percent relative humidity. During the afternoon of Friday, 12 September, the storage facility was inspected and no systems were found to be leaking. On the morning of Sunday, 14 September, the facility was again inspected and a very large concentration of ClF_5 vapors was found in the facility. After a thorough inspection it was determined that at least two tanks were leaking ClF_5, (one Group I 301 cryogenically stretch-formed AISI 301 stainless steel container, and one Group III integrated system with an AM350 steel tank). (Figures 8 & 9) (Appendix II). Numerous other tanks and systems were detanked because of corrosion damage to their external surfaces. The surfaces were cleaned and the tanks helium leak checked, and all tanks were or will be returned to test, since no leaks were found. The original leak was located in an aluminum tubing weld of a system containing ClF_5. The large concentration of HF (the product of ClF_5 hydrolysis) vapors resulting from the leaks also damaged the building's conditioning system which has been rebuilt.

SECTION VI

SUMMARY

The failure analyses have shown that a number of tanks have leaked from the external to the internal surface. This implies that the leakage may have been caused by leakage from another tank or by the leakage enlargement mechanism described in the introduction to this report. In order to prevent the leakage of one tank from affecting the test of another tank, the external surfaces of all tanks in test will be thoroughly cleaned to remove any corrosive contamination that may have formed when previous leaks occurred. The painting of the external surfaces to protect them is also being considered.

Although some pressure rises have been experienced in the storability testing of fuels, no conclusions can be made until more experience is gained.

REFERENCES

1. CR-46-145 "Improved Leak Detection, Correlation of Actual Leakage With Instrumentation Indications, Effect of Humidity of Leaks and Categorization of Leak Information", Final Report DSRS 10411, Contract AF04(611-576, C. Fateno et al, Martin Company, 16 June 1964.

2. "Long Term Storability of Propellant Tankage and Components", Technical Report AFRPL-TR-69-82, J. E. Branigan, Air Force Rocket Propulsion Laboratory, April 1969.

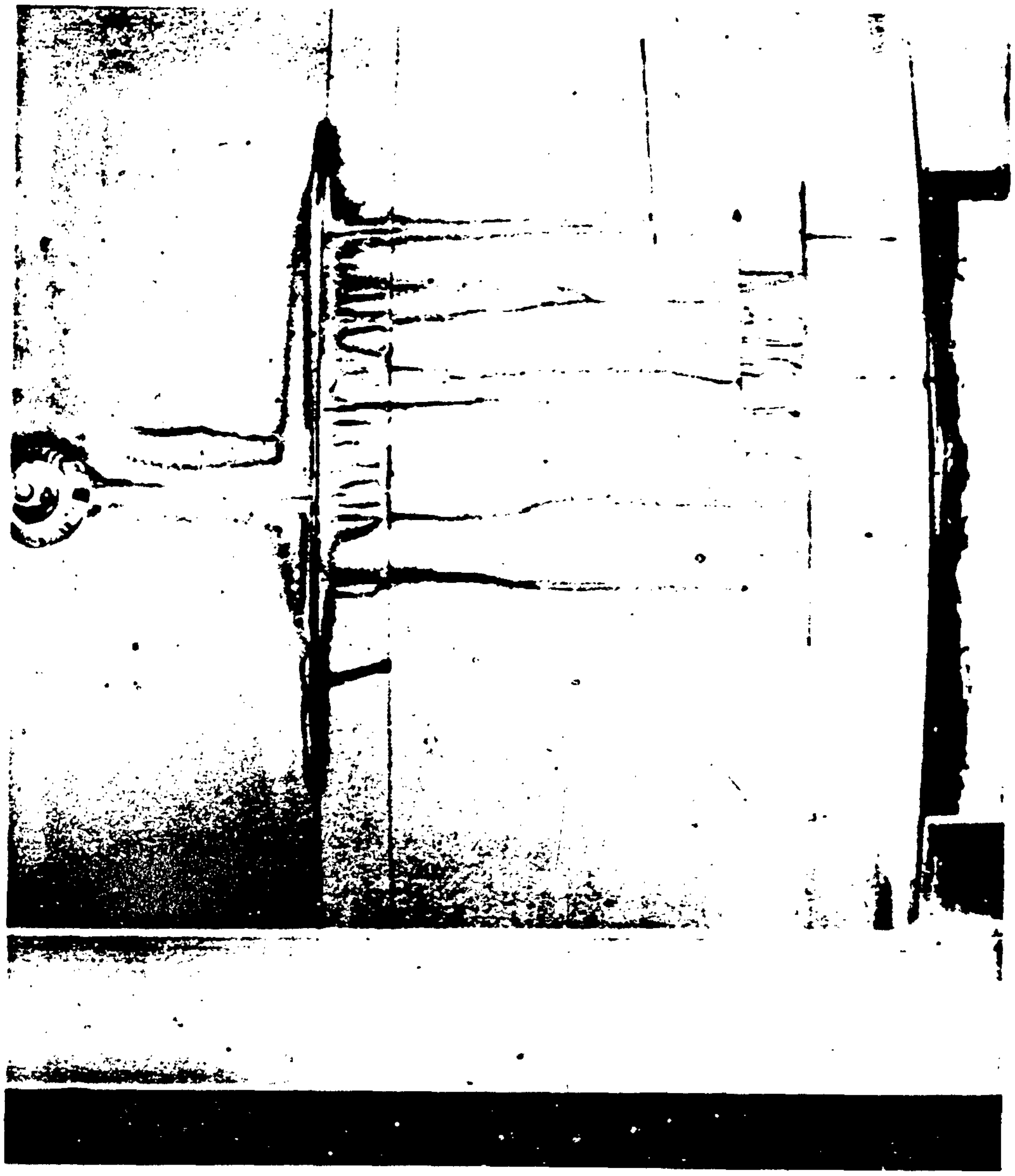


Figure 1. Hygroscopic Action of N_2O_4 Vapor

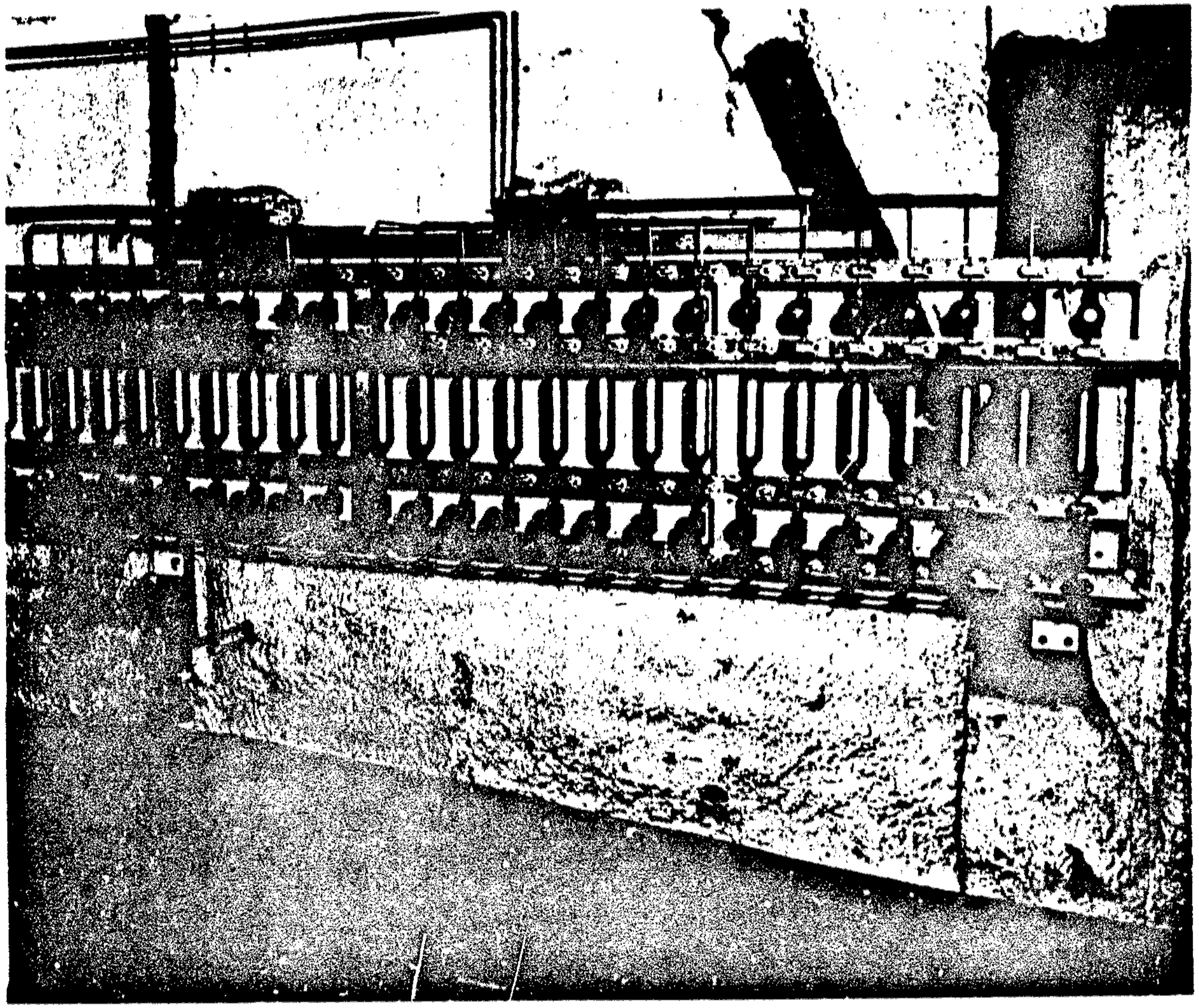


Figure 2. ARDE 301 Stainless Steel Cylinders

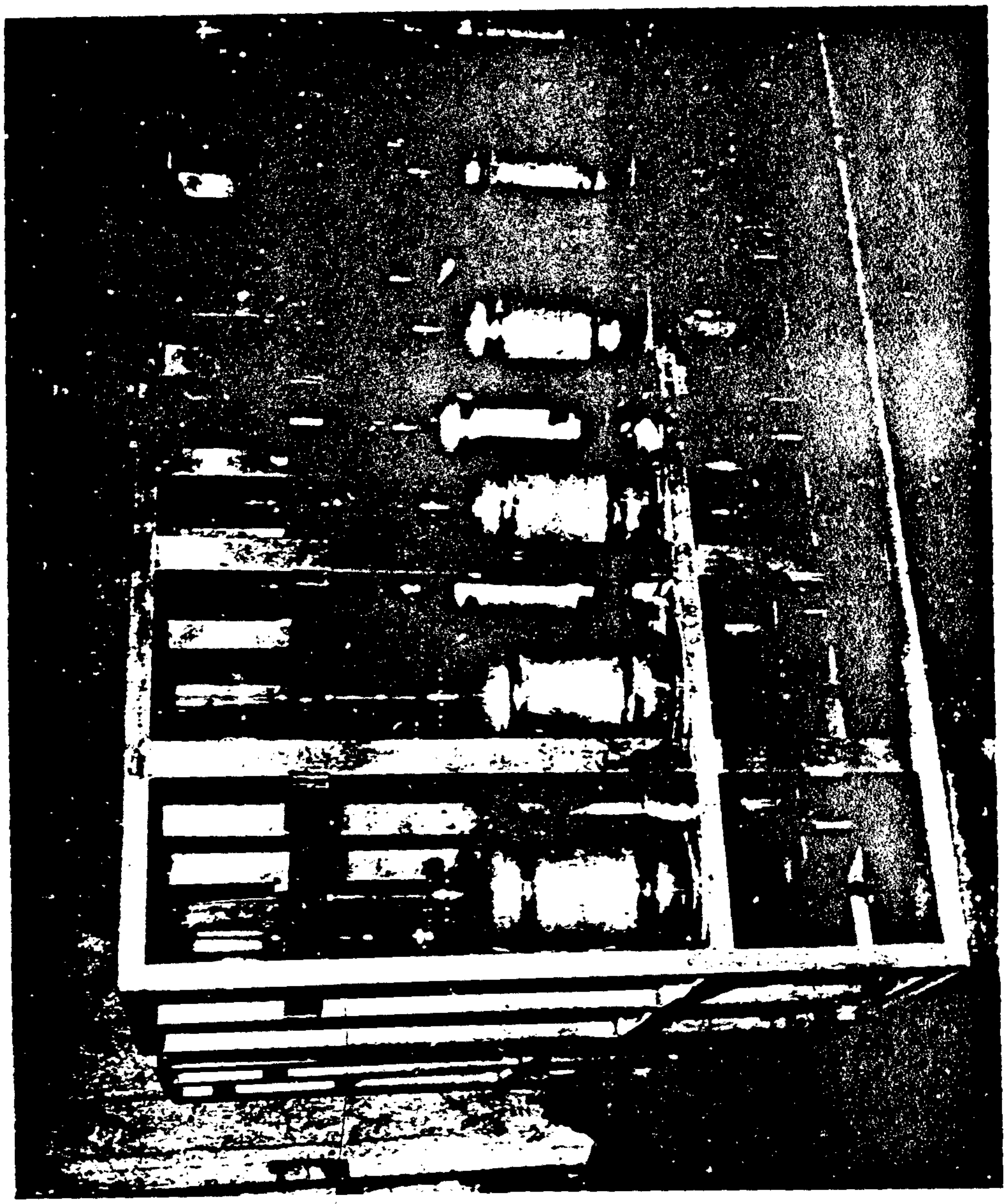


Figure 3. Martin 10 Gallon N_2H_4 Tanks

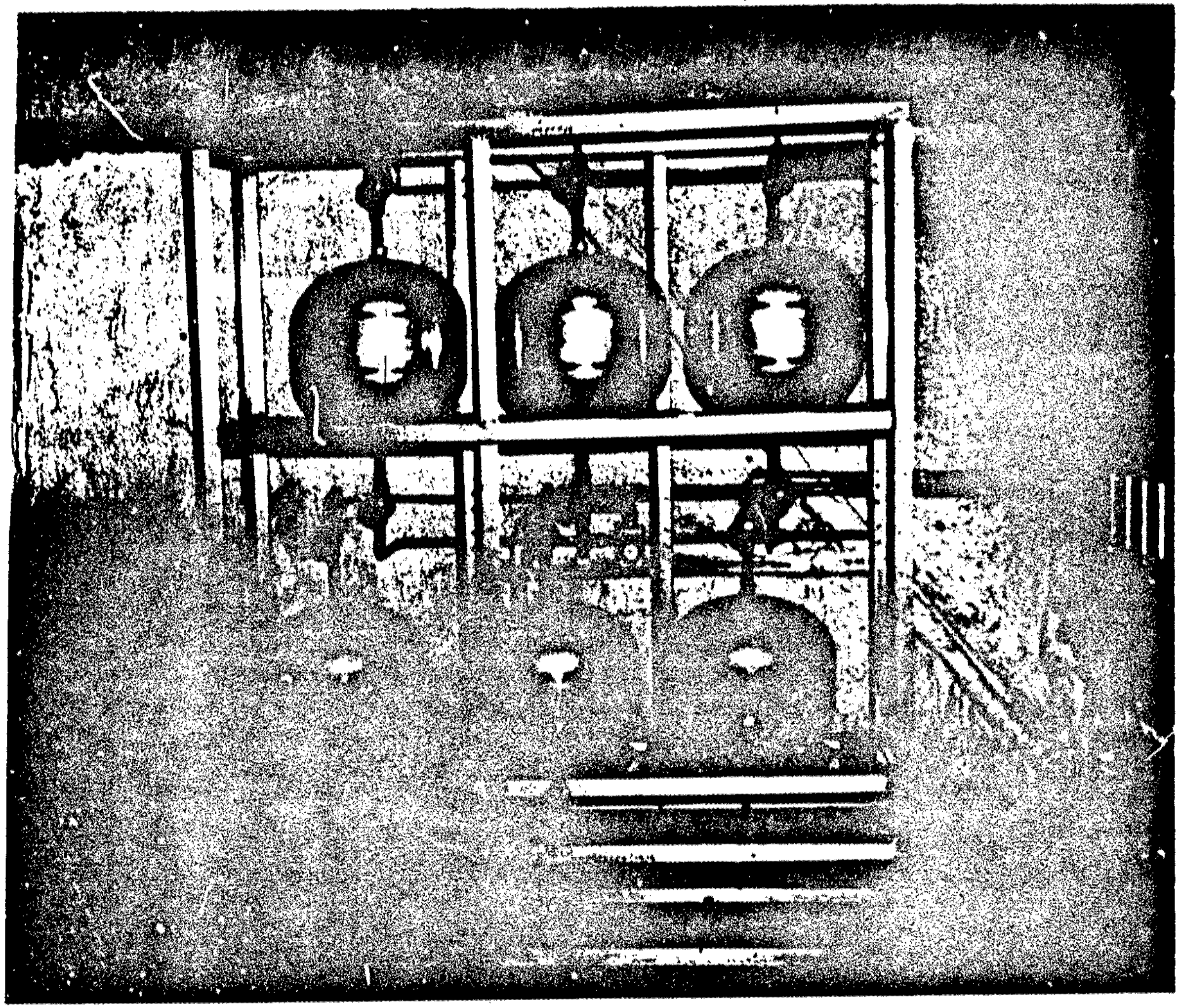


Figure 4. GD/C 15 Gallon N_2H_4 Tanks

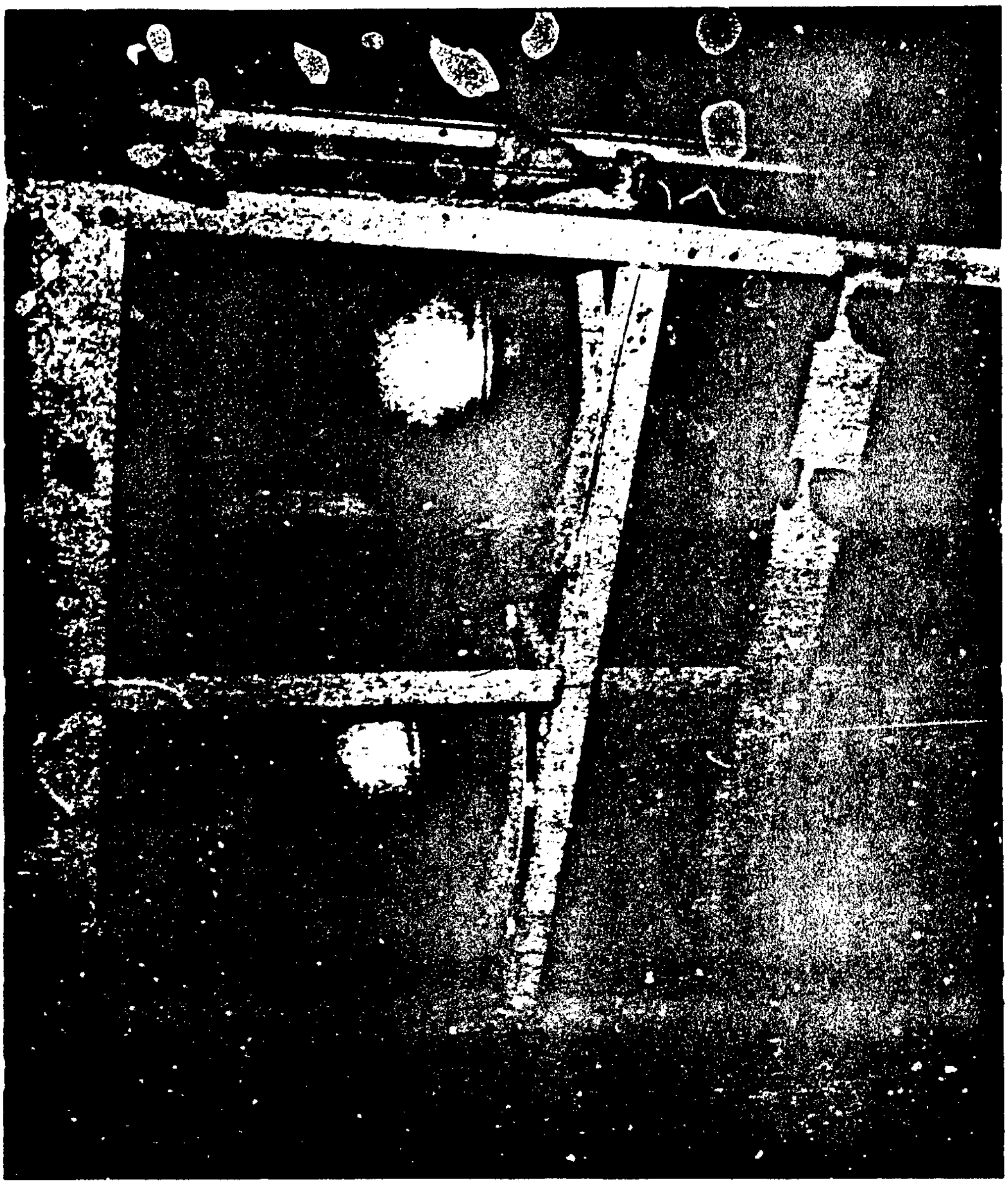


Figure 5. ARDE Ring Stiffened Diaphragm Tank

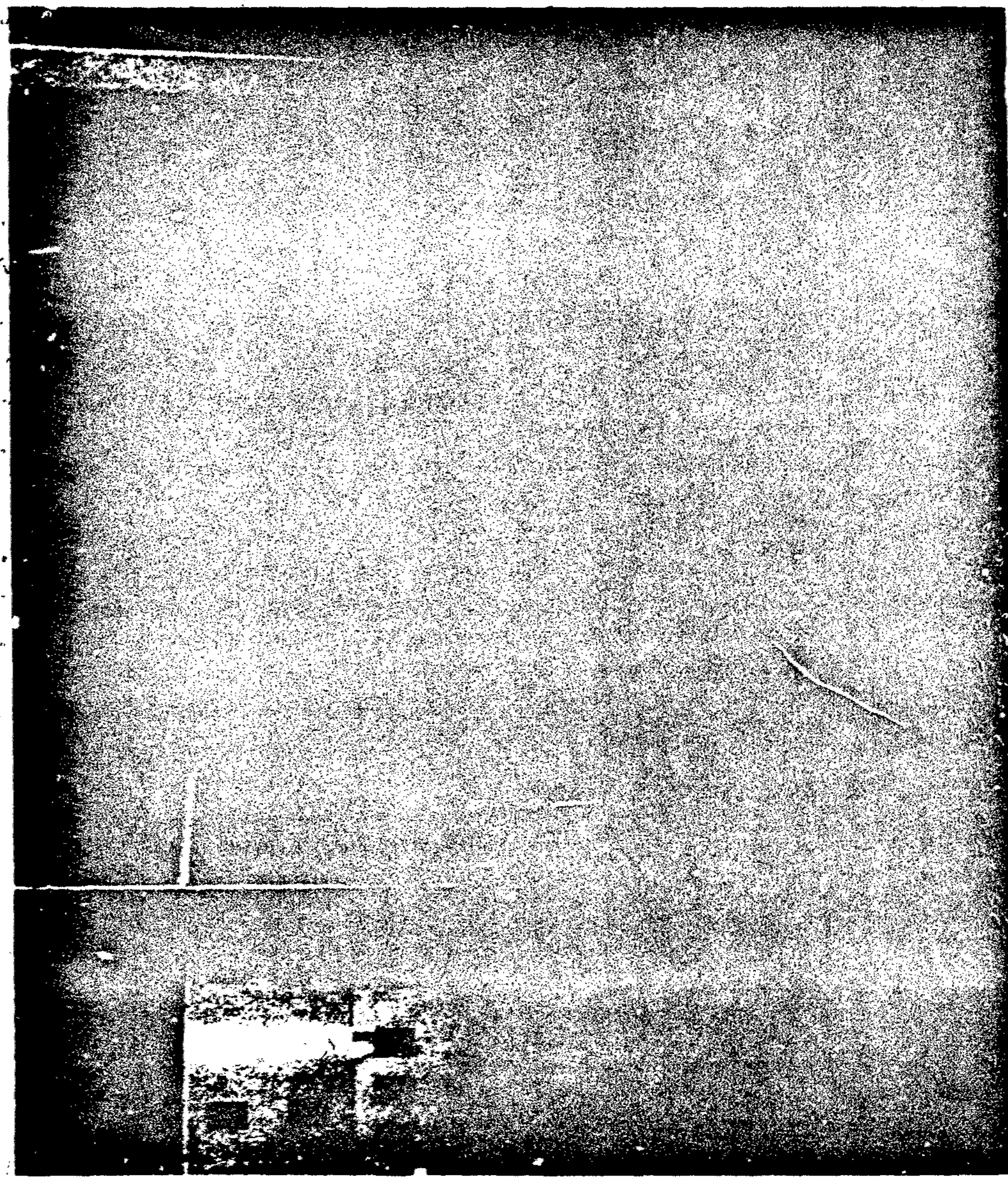


Figure 6. Fuel Storage Conditioning System

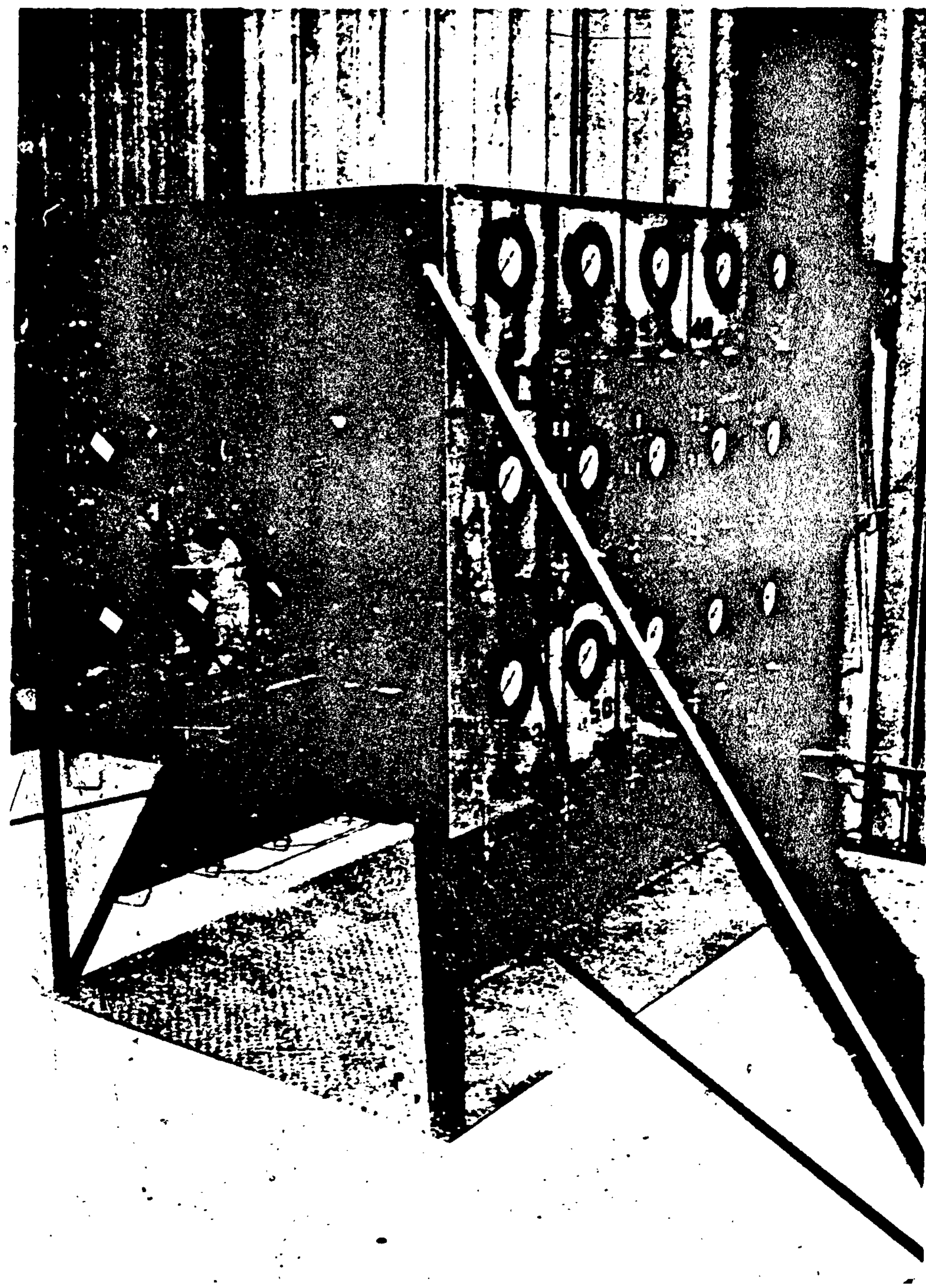


Figure 7. Fuel Storage Pressure Monitoring Panel

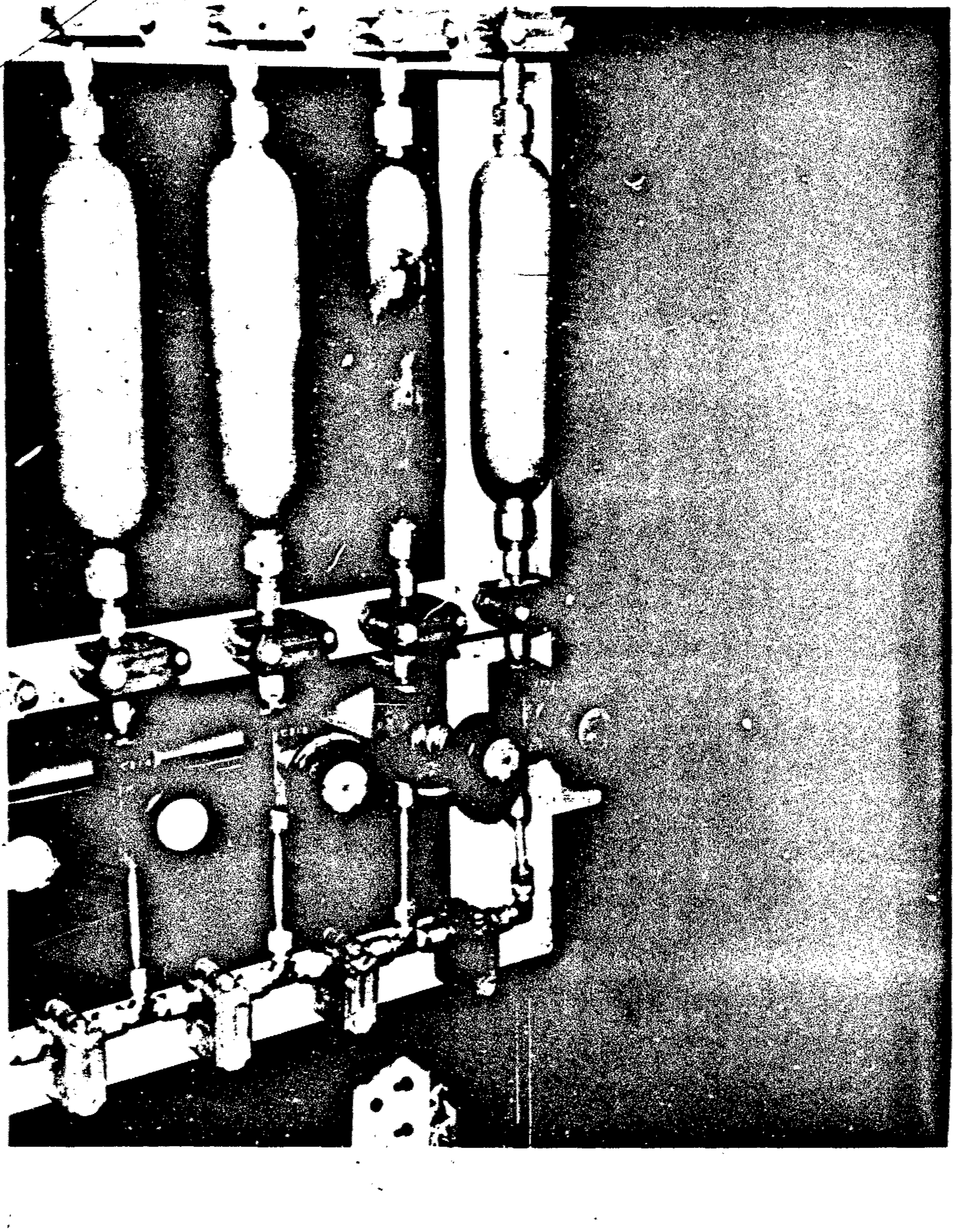


Figure 8. ARDE 301 Cylinder With ClF_5 Leak

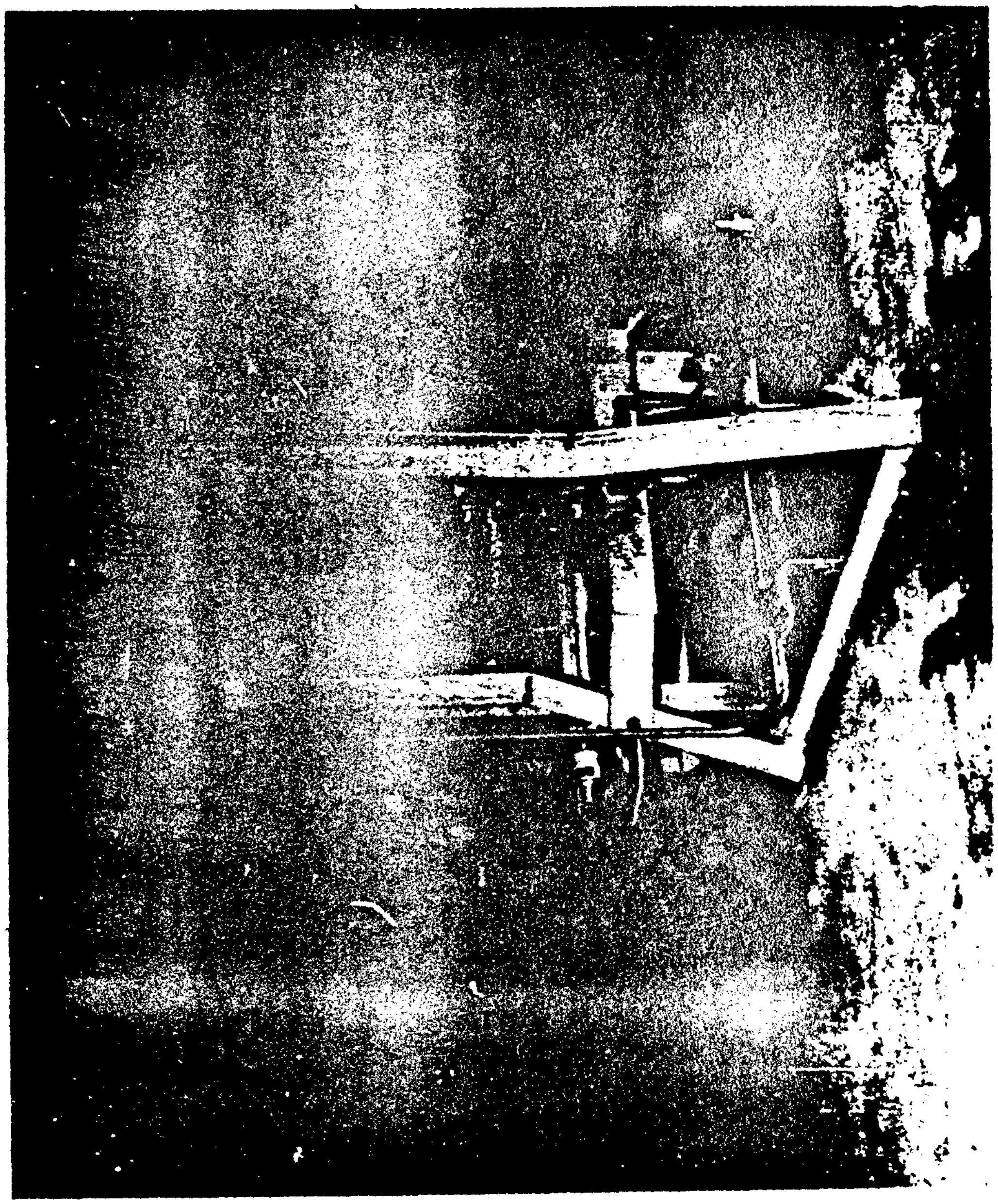


Figure 9. Integrated System With ClF_5 Leak

TABLE I. GROUP I - SUMMARY OF RESULTS

Propellant	Tank	Quantity	Tank Material	Test Initiated	Test Terminated	Days In Test
$^{+}N_2O_4$	3" X 6"	4	2014-T6	9-7-66	9-12-66	5
$^{+}N_2O_4$	3" X 6"	1	2014-T6	1-3-67	1-5-67	2
$^{+}N_2O_4$	3" X 6"	23	2014-T6	1-3-67		In Test
$^{+}N_2O_4$	Alcoa 1-qt	6	2014-T6	12-5-66		In Test
$^{+}N_2O_4$	Alcoa 1-qt	3	6016-T6	12-5-66		In Test
$^{+}N_2O_4$	Alcoa 1-qt	2	2219-T6	12-5-66		In Test
$^{+}N_2O_4$	Alcoa 1-qt	1	7007-T6	12-5-66		In Test
$^{+}N_2O_4$	Alcoa 1-qt	2	2021-T6	12-5-66		In Test
$^{+}N_2O_4$	Alcoa 1-qt	2	5456-T6	12-5-66		In Test
$^{+}N_2O_4$	Arde 1-pt Cryo Form	5	AISI 301 Aged	6-21-67		In Test
$^{+}N_2O_4$	Arde 1-pt Cryo Form	5	AISI 301 Unaged	6-21-67		In Test
ClF_5	Alcoa 1-qt	1	6061-T6	9-7-66	7-16-68	973
ClF_5	Alcoa 1-qt	1	6061-T6	9-7-66	5-14-69	616
ClF_5	Alcoa 1-qt	1	6061-T6	9-7-66	1-17-69	524
ClF_5	Alcoa 1-qt	3	6061-T6	4-7-66		In Test
ClF_5	Alcoa 1-qt	12	2014-T6	9-7-66		In Test
ClF_5	Alcoa 1-qt	1	2014-T6	9-7-66	5-22-67	57

+MIL-P-26539 Specification Grade

TABLE I. GROUP I - SUMMARY OF RESULTS (Cont'd)

Propellant	Tank	Quantity	Tank Material	Test Initiated	Test Terminated	Days In Test
ClF_5	Alcoa 1-qt	4	2219-T6	4-7-66		In Test
ClF_5	Alcoa 1-qt	4	2021-T6	9-7-66		In Test
ClF_5	Alcoa 1-qt	3	3003-T6	9-7-66		In Test
ClF_5	Alcoa 1-qt	4	5456-T6	9-7-66		In Test
ClF_5	Alcoa 1-qt	1	7007-T6	9-7-66		In Test
ClF_5	Alcoa 1-qt	1	7007-T6	9-7-66	8-11-69	635
ClF_5	Arde 1-pt Cryo Form	1	AISI 301 Aged	8-25-67	9-14-69	751
ClF_5	Arde 1-pt Cryo Form	4	AISI 301 Aged	8-23-67		In Test
ClF_5	Arde 1-pt Cryo Form	5	AISI 301 Unaged	8-23-67		
N_2H_4	Arde 1-pt Cryo Form	15	AISI 301 Aged	7-1-69		In Test Self-Passivating
N_2H_4	Arde 1-pt Cryo Form	14	AISI 301 Unaged	7-1-69		In Test Self-Passivating

TABLE II. GROUP II - SUMMARY OF RESULTS

Propellant	Tank	Quantity	Tank Material	Test Initiated	Test Terminated	Days In Test
+N_2O_4	Martin	1	2014-T6	1-3-67	1-25-67	22
+N_2O_4	Martin	1	2014-T6	1-3-67		In Test
+N_2O_4	GD/C	2	2014-T6	1-3-67		In Test
+N_2O_4	Martin	1	6Al-4V	1-3-67	1-13-67	10
N_2O_4	Martin	1	6Al-4V	1-3-67	2-7-67	34
N_2O_4	Martin	1	6Al-4V	1-3-67	2-8-67	35
N_2O_4	GD/C	1	5Al-2.5SN	1-3-67	1-17-67	14
N_2O_4	GD/C	1	5Al-2.5SN	1-3-67	1-19-67	16
N_2O_4	GD/C	2	6061-T6	1-3-67		In Test
N_2O_4	Martin	1	7039-T6	1-3-67	7-11-68	555
N_2O_4	Martin	1	7039-T6	1-3-67		In Test
N_2O_4	GD/C	1	AM350	1-3-67	10-24-67	294
N_2O_4	Martin	1	17-7PH	1-3-67	10-25-67	295
*N_2O_4	GD/C	3	2021-T8-X	8-4-69		In Test
*N_2O_4	GD/C	3	6Al-4V	8-4-69		In Test
ClF_5	Martin	1	2014-T6	1-3-67	3-3-67	58

*MSC-PPO-2A Specification Grade
+MIL-P-26539 Specification Grade

TABLE II. GROUP II - SUMMARY OF RESULTS (Cont'd)

Propellant	Tank	Quantity	Tank Material	Test Initiated	Test Terminated	Days In Test
ClF_5	GD/C	1	2014-T6	1-3-67		In Test
ClF_5	GD/C	1	AM350	1-3-67	10-24-67	294
ClF_5	GD/C	1	AM350	1-3-67	10-25-67	295
ClF_5	GD/C	1	6061-T6	1-3-67		In Test
ClF_5	Martin	1	7039-T6	1-3-67		In Test
ClF_5	Martin	1	17-7PH	1-3-67	3-9-67	64
ClF_5	Martin	1	17-7PH	1-3-67	10-23-67	293
N_2H_4	Martin	5	17-7PH	5-22-69		Some Pressure Rise
N_2H_4	Martin	5	AM350	5-22-69		Some Pressure Rise
N_2H_4	Martin	5	A286	5-22-69		Self Passivated
N_2H_4	Martin	5	2021	5-22-69		Self Passivated
N_2H_4	Martin	5	2014	5-22-69		Self Passivated
N_2H_4	Martin	5	2219	5-22-69		Self Passivated
N_2H_4	Martin	5	6AL4V	5-22-69		Self Passivated
*N_2O_4	Bullpup	3	2014	6-10-68		In Test
*N_2O_4	ULPR	2	2219	5-21-68		In Test

*MSC-PPO-2A Specification Grade

TABLE III. GROUP III - SUMMARY OF RESULTS

Propellant	Number	Press System	Exp System	Test Initiated	Test Terminated	Days In Test
MHF-5	2	LGG	R. D.	6-9-67		In Test
MHF-5	2	SGG	R. D.	6-9-67		In Test
MHF-5	1	H	R. D.	6-9-67		In Test
MHF-5	2	LGG	S. T.	6-9-67		In Test
MHF-5	2	SGG	S. T.	6-9-67		In Test
MHF-5	2	H	S. T.	6-9-67		In Test
$+N_2O_4$	2	LGG	R. D.	5-22-67		In Test
$+N_2O_4$	2	SGG	R. D.	5-22-67		In Test
$+N_2O_4$	2	H	S. T.	5-22-67		In Test
ClF_5	1	SGG	R. D.	6-20-67	10-7-67	20
ClF_5	1	H	S. T.	8-4-67	10-23-67	80
ClF_5	1	H	S. T.	8-4-67		In Test
$*N_2O_4$	2	LGG	R. D.	5-10-67		In Test
$*N_2O_4$	1	SGG	R. D.	5-10-67		In Test
$*N_2O_4$	1	H	R. D.	5-10-67		In Test

*MSC-PPO-2A Specification Grade
+MIL-P-26539 Specification Grade

LGG Liquid Gas Generator
SGG Solid Gas Generator
H Stored Helium
ST Surface Tension
RD Rolling Diaphragm

TABLE IV. GROUP III - SUMMARY OF RESULTS

Propellant	Tank	Quantity	Expulsion Device	Material	Test Start	Test Terminated	Days In Test
*N_2O_4	Arde	2	Ring Stiffened Diaphragm	AISI 301 Cryo Form	7-3-69	7-3-69	In Test
ClF_5	Arde	2	Ring Stiffened Diaphragm	AISI 301 Cryo Form	7-3-69		In Test
N_2H_4	Arde	2	Ring Stiffened Diaphragm	AISI 301 Cryo Form	7-20-69		No Pressure Rise

*MSC-PPO-2A Specification Grade

APPENDIX NO. 1

MARTIN-MARIETTA FAILURE ANALYSIS REPORTS

Martin Marietta Corporation — 18 July 1969

Materials Research and Engineering — Page 1 of

Failure Analysis of Small Tank AFRPL S/N 1,
Ti-5Al-2.5 Sn Titanium Alloy

Report No. 69/31R

Author: ____________________
Lawrence W. Loechel
Senior Engineer-Metals
Materials Research and Engineering

Approved: ____________________
A. W. O'Brien, Jr.
Chief
Materials Research and Engineering

Author: ____________________
Howard J. Brown
Unit Head - Metals
Materials Research and Engineering

Reference: (1) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 2, Ti-6Al-4V Titanium Alloy," 31 March 1969, Materials Research and Engineering Report No. 69/14R.

(2) "Electron Fractography Handbook" - Technical Report ML-TDR-64-416, January 31, 1965. Page 4-132.

(3) DMIC Review of Recent Developments, "Corrosion and Compatibility", W. E. Berry, February 28, 1968.

(4) L. W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 5, 7039-T651, Aluminum Alloy", 23 April 1969, Materials Research and Engineering Report No. 69/16R.

(5) C. F. Tiffany and J. N. Masters, "Investigation of Flaw Growth Characteristics of Ti-6Al-4V Titanium Used in Apollo Space Craft Pressure Vessels. NASA CR-65586.

(6) L. W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr. "Failure Analysis of Small Tank AFRPL S/N 3, 6Al-4V Titanium Alloy," 27 June 1969, Materials Research and Engineering Report No. 69/28R.

INTRODUCTION

Tank S/N 1 is a Ti-5Al-2.5 Sn titanium alloy tank that had been exposed to uninhibited N_2O_4 for 14-16 days when the tank failed by leaking in the dome area.

OBJECTIVE

The objective of this analysis was to determine the metallurgical cause of failure of tank number 1.

CONCLUSIONS

1. The failure was caused by stress-corrosion cracking occurring in the heat affected zone of the beanie-to-dome segment welds in each end of the tank.

2. The stress-corrosion cracking was caused by internal attack by the uninhibited N_2O_4.

RECOMMENDATIONS

For exposure of titanium to nitrogen tetroxide, only nitrogen tetroxide containing 0.4 to 0.8 percent NO should be used to prevent stress corrosion.

RESULTS AND DISCUSSION

1. Macroexamination - Two small cracks were visible on the external surface of the tank. The cracks were in the heat affected zone (HAZ) of a dome segment-to-fitting weld. Except for these cracks the overall appearance of the tank was good, Figure 1.

2. Leak Test - The tank was baked at 250°F for one hour. It was then pressurized with 100% helium for 30 hours. The tank was then leak checked by the hand probe method, using a CEC helium mass spectrometer. One leak was found in the bottom of the tank. This leak had a magnitude of 8.4×10^{-6} atm. cc/sec. One leak having a magnitude of 1.6×10^{-9} was also found in the top of the tank, Figure 2.

3. X-Ray Inspection - The dome ends were cut from the tank and X-rayed. The X-rays of the dome segment welds showed numerous small cracks in the HAZ's of the welds. The cracks, which were oriented perpendicular to the weld, were not visible in the original X-rays of the tank.

4. Metallographic Examination - The areas showing cracks in the X-rays were visibly inspected and numerous small cracks were found in the internal surface of the tank, Figures 4, 5, and 6. Microsections were taken through several of the cracks. As shown in Figures 7, 8, and 9, the cracks were typical of N_2O_4 induced stress corrosion.

5. Electron Microscopy - Electron fractography of the fracture surfaces was not possible since the fractures were too small to replicate.

6. Chemical Analysis - Although the chemical analysis of the Ti-5Al-2.5 Sn was required to be the extra low interstitial grade (ELI), the analysis of the failed tank showed the material was more closely the normal interstitial grade. This analysis, however, would not result in more stress corrosion occurring than in the ELI grade.

Element	Al	Sn	Fe max.	C max.	N max.	H max.	O max.	Others, Total max.
Requirements of MIL-T-9046 normal interstitial	4.6	2.3	0.50	0.15	0.17	0.020	0.20	0.40
Requirements of MIL-T-9046 for ELI	4.25-5.75	2.3	0.15	0.05	0.04	0.018	0.12	0.30
Analysis	6.50	2.52	-	-	0.078	0.016	0.124	0.01
Check Analysis MIL-T-9046	±0.40	±0.15	+0.15	+0.02	+0.02	+0.002	+0.04	

7. Mechanical Properties - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained:

Specimen	Ftu (ksi)	Fty (ksi)	Percent Elongation 2" gage, in/in
Ti-1	120.8	119.7	16
Ti-2	121.2	117.6	15
Ti-3	138.8	121.8	19
Ti-4	125.6	122.7	16
MIL-T-9046 Minimum for normal interstitial	120.0	113.0	10
MIL-T-9046 Minimum for ELI	100.0	95.[illegible]	8 - ≤0.025" 10 - >0.025"

As may be seen the tensile properties show the material to be normal interstitial material properties and not the ELI grade of Ti-5Al-2.5 Sn titanium alloy as required by GD/C-TSP-001.

8. Dimensions - The tank thicknesses were as follows:

   a. Dome gore segments
   b. Barrel panels
   c. -41 ring detail - Tapered from 0.040" to 0.102" thickness.

These dimensions were within the drawing requirements of GD/C-TSP-001

However, a peculiarity was observed when checking the drawing for dimensions, i.e., the -43 and -41 are all one piece, probably machined from bar stock, whereas, the drawing required there to be two pieces.

9. Corrosion Product Analysis - Corrosion products present on the tank were in insufficient quantities such that, an analysis could not be made. However with the remainder of the metallurgical analyses showing typical stress corrosion failure and with the knowledge that uninhibited N_2O_4 was used, the mode of failure was determinable.

10. Uninhibited N_2O_4 - Reference (5) presents flaw growth characteristics and threshold stress level of Ti-6Al-4V titanium subjected to various environments including inhibited N_2O_4. N_2O_4 inhibited with 0.4 to 0.8% NO must be used in contact with titanium, since several investigations after the failure of several Apollo propellant tanks in 1965 and 1966 indicated that uninhibited N_2O_4 will cause stress corrosion in titanium at stress levels around 40,000 psi.

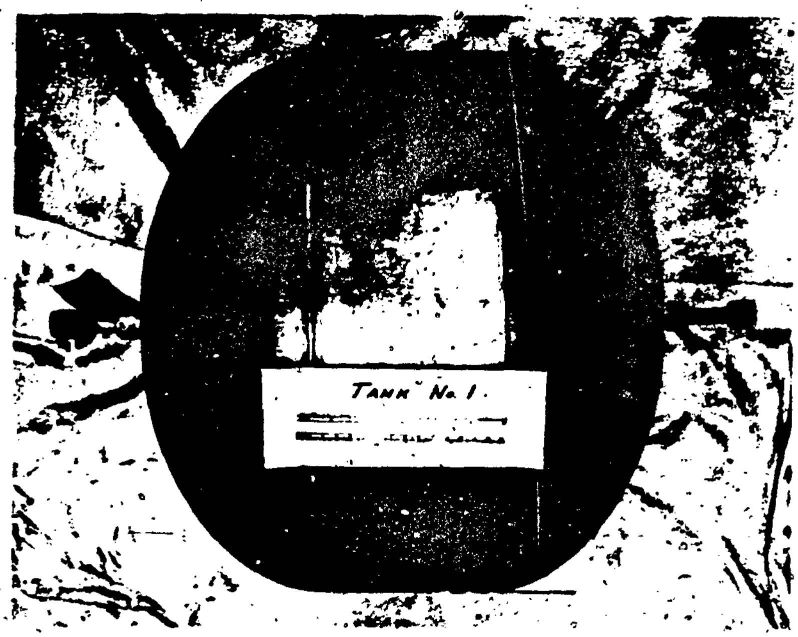


Figure 1. Side Views of Tank No. 1. 0.2X

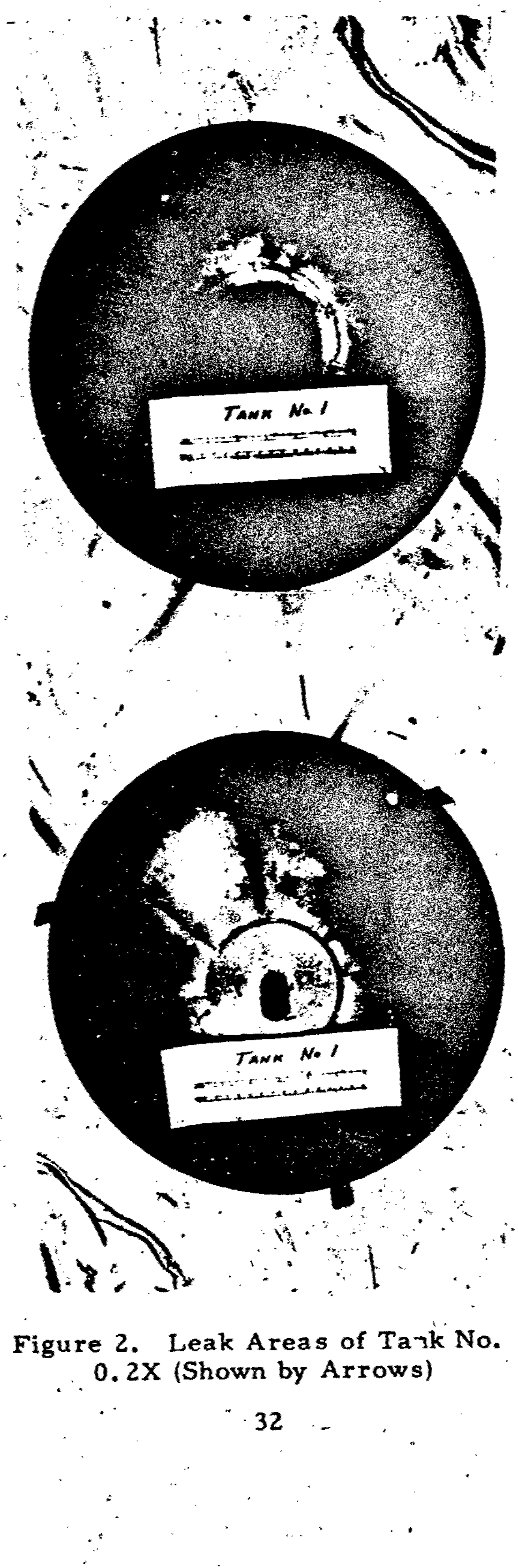


Figure 2. Leak Areas of Tank No. 1
0.2X (Shown by Arrows)

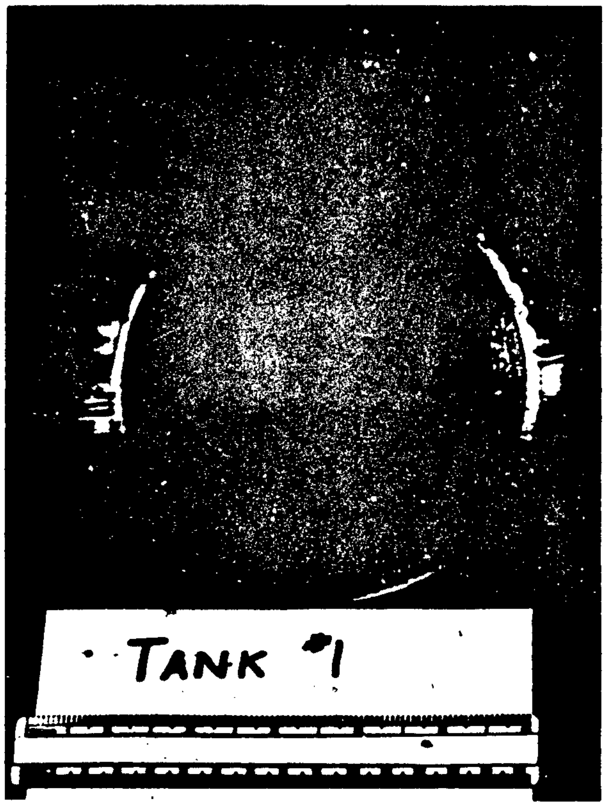


Figure 3. Circled Areas in Bottom of Tank Where Cracks Were Found (Inside View)

Figure 4. Photomacrograph of Crack in the Bottom of Tank No. 1

Figure 5. Internal Stress-Corrosion Crack in Top of Tank No. 1 (≈30X)

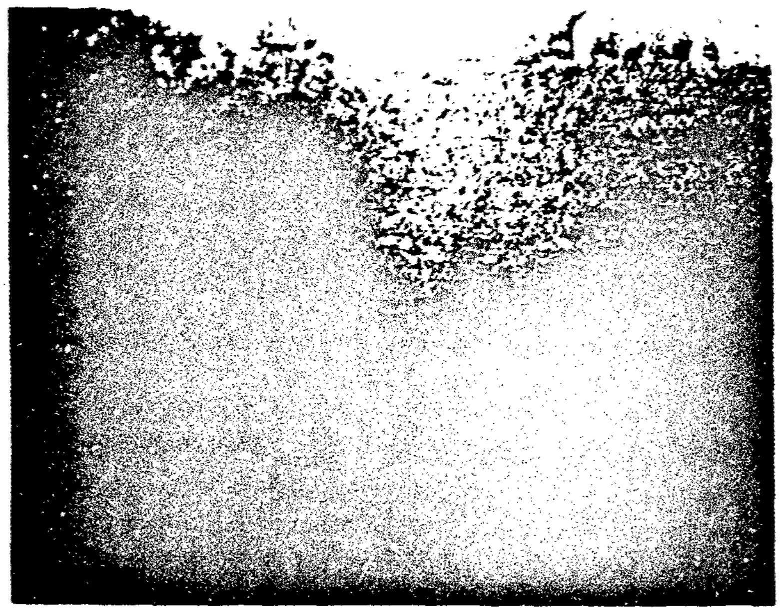


Figure 6. Internal Stress Corrosion Crack in Bottom of Tank No. 1 (≈20X)

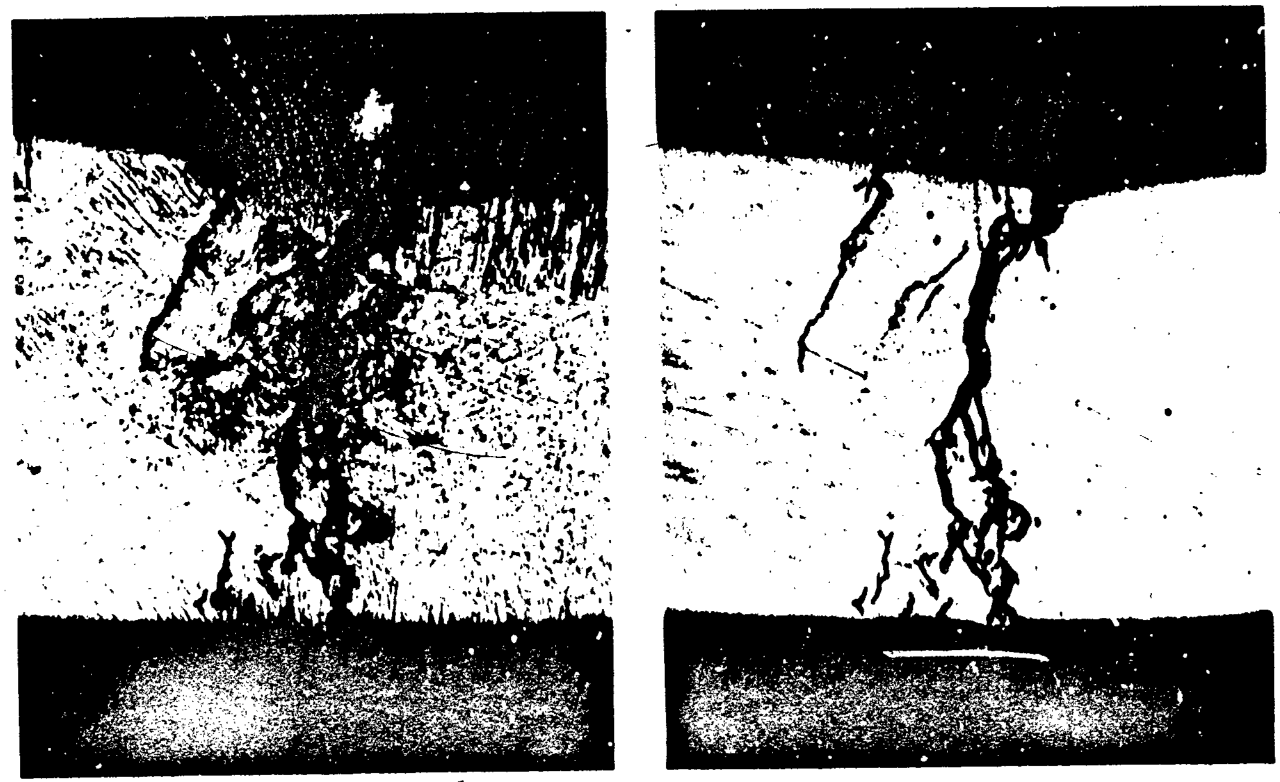


Figure 7. Microsection of Stress-Corrosion Crack in Bottom of Tank (150X)

Figure 8. Microsection of Stress-Corrosion Crack in Bottom of Tank No. 1 (150X)

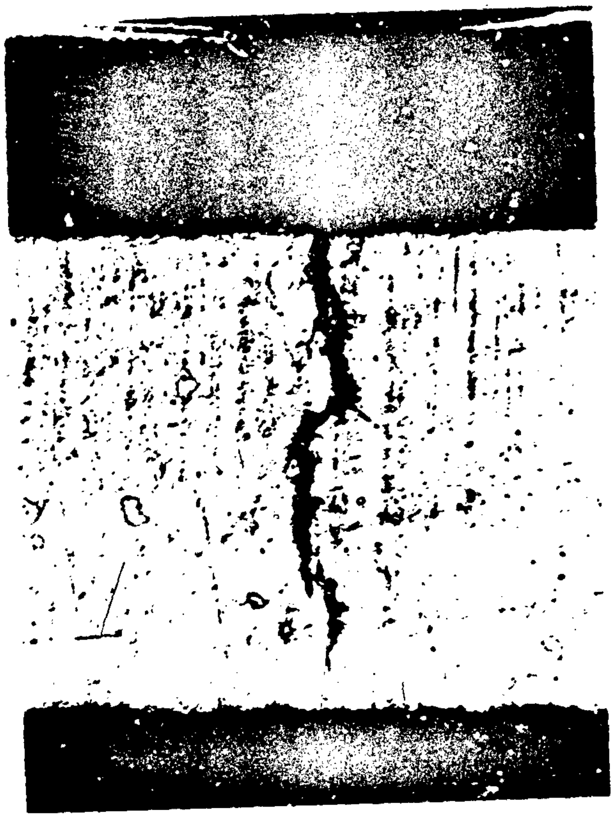


Figure 9. Microsection of Stress-Corrosion Crack in Top of Tank No. 1 (150X)

Failure Analysis of Small Tank AFRPL S/N 2,
Ti-6Al-4V-Titanium Alloy

Report No. 69/14R

Author:
Lawrence W. Loechel
Senior Engineer-Metals
Materials and Process Technology

Approved:
A. W. O'Brien, Jr.
Chief
Materials and Process Technology

Author:
Howard J. Brown
Head - Metals Unit
Materials and Process Technology

INTRODUCTION

Tank S/N 2 is a Ti-6Al-4V-Titanium Alloy tank that had been exposed to N_2O_4 for 34 days.

OBJECTIVE

The object of this failure analysis was to determine the metallurgical cause for the failure of AFRPL S/N 2, Ti-6Al-4V titanium alloy tank.

CONCLUSIONS

1. The origin of failure of small tank AFRPL S/N 2 was a hot-short crack in the fusion zone (weld bead edge) of a repair weld.
2. Insufficient inert gas coverage, in repair welding the tank, resulted in the formation of stabilized alpha on the surface of the titanium in the weld heat affected zone. This created an embrittled surface and an area of stress concentration.

RECOMMENDATIONS

1. More extensive radiographic coverage should be provided for all welds in propellant tanks.

2. All propellant tanks should be welded under conditions which make all repair welds accountable to the cognizant Air Force representative. Repair welds have always presented a problem to all manufacturers.

3. No propellant tanks should be accepted with discoloration showing on welds until it is proven the discoloration formed in a harmless manner, e.g., discoloration can form if the metal, while still above 600°F but less than 1200°F, passes out from under the trailing shield, this would not be harmful. If air contacts the titanium while above 1200°F, embrittlement of the weld can occur.

4. As has been recommended previously, no propellant tanks should be exposed to fumes from leaking vessels while in the humid exposure environment. HNO_3 formed can cause stress and pitting corrosion of the propellant tanks.

RESULTS AND DISCUSSION

The following procedures were followed during failure analysis of tank No. 2.

1. Macroexamination - The tank appeared to be in good condition with the exception of some discolored weld areas and a crack in the fusion zone of a repair weld, Figures 1, 2, 3, and 4.

2. Leak Test - The tank was baked at 250°F for one hour. It was then pressurized with 100% helium for 16 hours. The tank was then leak checked by the hand probe method, using a CEC helium mass spectrometer. One leak was found in the area shown in Figure 2. The leak was determined to be 2×10^{-5} atm-cc/sec.

3. Metallographic Examination - A microsection was made through the leak area, Figure 5. It was apparent from the microsection that the leak was caused by a hot-short crack in the fusion zone of the repair weld. A contributing factor to the hot-short cracking was the fact the repair weld appeared to have been made with insufficient heat in tailing off. Another microsection was made through a repair area that showed excessive weld discoloration, Figure 6. This area also showed crack indications in x-rays that were made of the area. Cracks were also found in the microsection, Figure 7.

These cracks were stress-corrosion cracks originating at the outside surface of the tank. Also apparent in the etched photomicrograph is a surface layer of stabilized alpha caused by oxygen enrichment of the surface due to insufficient inert cover gas during repair welding. Although not part of the origin of failure in this case, the stress corrosion cracking ultimately would have caused leakage of the tank. Therefore, efforts should be made to prevent condensation of nitric acid on the outer surfaces of the tank.

4. Chemical Analysis

	Element	
Sample No.	Aluminum	Vanadium
2C1	5.92	4.3
2C2	5.61	4.2

5. X-Ray Inspection - The dome welds from the leaking end of the tank were x-rayed. Numerous defects, such as porosity, cracks, and lack of fusion were found. The defects in the area that were microsectioned were also apparent.

6. Mechanical Tests - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained.

	Ftu (ksi)	Fty (ksi)	Percent Elongation (in/in)
	140.2	133.1	11.0
	140.2	131.5	12.5
	139.3	128.1	12.5
	138.6	127.7	12.0
Drawing Requirements	130	120	10.0

The hardness was determined to be R_a67.

7. Dimensional Checks.- The tank was measured and determined to be within drawing requirements.

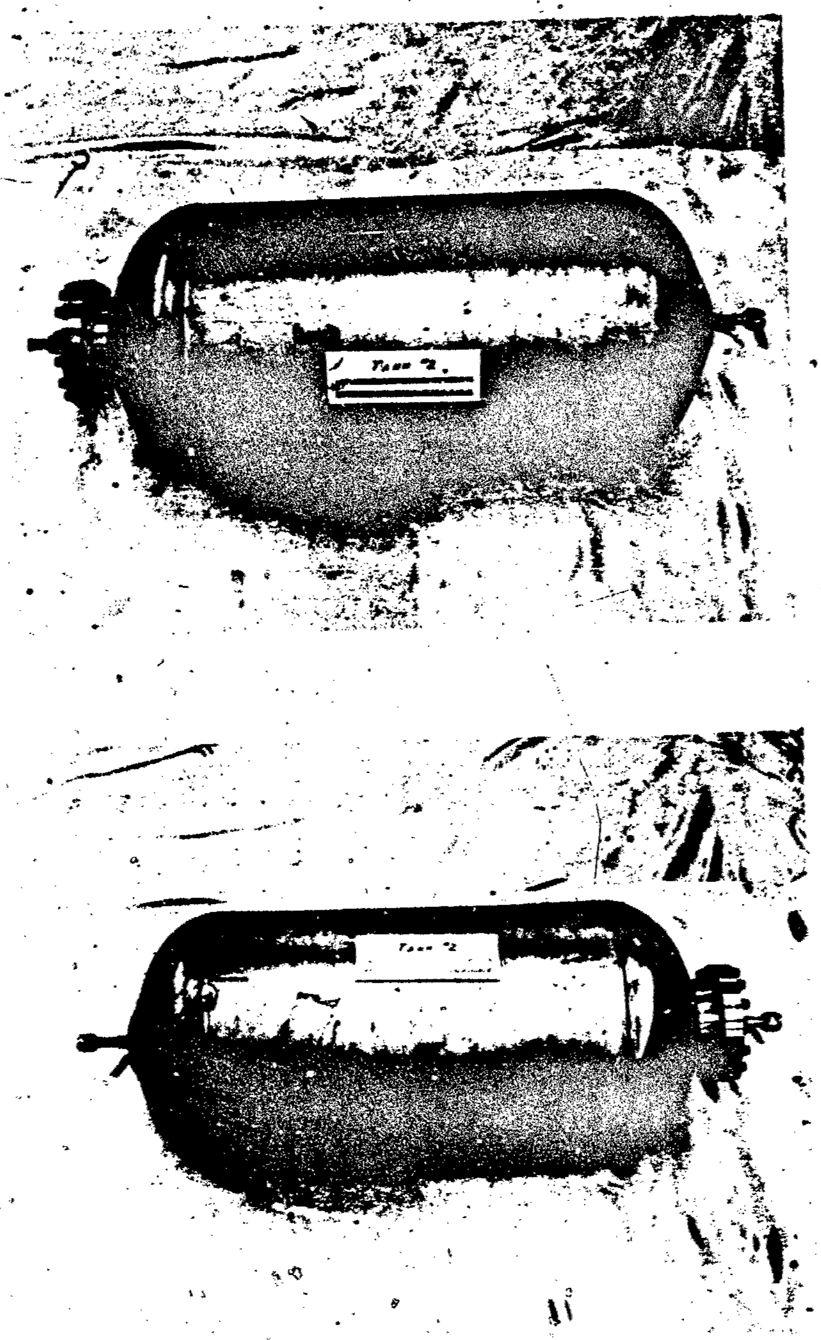


Figure 1. Side View of Tank No. 2

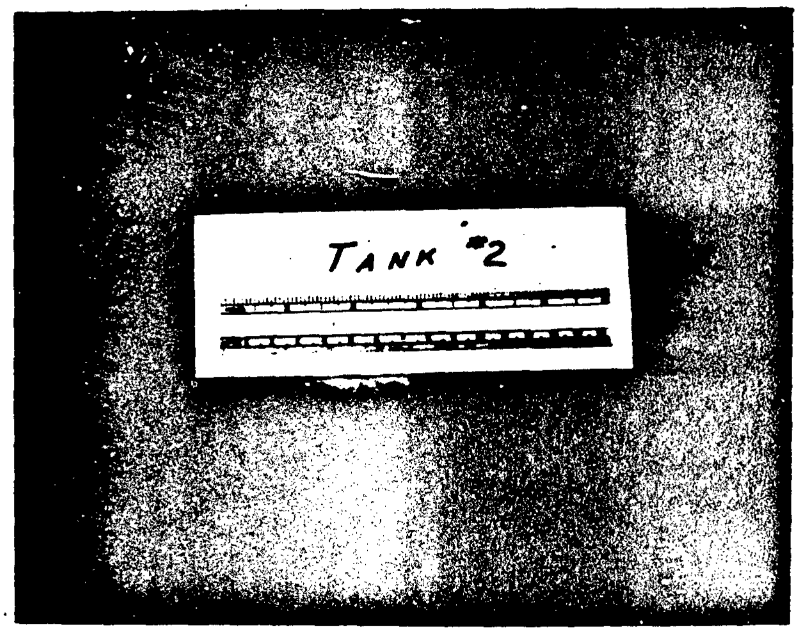


Figure 2. Closeup of Leak Area in Repair Weld Area

Figure 3. Photomacrograph of Crack (5X)

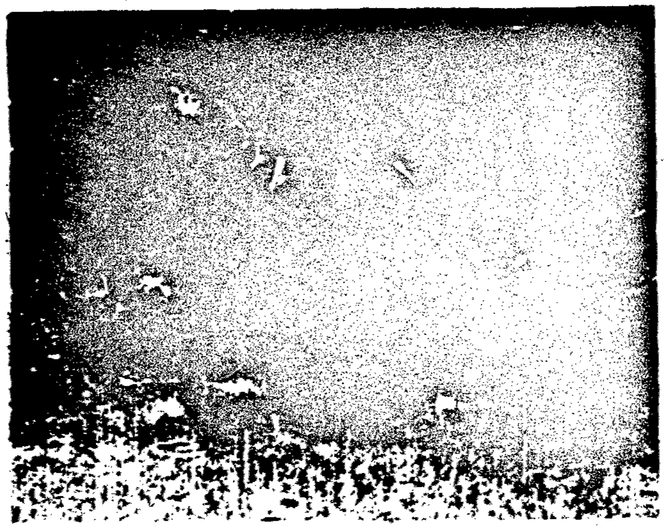


Figure 4. Photomacrograph of Crack from Inside of Tank (20X)

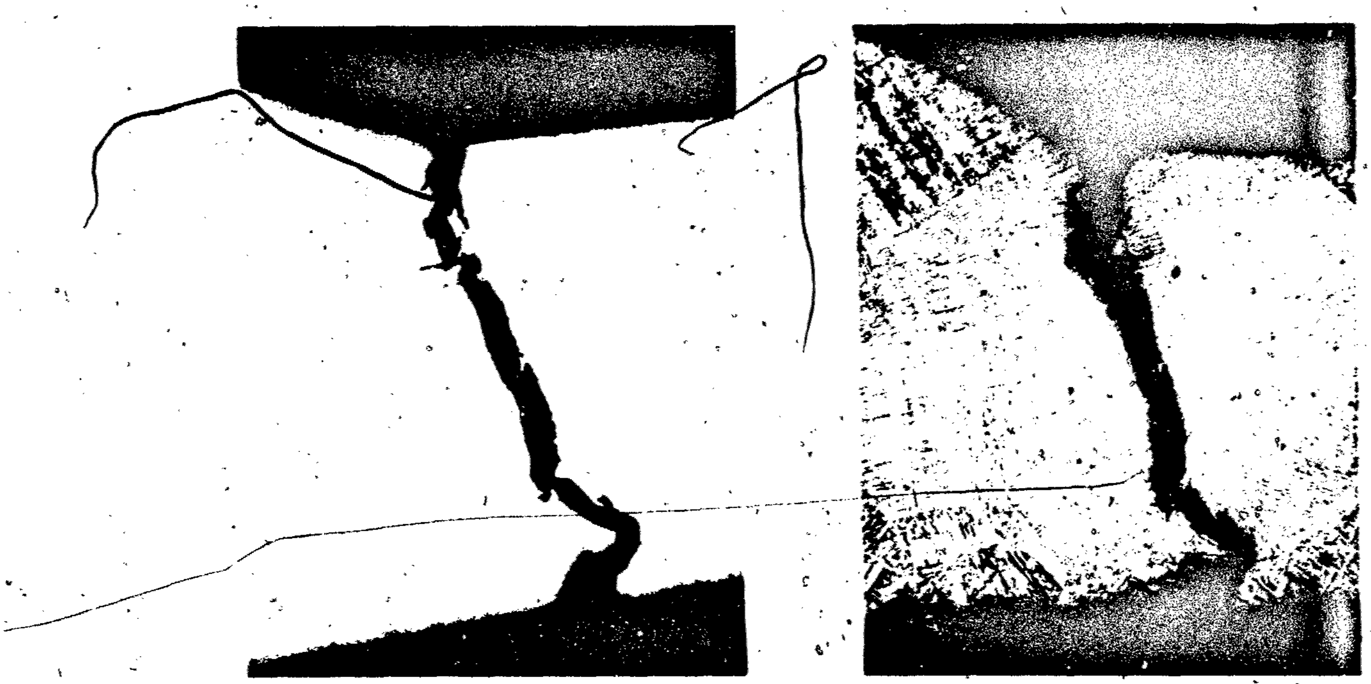


Figure 5. Photomicrographs of Hot-Short Crack in Leak Area Unetched and Etched (100X)

Figure 6. Photomacrograph of Discolored Area in Repair Weld (5X)

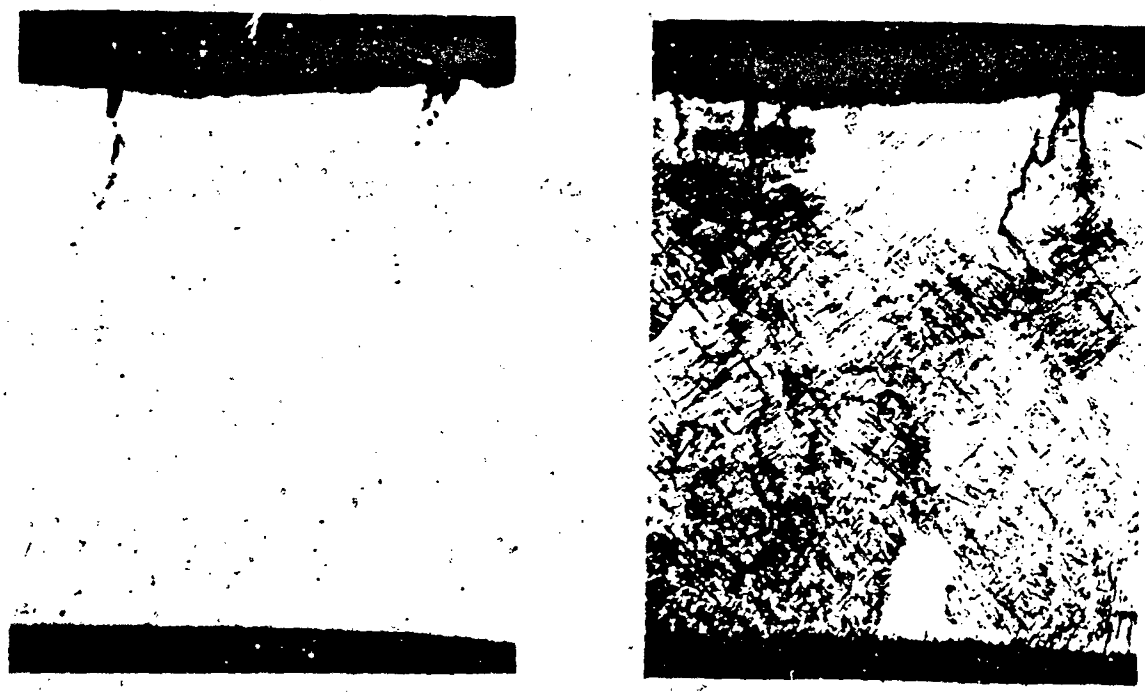


Figure 7. Stress-Corrosion Cracks and Alpha Case in Discolored Area, Unetched and Etched. (100X)

Failure Analysis of Small Tank AFRPL S/N 3, 6Al-4V Titanium Alloy

Report No. 69/28R

Author: ______________________
Lawrence W. Loechel
Senior Engineer-Metals
Materials Research and Engineering

Approved: ______________________
A. W. O'Brien, Jr.
Section Chief
Materials Research and Engineering

Author: ______________________
Howard J. Brown
Unit Head - Metals
Materials Research and Engineering

Reference: (1) Lawrence W. Loechel, Howard J. Brown and A. W. O'Brien, Jr. "Failure Analysis of Small Tank AFRPL S/N 2, Ti-6Al-4V Titanium Alloy," 31 March 1969, Materials Research and Engineering Report No. 69/14R.

(2) "Electron Fractography Handbook" - Technical Report ML-TDR-64-416, January 31, 1965. Page 4-132.

(3) DMIC Review of Recent Developments, "Corrosion and Compatibility", W. E. Berry, February 28, 1968.

(4) L. W. Loechel, Howard J. Brown and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 5, 7039-T651 Aluminum Alloy", 23 April 1969, Materials Research and Engineering Report No. 69/16R.

(5) C. F. Tiffany and J. N. Masters, "Investigation of Flaw Growth Characteristics of Ti-6Al-4V Titanium Used in Apollo Space Craft Pressure Vessels. NASA CR-65586.

INTRODUCTION

Tank S/N is a Ti-6Al-4V titanium alloy tank that had been exposed to uninhibited N_2O_4 for 35 days when the tank failed by leaking in the dome area.

OBJECTIVE

The objective of this analysis was to determine the metallurgical cause of failure of tank number 3.

CONCLUSIONS

1. The failure was caused by stress-corrosion cracking occurring in the heat affected zone of the beanie-to-dome segment weld.

2. The stress--corrosion cracking was caused by internal attack by the uninhibited N_2O_4.

RECOMMENDATIONS

For exposure of titanium to nitrogen tetroxide, only nitrogen tetroxide containing 0.4 to 0.8 percent NO should be used to prevent stress corrosion.

RESULTS AND DISCUSSION

1. Macroexamination. One small crack was visible on the external surface of the tank. The crack was in the heat affected zone (HAZ) of a dome segment-to-fitting weld, Figure 1. Except for this one crack the overall appearance of the tank was good, Figures 2 and 3.

2. Leak Test. The tank was baked at 250°F for one hour. It was then pressurized with 100% helium for 30 hours. The tank was then leak checked by the hand probe method, using a CEC helium mass spectrometer. One leak was found in the crack shown in Figure 1. This leak was determined to be 1.6×10^{-6} atm. cc/sec.

3. X-Ray Inspection. The dome end which contained the crack was cut from the tank and X-rayed. The X-rays of the dome segment welds showed numerous small cracks in the HAZ's of the welds. The cracks, which were oriented perpendicular to the weld, were not visible in the original X-rays of the tank.

4. Metallographic Examination. The areas showing cracks in the X-rays were visibly inspected and numerous small cracks were found in the internal surface of the tank, Figure 4. Microsections were taken through several of the cracks. As shown in Figures 5, 6, 7 and 8, the cracks were typical of N_2O_4 induced stress corrosion.

5. Electron Microscopy. A replica was made of the fracture surface of one of the cracks after it had been broken apart, Figure 9. The fracture appearance is indicative of stress-corrosion cracking (Reference 2).

6. Mechanical Properties. Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained:

	Ftu (ksi)	Fty (ksi)	% e (in./in.)
	140.4	[illegible]	13
	139.9	123.6	12
	140.4	126.3	13
MMS1669 Rqmt.	130	120	10

7. Interstitial Analysis. The oxygen, nitrogen and hydrogen content of the welds and parent material were determined to ascertain whether hydrogen or oxygen embrittlement may have contributed to the failure. The analysis showed that these elements were all within the maximum limits allowed by MMS 1669, and consequently, did not contribute to the failure.

8. Dimensional Check. The tank was measured and was found to be within drawing requirements.

9. Uninhibited N_2O_4. Reference (5) presents flaw growth characteristics and threshhold stress level of Ti-6Al-4V titanium subjected to various environments including inhibited N_2O_4. N_2O_4 inhibited with 0.4 to 0.8% NO must be used in contact with titanium, since several investigations after the failure of several Apollo propellant tanks in 1965 and 1966 indicated that uninhibited N_2O_4 will cause stress corrosion in titanium at stress levels around 40,000 psi.

Figure 1. Leak Area of Tank No. 3

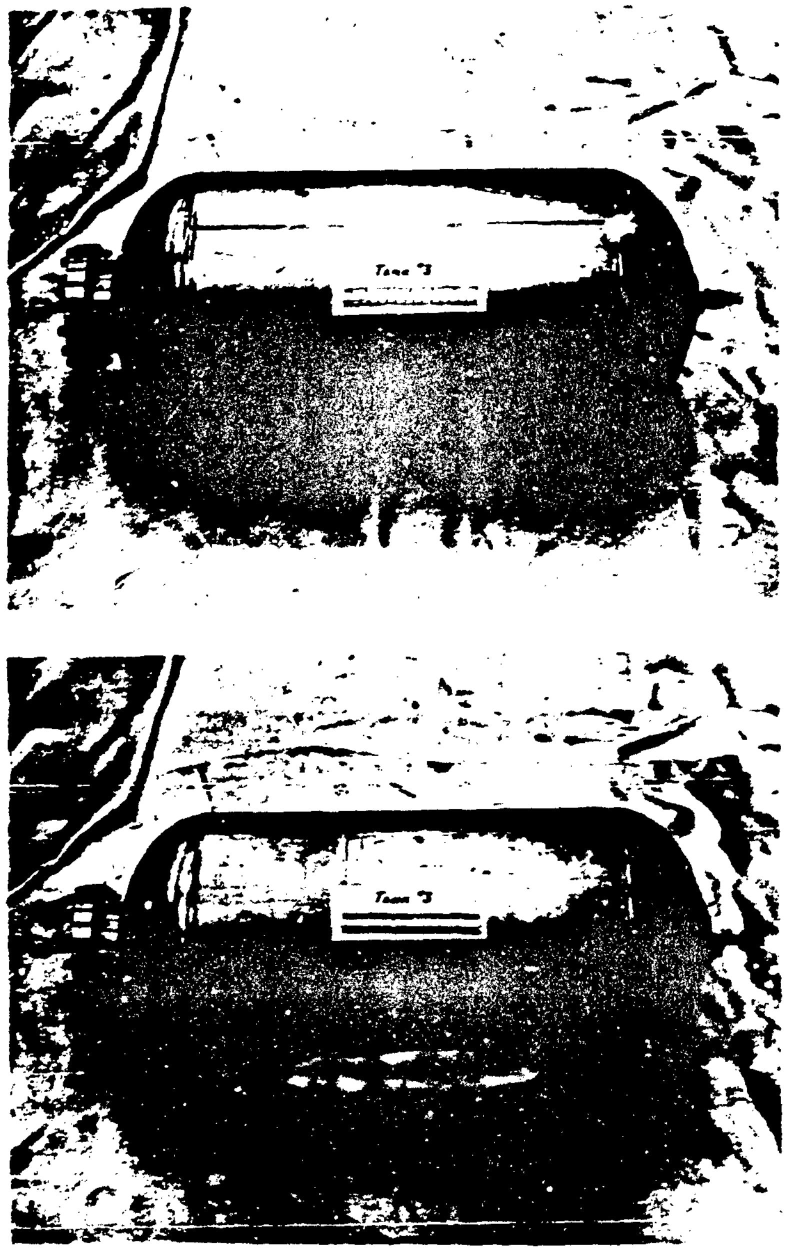


Figure 2. Side Views of Tank No. 3

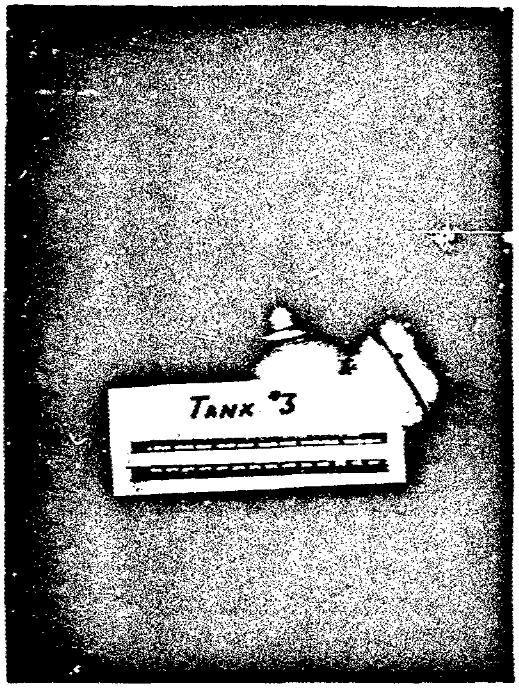


Figure 3. End Views of Tank No. 3

Figure 4. Photomacrograph Showing the Appearance of the Inside Surfaces of Tank Serial No. 3 (20X)

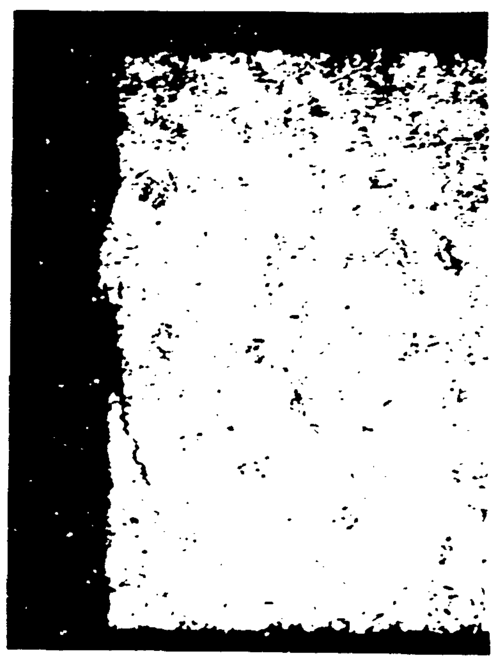


Figure 5. Photomicrograph Showing the Microstructure of the Ti-6Al-4V Titanium Alloy on the Area of the Leak (100X)

Figure 6. Photomicrograph Showing the Microstructure of the Ti-6Al-4V Titanium Alloy at a Stress Corrosion Crack (250X)

Figure 7. Photomicrograph Showing the Microstructure of the Ti-6Al-4V Titanium Alloy at a Stress Corrosion Crack (100X)

Figure 8. Photomicrograph Showing the Microstructure of the Ti-6Al-4V Titanium at a Stress Corrosion Crack (100X)

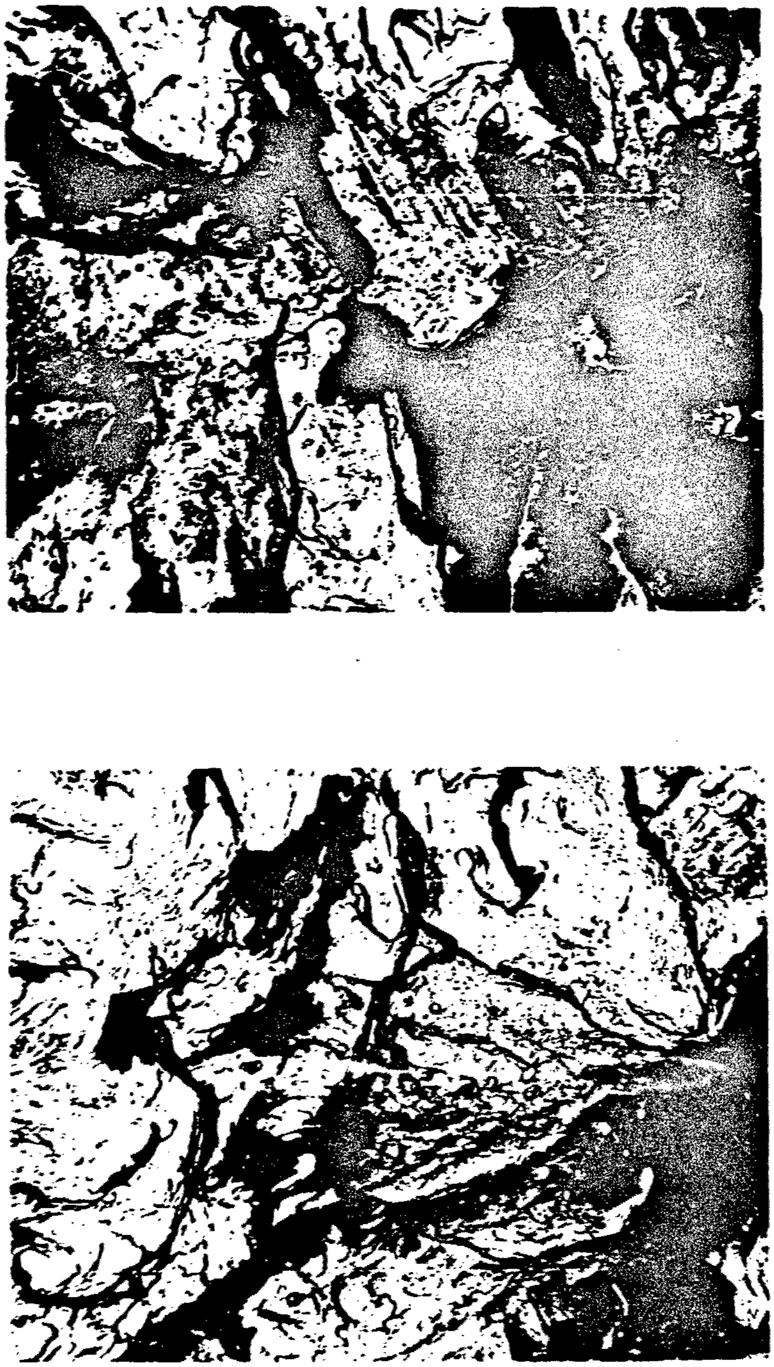


Figure 9. Electronophotomicrograph Showing Evidence of Stress Corrosion (6500X)

Martin Marietta Corporation 3 January 1969

MCR 69-27 Materials and Process Technology

Failure Analysis of Small Tank S/N 4, AM350 Precipitation Hardening Stainless Steel

Report No. 68/77R

Author:________________________
Lawrence W. Loechel
Senior Engineer-Metals
Materials and Process Technology

Approved:________________________
A. W. O'Brien, Jr.
Chief
Materials and Process Technology

Author:________________________
Howard J. Brown
Head - Metals Unit
Materials and Process Technology

INTRODUCTION

The first small tank to be failure analyzed as required by AF Contract No. F42600-68-A-2327 was Tank AFRPL S/N 4. This tank had been immersed in N_2O_4 for 294 days at Edwards AFB, California. Tank S/N 4 was an AM350 Precipitation Hardening Stainless Steel Alloy and was badly pitted and rusted.

REFERENCES

(1) NASA Tech Brief, April 1967, Brief #67-10069, "Controlled Ferrite Content Improves Weldability of Corrosion - Resistant Steel".

(2) H. Kihara, "Weld Cracks & Notch - Toughness of Heat-Affected Zone in High-Strength Steels," July 15, 1968.

(3) R. G. Baker, "Weld Cracking - a modern insight", British Welding Journal, June 1968.

(4) Martin Marietta Corporation, Materials & Process Technology Report No. M. E. 68/60R, 10/23/68, "Use of 347 Stainless Steel Alloy to Preclude Hot Short Cracking."

OBJECTIVE

The objective of this failure analysis was to determine the metallurgical cause for the failure of S/N #4 AM350 Precipitation Hardening Stainless Steel Tank.

CONCLUSIONS

1. The cause for the failure of the AM350 Precipitation Hardening Steel Alloy tank was a hot short crack which had occurred in a repair weld at the top of the tank.

2. After initial leakage occurred through the hot short crack area, N_2O_4 leaking to the atmosphere formed HNO_3, and the heat affected zones of welds on the bottom of the tank caused excessive corrosion and pitting resulting in further leakage.

3. The potential defect should have been examined more closely on initial inspection of the finished tank.

4. The mechanical properties were lower than required by drawing.

RECOMMENDATIONS

1. Weld acceptance criteria used to initially accept this tank should be reviewed for future orders. The criteria should be strengthened in the area of acceptable radiographic defects and also on the allowable visual defects such as repair weld build-up, undercut, and cratering.

2. Weld parameters must be adjusted on initial qualifications and certifications to assure that the production articles will be free from hot tearing.

RESULTS AND DISCUSSION

The following procedures were followed during failure analysis of tank No. 4.

1. Macroexamination - The tank was badly corroded, particularly near the bottom, Figures 1, 2, 3, and 4. Numerous corrosion pits were found near the weld cross overs on the bottom portion of the tank. A hot-short crack was later found in a repair weld in the beanie weld at the top of the tank.

2. Leak Test - The tank was baked at 250°F for 1 hour. Then it was pressurized with 100% helium. The pressure dropped to zero in 16 hours. Since the leakage was so profuse it was not necessary to chamber leak tests the tank. Instead the tank was checked by the hand probe method using a CEC He mass spectrometer.

   Seven leaks were found in the bottom of the tank, all of them off scale, Figure 5. Each leak occurred in the weld cross overs or in their heat affected zones. And each leak was apparently caused by HNO_3 corrosion pits extending through the tank wall. Figure 6.

   A leak was found in a repair weld at the top of the tank, Figure 7. The leak was measured to be 2.6×10^{-7} atmcc/sec, and was caused by a hot short crack in the repair, Figure 8.

3. Metallographic Examination - Microsections of each leak were made. All of the leaks at the bottom of the tank were caused by external corrosion pitting through the tank wall. Typical microsections shown in Figures 9A and 9B.

   A microsection through the leak area at the top of the tank verified that leakage was caused by a hot-short crack in the repair weld area, Figure 10.

4. Corrosion Product Analysis - Corrosion products taken from the external surface of the tank were identified as Fe_3O_4 by electron diffraction. This would indicate the corrosion products were results of corrosion by a strong oxidizing acid such as HNO_3. X-ray fluorescence showed the corrosion products were strong in Fe, Cr, and Ni which would be the normal corrosion oxide products if the AM350 precipitation hardening stainless steel were attacked by nitric acid. Also shown by X-ray fluoresence in weaker concentration were the elements Mn, Mo, Cu, and Zn. These elements are also present in AM350 in small amounts and therefore should appear in an analysis of the corrosion products.

5. Chemical Analysis

Mn - 0.71
Si - 0.49
Ni - 4.30
Cr - 16.94
Mo - 2.40

This analysis indicated the material met the requirements of the drawing.

6. X-Ray Inspection - The leak areas were x-rayed prior to sectioning. No defects were visible in the bottom welds, other than corrosion pits. The hot short crack was plainly visible in the x-ray of the top welds.

7. Mechanical Tests - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained.

	Ftu ksi	Fty ksi	Percent Elongation Percent in 2 inch
	162	156	14
	158	150	13
	160	155	11.5
	163	157	12.5
Drawing Callout	185	150	

The hardness was determined to be R_a 70.

Although the mechanical properties did not enter into the reasons for failure of the tank, in this instance, the ultimate tensile strength was below the value required by drawing.

8. Dimensional Checks - The barrel thickness was 0.030 inch. The dome thickness ranged from 0.025 to 0.027 inch. The thickness of the boss end plugs tapered from 0.050 to 0.090 inch. These dimensions were within the requirements of the drawing, GD/C-TSP-001.

9. Internal tank Examination - The inside of the tank was clean and bright as evidenced by the appearance shown in Figure 14. There was no corrosion in evidence on the internal surfaces of the tank.

CAUSES OF WELD CRACKING

According to references 1, 2, 3, and 4, the chromium-nickel ratio must be maintained higher than 1.7 to control ferrite to a range of 3 to 6%, preferably 4%. The degree of cracking is determined by the chemical composition and is aggravated by higher levels of phosphorous, carbon, sulfer, silicon, columbium, and residual elements. In addition to these controls, welding procedures must be adjusted and craters must be avoided in either start-up or run out.

One of the theories of weld cracking at elevated temperatures (hot short cracking) is the strain theory of hot tearing. This theory is; that, hot tearing is caused by locallized strains set up by thermal contraction under restraint from weld fixtures, heavy sections, etc., tend to pull apart solid masses of material separated by essentially continuous thin liquid films of sulfides, phosfides, silicides, etc., which are eutectic films formed at the grain boundaries when the steel is melted for welding.

The above discussion is presented as a short discourse explaining the mechanism of hot tearing. In the steel under consideration, AM350 precipitation hardening steel, the hot tearing is always a possibility, since the ferrite content can vary and the elements, sulfur, phosphorous, silicon, carbon, etc., are present. However, the steel is considered to have excellent weldability, except that welding parameters should be carefully controlled. In the case in point, there was a crater which occurred in a repair weld. Under this condition of high heat, restraint and stress concentration, the material cracked on cooling from the welding temperatures.

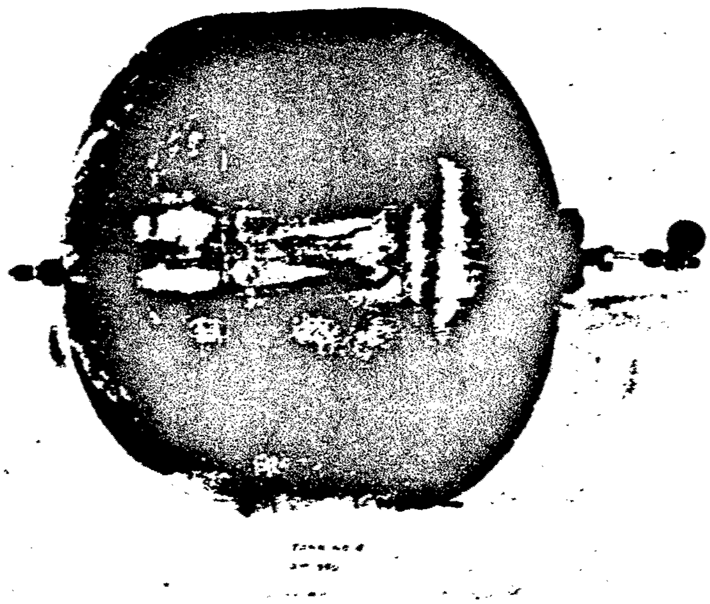


Figure 1. Photomacrograph Showing the Overall Appearance of the Failed AM350 Small Tank A/F Serial No. 4 1/4X

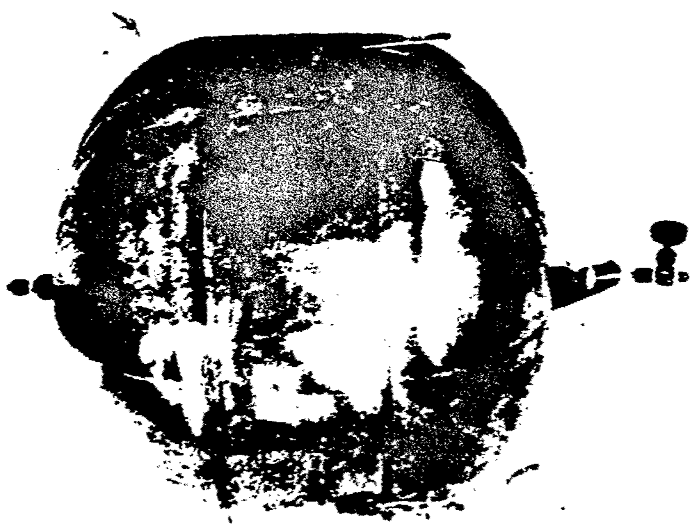


Figure 2. Another View of Tank Shown in Figure 1 1/4X

Figure 3. Photomacrograph Showing the Bottom End of the Failed Tank. 1/4X

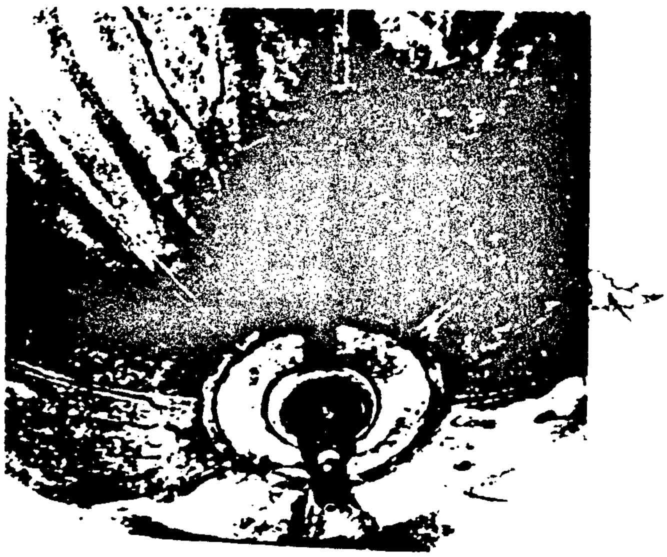


Figure 4. Photomacrograph Showing a View of the Tank Bottom at Higher Magnification. 1/2X

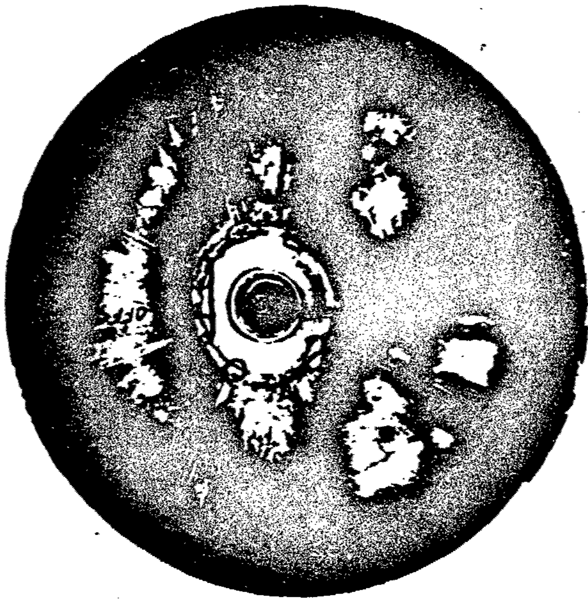


Figure 5. Photomacrograph Showing the Leak Areas on the Bottom of the Failed Tank. 1/4X

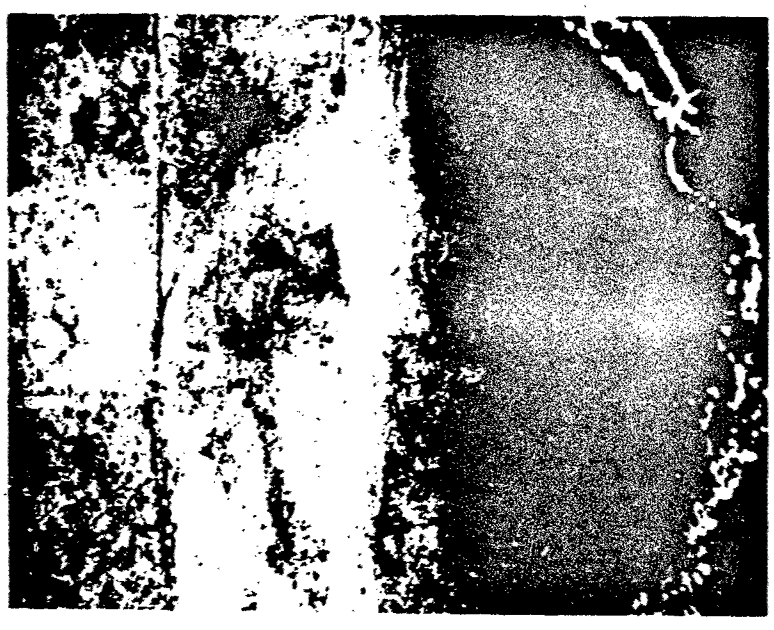


Figure 6. Photomacrograph Showing a Leak in the Bottom of the Failed Tank. 10X

Figure 7. Photomacrograph Showing An Overall View of The Top of The Failed Tank. The Arrow Indicates The Origin of Failure of The Tank.

Figure 8. Photomacrograph Showing The Inside Of The Top of The Failed Tank. Note The Crack In The Repair Weld Stop Area. 10X

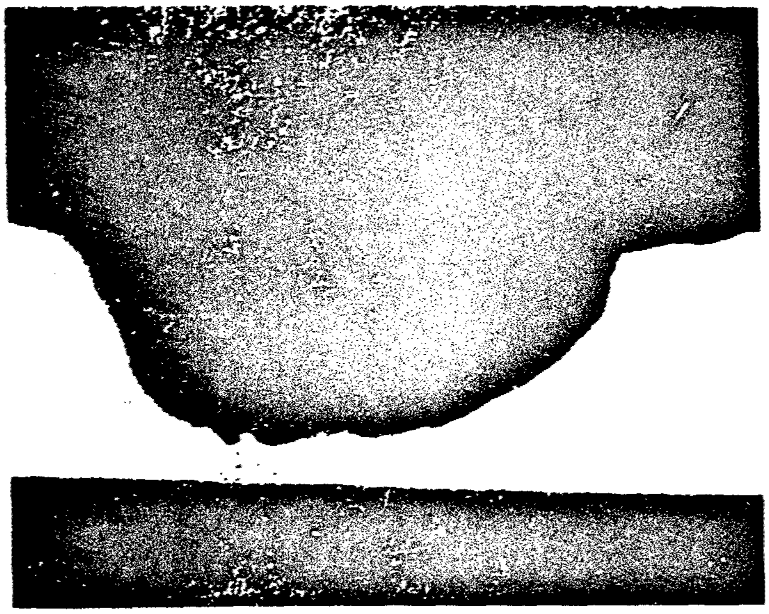


Figure 9A. Photomicrograph Showing a Cross Section of a Pit in the Bottom of the Failed Tank. Unetched 60X

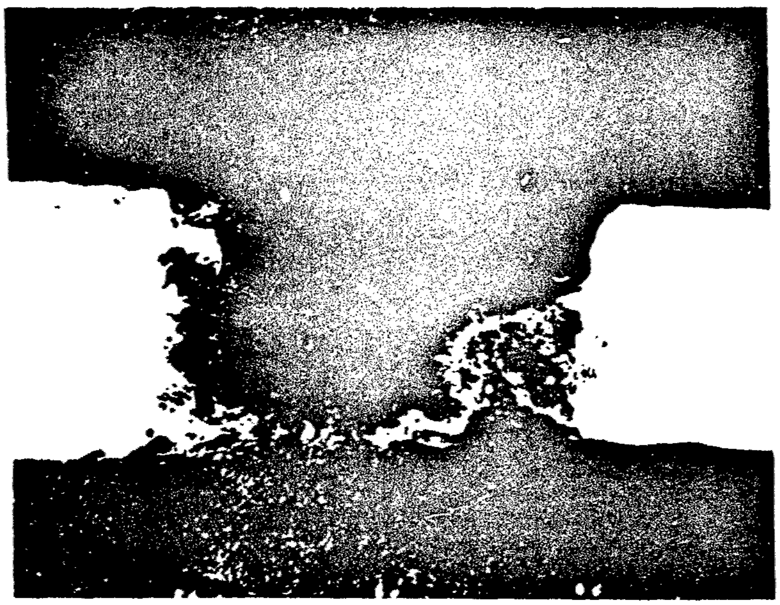


Figure 9B. Photomicrograph Showing Another Cross Section of a Pit in the Bottom of the Failed Tank. Unetched 60X

Figure 10. Photomicrograph Showing a Cross Section Through the Hot Short Crack in the Origin of the Failure of Tank Serial Number AF-4
Unetched 60X

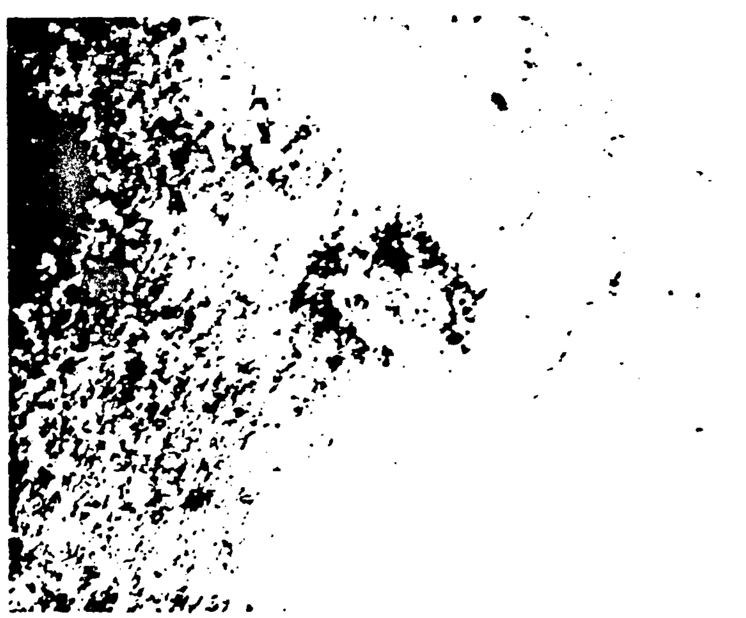


Figure 11. Photomacrograph Showing a Leak Area on the Inside Bottom of the Failed Tank 10X

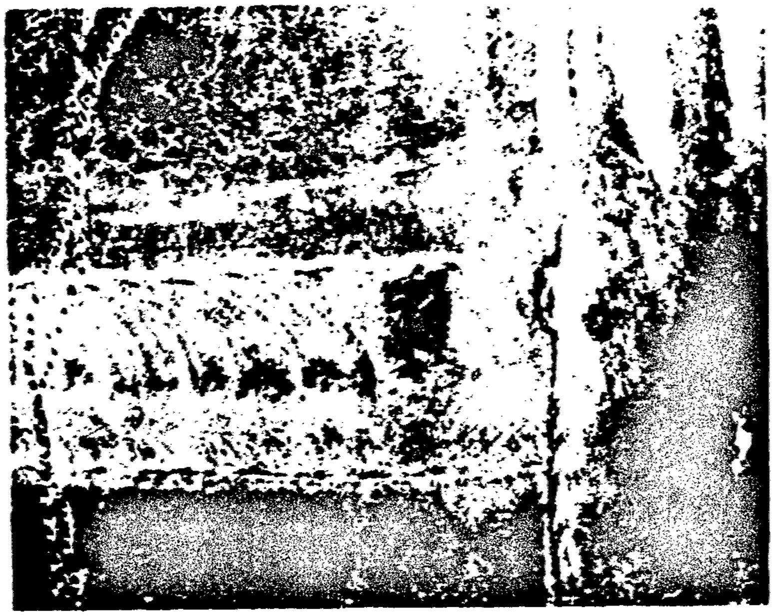


Figure 12. Photomacrograph Showing Pitting Corrosion Near a Weld Cross-Over on the Outside Bottom of the Failed Tank 10X

Figure 13. Photomacrograph Showing Pitting Corrosion in a Ground Area of a Weldment on the Outside Bottom of the Failed Tank 10X

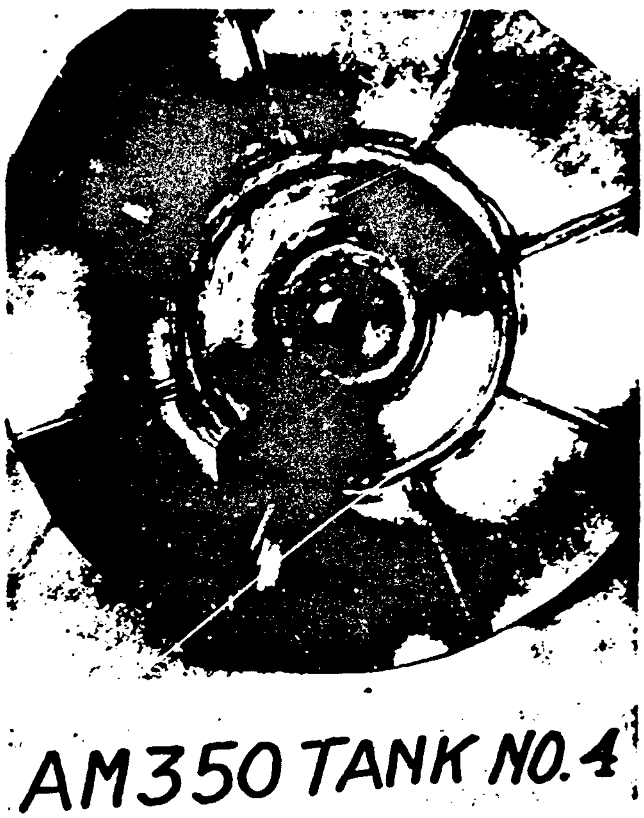


Figure 14. Photomacrograph Showing a Representative Surface on Inside of Tank Serial No. AF-4 1/3X

Failure Analysis of Small Tank AFRPL S/N 5, 7039-T651 Aluminum Alloy

Report No. 69/16R

Author:____________________
Lawrence W. Loechel
Senior Engineer-Metals
Materials Research and Engineering

Approved:____________________
A. W. O'Brien, Jr.
Chief
Materials Research and Engineering

Author:____________________
Howard J. Brown
Head - Metals Unit
Materials Research and Engineering

Reference: (1) Lawrence W. Loechel, Howard J. Brown and A. W. O'Brien, "Failure Analysis of Small Tank AFRPL S/N 2, Ti-6Al-4V Titanium Alloy," 31 March 1969, Materials Research and Engineering Report No. 69.14R.

(2) "Electron Fractography Handbook" - Technical Report ML-TDR-64-416, January 31, 1965. Page 4-132.

(3) Martin Material Specification, MMS 1151, Aluminum Alloy 7039 Bare Sheet and Plate, May 19, 1965.

(4) "Weldable/Heat Treatable Aluminum Alloy 7039," Kaiser, June 1965.

(5) DMIC Review of Recent Developments, "Corrosion and Compatibility," W. E. Berry, February 28, 1968.

(6) "Stress-Corrosion Cracking of Aluminum Alloys," DMIC Memo No. 231, August, 1967.

INTRODUCTION

Tank S/N 5 is a 7039 aluminum alloy tank that had been exposed to N_2O_4 for 55 days when the tank failed by leaking in the flange neck area.

OBJECTIVE

The objective of this analysis was to determine the metallurgical cause of failure of tank number 5.

CONCLUSIONS

1. Leakage occurred as a result of stress corrosion cracking from external to internal surfaces along short transverse grain boundaries of the outlet flange. This was the primary failure.

2. Leakage also occurred as a result of intergranular and stress corrosion cracking in the area of hot short cracks in the outlet tube weld.

RECOMMENDATIONS

1. For future designs, those alloys which are quite susceptible to stress corrosion in short transverse grain directions should not be highly stressed in that direction.

2. As has been recommended previously, reference (1), no propellant tanks should be exposed to fumes or spills from other leaking vessels while in a humid environment.

RESULTS AND DISCUSSION

1. Macroexamination - One large crack and numerous secondary cracks were visible in the outlet flange of the tank, Figure 1. Numerous cracks were also found in the weld area joining the tube to the outlet cover plate, Figure 2. The remainder of the tank was in fairly good condition, except for some areas of light general corrosion, Figure 3 and 4.

2. Leak Test - The tank was baked at 250°F for one hour. It was then pressurized with 100% helium for 16 hours. The tank was then leak checked by the hand probe method, using a CEC helium mass spectrometer. One leak was found in the crack shown in Figure 1. This leak was determined to be 1.2 x 10^{-5} atm. cc/sec.

3. Metallographic Examination - A microsection was made through the crack in the outlet flange, Figures 5 and 6. The fracture and the many secondary cracks were caused by stress-corrosion cracking originating at the external surface of the flange.

   The cracks in the outlet-tube weld area were in the parent metal adjacent to the fillet weld, Figure 7. A microsection through one of these cracks is shown in Figure 8. These cracks were caused by hot-short cracking in the heat-affected-zone of the 7039 cover plate. Another microsection was made through an area that showed crack indication in x-rays of the area. Figure 9 is a photomacrograph of the internal surface of this area. Here a crack running parallel to the weld in the heat-affected zone is visible. This was also a hot-short crack as indicated in Figure 10. Figure 11 is the external surface across from the hot-short crack. Intergranular corrosion and the beginning of stress corrosion are apparent.

4. Electron Microscopy - Replicas of the fracture surface of the large outlet crack were made for examination with the electron microscope. Figure 12 is an electron photomicrograph of the fracture surface. These photos show a "mud crack" fracture appearance that is very typical of stress-corrosion cracking in 7000 series alloys. "Mud Crack" is terminology which is used in reference (2) to identify areas typical of stress-corrosion cracking.

5. Corrosion Product Identification - The only element in the corrosion product that was postively identified was phosphorus. Up to 3.9% P was found by electron-microprobe analysis. It is believed that the product was a mixture of aluminum oxides and phosphates, the phosphates probably resulting from residues from decontaminating procedures.

6. Chemical Analysis - The tank was determined to have been made from 7039 aluminum alloy and conformed to the MMS 1151 requirement, reference (3).

7. Mechanical Tests - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained.

	Ftu (ksi)	Fty (ksi)	Percent Elongation (in/in)
	59.0	50.7	10.5
	59.0	51.5	11.0
	58.1	50.0	13.0
	58.8	50.0	12.5
MMS 1151 requirement	55	45	10

The hardness was determined to be R_B78 which is acceptable per MMS 1151.

8. Dimensional Checks - The tank was measured and determined to be within drawing requirements.

9. X-ray Inspection - The dome welds from the leaking end of the tank were x-rayed. Numerous defects, such as porosity, cracks, and lack of fusion were found. The defects in the area that were microsectioned were also apparent.

10. 7039-T651 Aluminum Alloy has shown corrosion and stress corrosion cracking resistance similar tc 5083 and 5086 and has shown to be superior to 7079-T6, 7075-T6, and 2014-T6 in the long transverse and longitudinal grain directions, references (4) and (5) at 75% of Fty for 500 hours.

    In the short transverse grain directions, 7039-T651 has not shown to be as good as 5083 and better than 7079-T6, 7075-T6 and 2014-T6, reference (4).

    Reference (6) indicates an alloy similar to 7039, Al Zn Mg, has a high tendency to stress corrosion cracking. Alloys containing 7 percent and more of Zn and Mg were highly sensitive to stress corrosion.

    Actually, 555 days in a corrosive environment exposed in the short transverse grain direction is a severe test and does indicate the 7039-T65 aluminum alloy is relatively corrosion resistant.

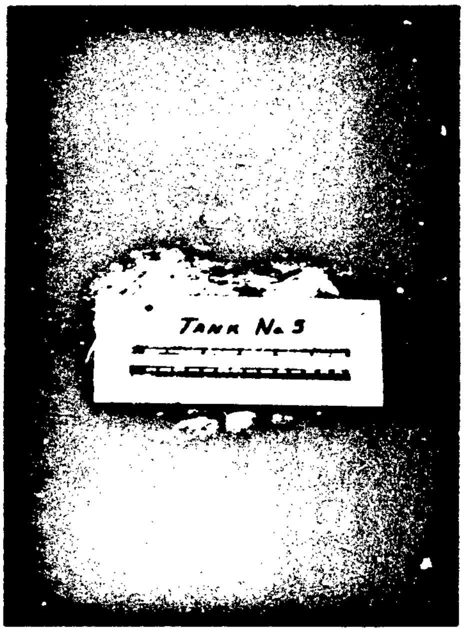


Figure 1. Crack in Outlet Flange of S/N 5 1/4X

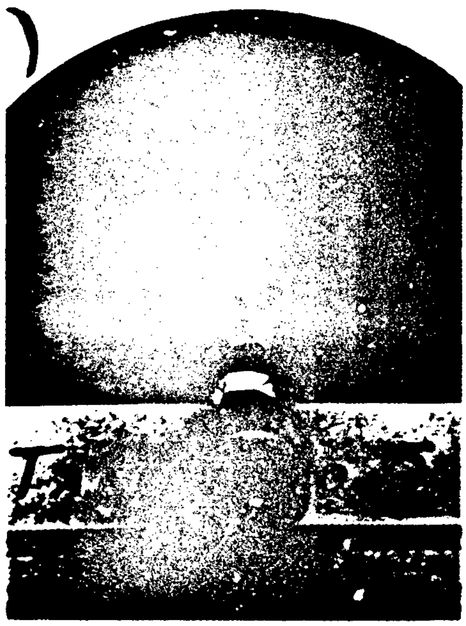
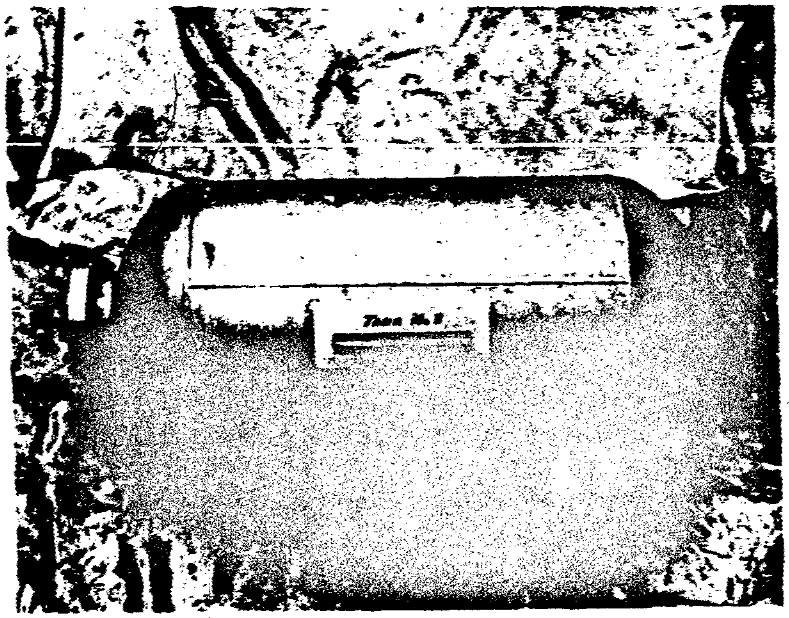
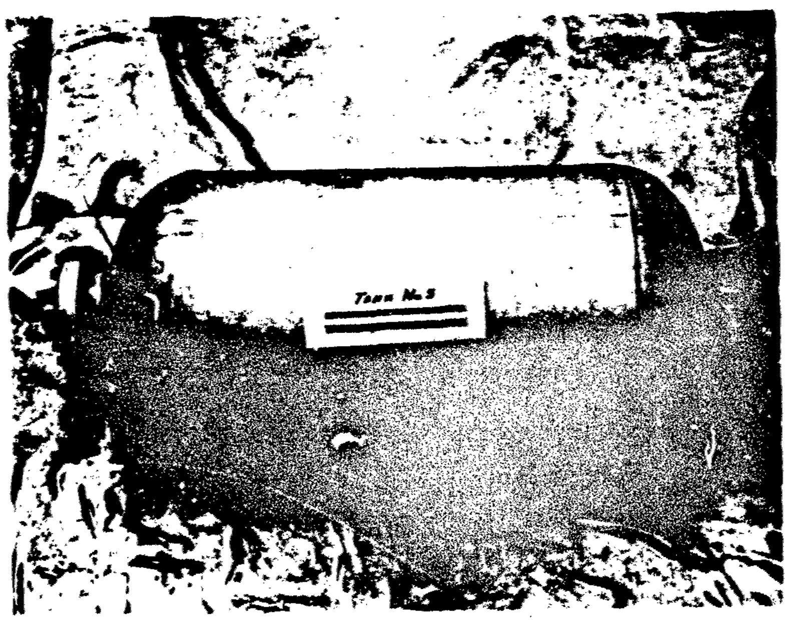


Figure 2. Crack in Tube Weld on Outlet Cover 3/4X



a



b

Figure 3. Sideviews of Small Tank S/N 5 1/8X

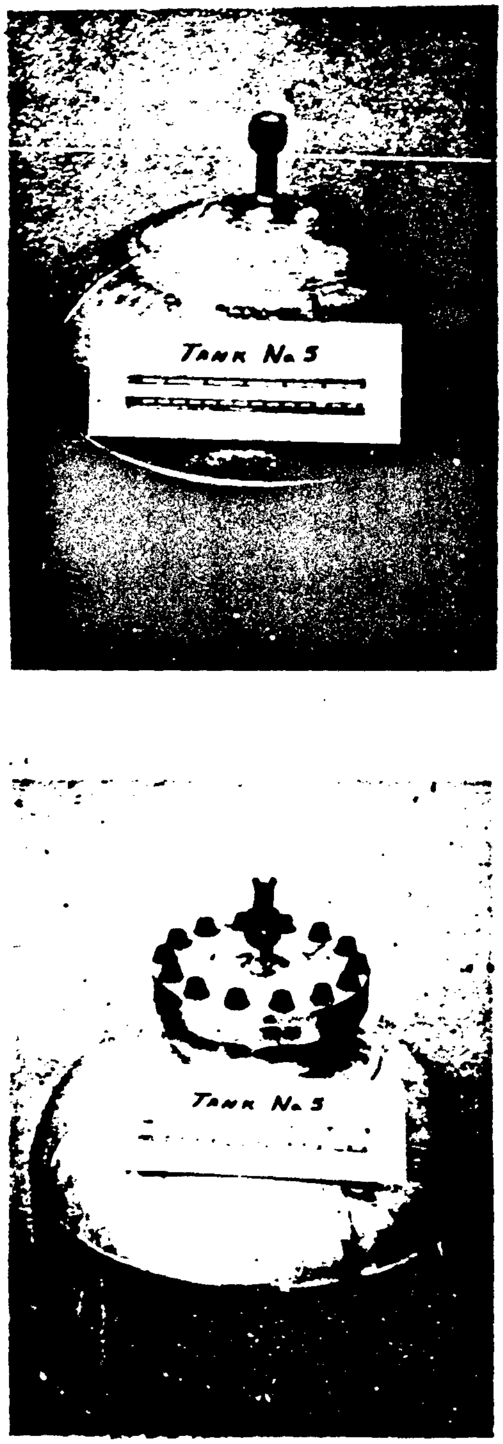


Figure 4. End Views of Small Tank S/N 5 1/4X

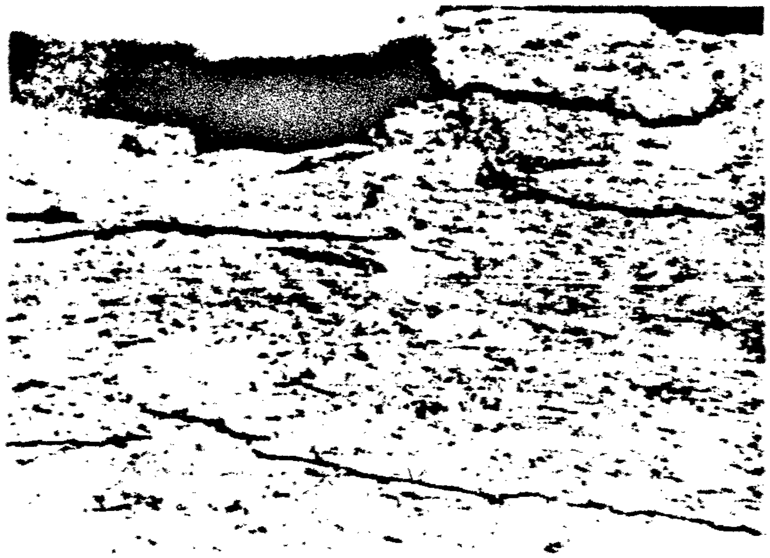


Figure 5. Photomacrograph of Secondary Cracks Near Fracture. (Fracture Surface is indicated by arrow) 20X

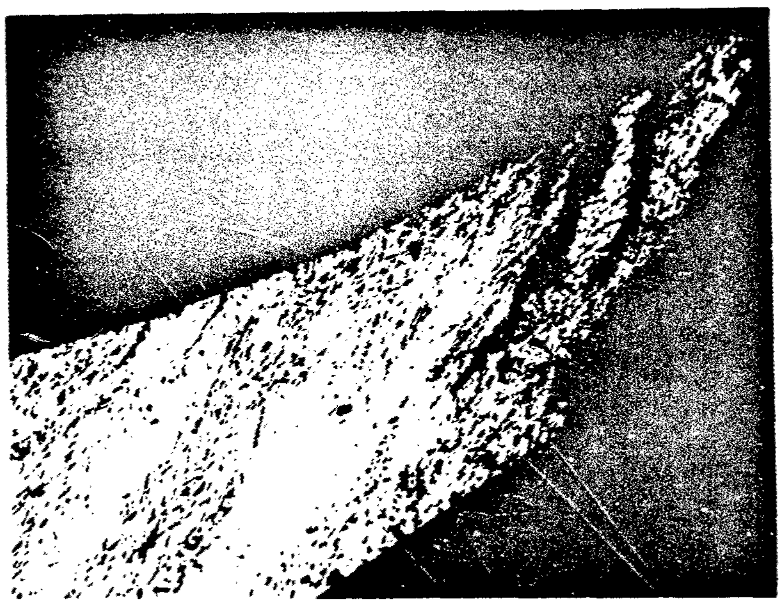


Figure 6. Microsection Through Area Shown in Figure 5. (25X)

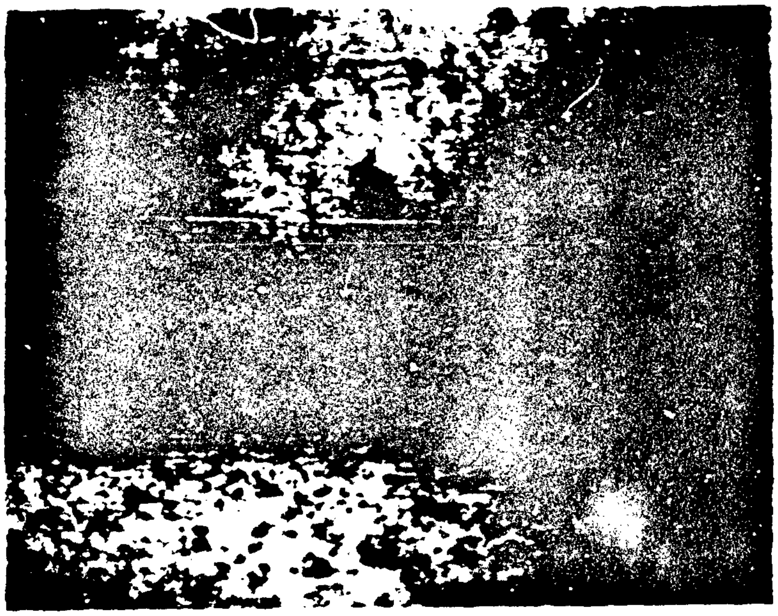


Figure 7. Photomacrograph of Cracks Near Fillet Weld of Tube Assembly (20X)

Figure 8. Microsection Through Crack Shown in Figure 7. (50X)

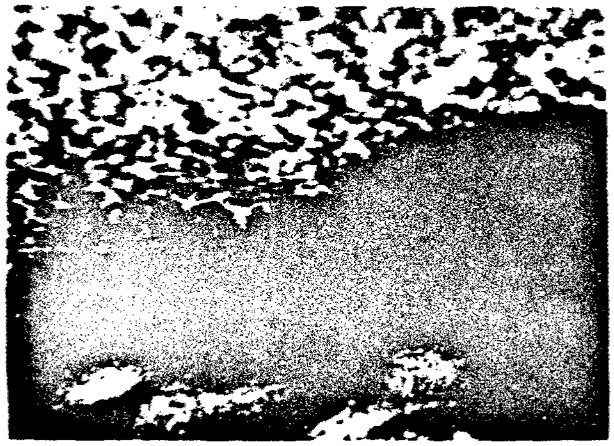


Figure 9. Photomacrograph of Crack Near Fusion Weld. (20X)

Figure 10. Microsection Through Hot-Short Crack in Figure 9. (50X)

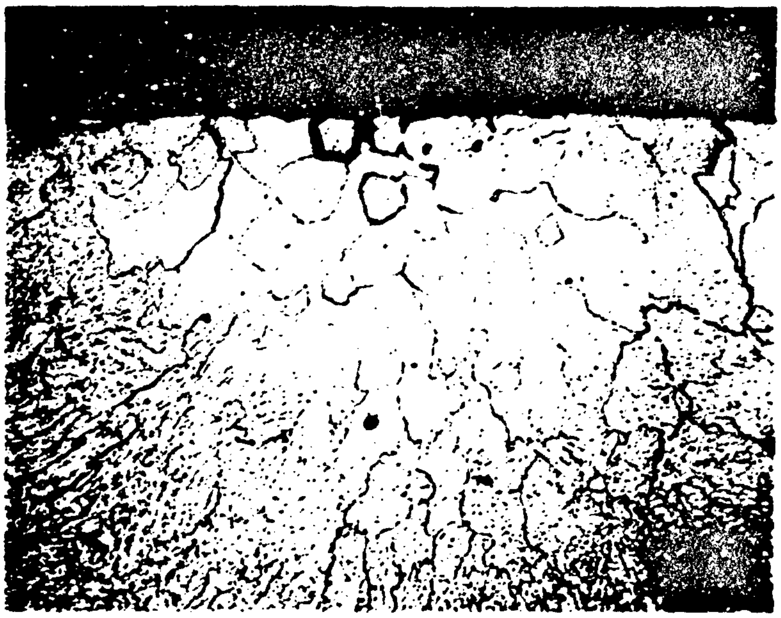


Figure 11. Photomicrograph of Intergranular Corrosion and Stress-Corrosion Cracks on External Surface of Area Shown in in Figure 10. (50X)

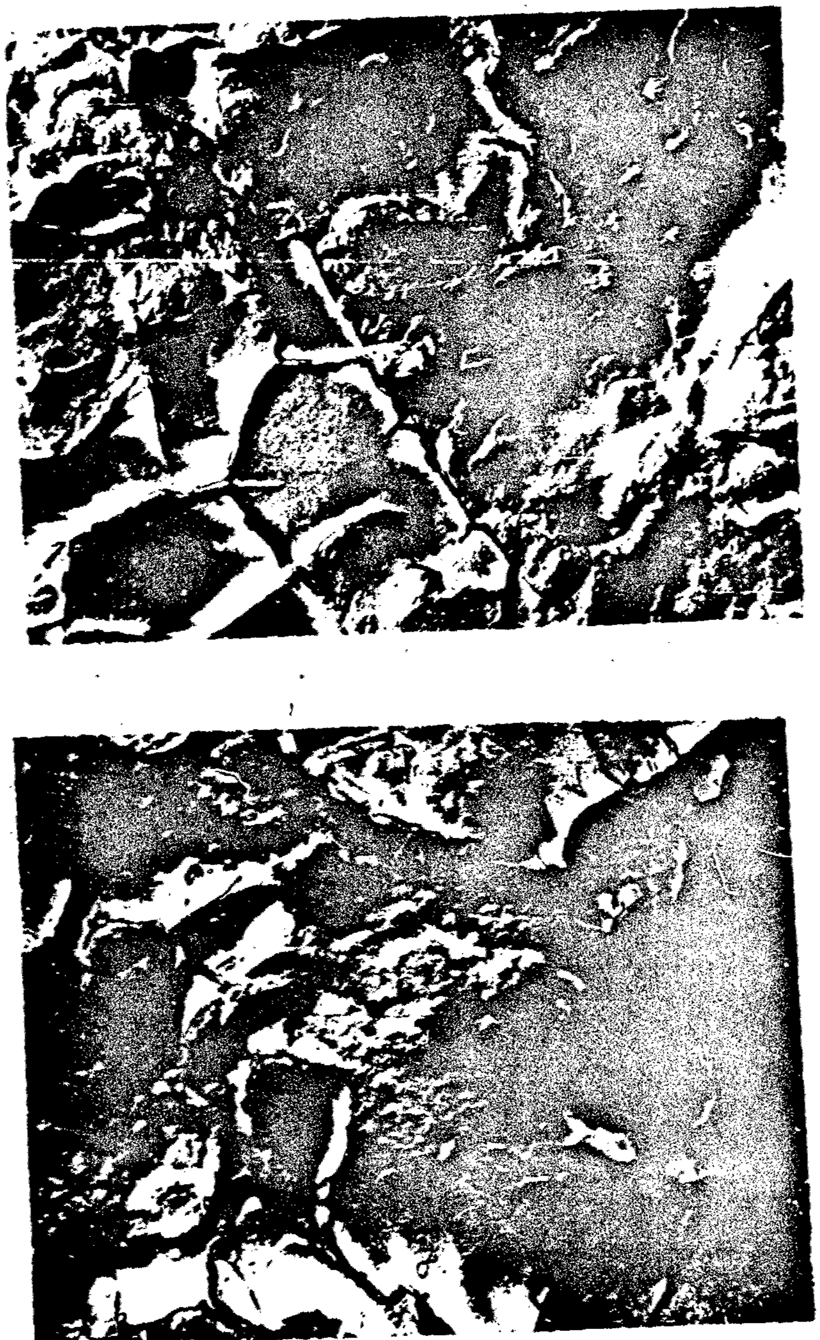


Figure 12. Electron Photomicrographs of Fracture Surface of Outlet Crack. (6500X)

Failure Analysis of Small Tank AFRPL S/N 6, 17-7PH Stainless Steel

Report No. 69/24R

Author:______________________
Lawrence W. Loechel
Senior Engineer-Metals
Materials Research and Engineering

Approved:______________________
A. W. O'Brien, Jr.
Chief
Materials Research and Engineering

Author:______________________
Howard J. Brown
Head - Metals Unit
Materials Research and Engineering

INTRODUCTION

Tank S/N 6 is a 17-7PH precipitation hardening stainless steel tank that had been exposed to N_2O_4 for 295 days.

OBJECTIVE

The object of this failure analysis was to determine the metallurgical cause for the failure of AFRPL S/N 6.

CONCLUSIONS

1. The tank failed because of corrosion through by nitric acid from the exterior surface of the tank.

2. The nitric acid apparently formed on the failed tank by condensation of water (85% relative humidity) and N_2O_4 from a nearby leaking N_2O_4 bessel.

3. One leak may have occurred through a hot-short crack in a dome weld.

RECOMMENDATIONS

1. Test conditions should be regulated so that when other test specimens fail, the by-products of that failure should not be allowed to interfere with another test in progress.

2. Weld acceptance criteria used to initially accept this tank should be reviewed for future orders. The criteria should be strengthened in the area of acceptable radiographic defects.

3. Weld parameters must be adjusted on initial qualifications and certifications to assure that the production articles will be free from hot tearing.

RESULTS AND DISCUSSION

1. Macroexamination - The tank was examined with the unaided eye and with magnifications to 30X with a stereomicroscope.

2. Leak Test - The tank was baked at 250°F for 1 hour. After cooling to room temperature, it was pressurized with 100% helium, and allowed to soak for 16 hours. The tank was then leak tested by the hand probe method using a CEC helium mass spectrometer. Seven leaks were found in the dome areas of the tank. The magnitude of the leakage ranged from 7×10^{-9} to 1.6×10^{-5} atm cc/sec. Photographs of the ends showing several of the leak areas are shown in Figures 3 and 4.

3. Metallographic Examination - Before sectioning and mounting the leak areas, each one was examined under the stereomicroscope. All but one of the leaks appeared to be the result of external corrosion. Representative photomicrographs of cross sections of the leaks are shown in Figures 5 and 6.

   It was apparent from the microsections that all of the leaks except one were caused by external corrosion. One leak apparently occurred through a hot-short crack in a dome weld, Figure 6.

4. X-ray Examination - The dome welds from both ends of the tank were x-rayed. In addition to the corrosion pits, three hot-short cracks were visible in the weld x-rays.

5. Mechanical Tests - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained.

	Ftu (ksi)	Fty (ksi)	Percent Elongation (in/in) (2 inch gage)
	192.2	178.4	6
	192.6	174.5	6
	191.2	172.1	6
	191.2	173.5	5
Drawing Requirements	180	150	6

6. Dimensional Checks - The Tank dimensions were within drawing specifications.

7. Chemical Analysis - The Tank was confirmed to have been made from 17-7PH.

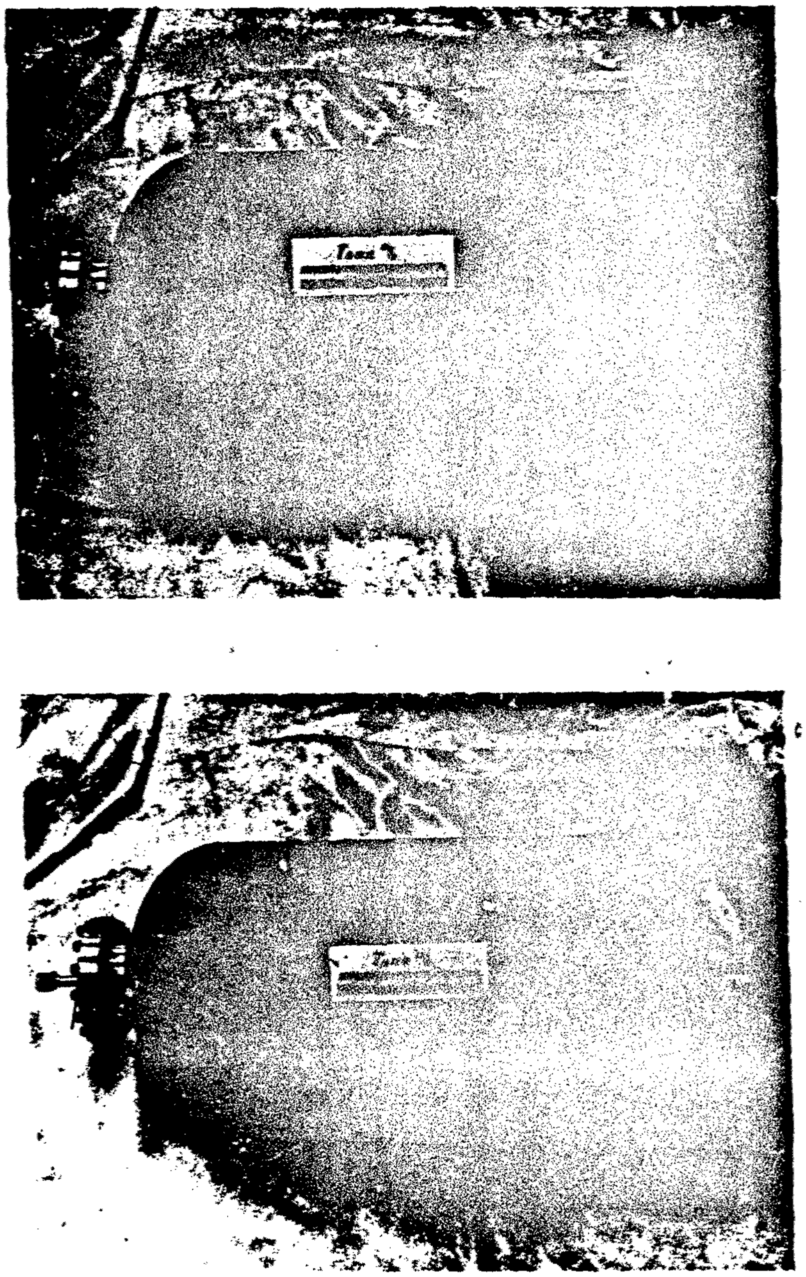


Figure 1. Side views of Tank No. 6.

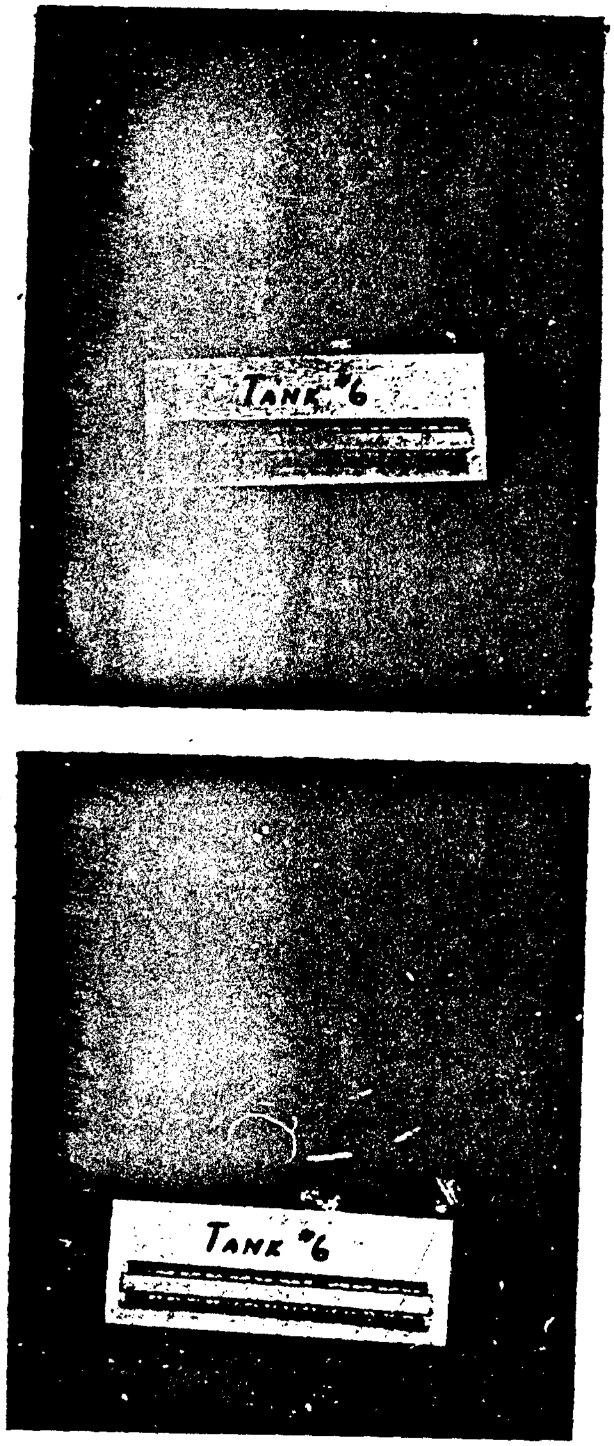


Figure 2. End views of Tank No. 6.

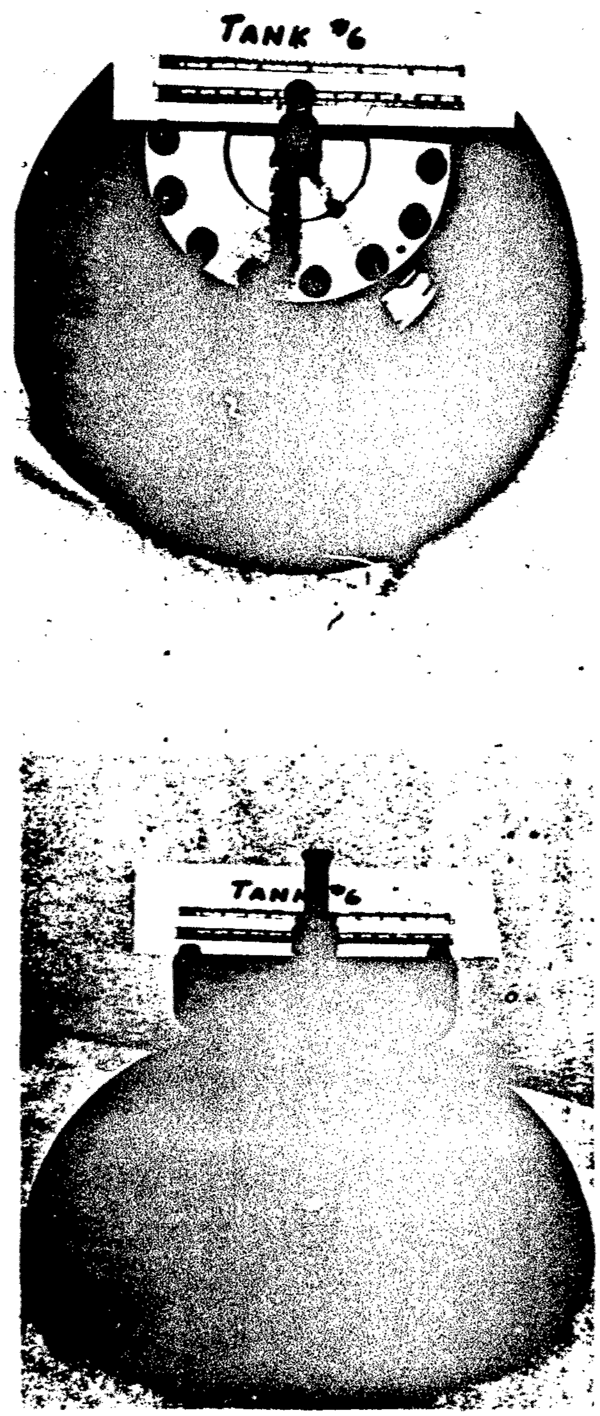


Figure 3. Flanged End of Tank No. 6.

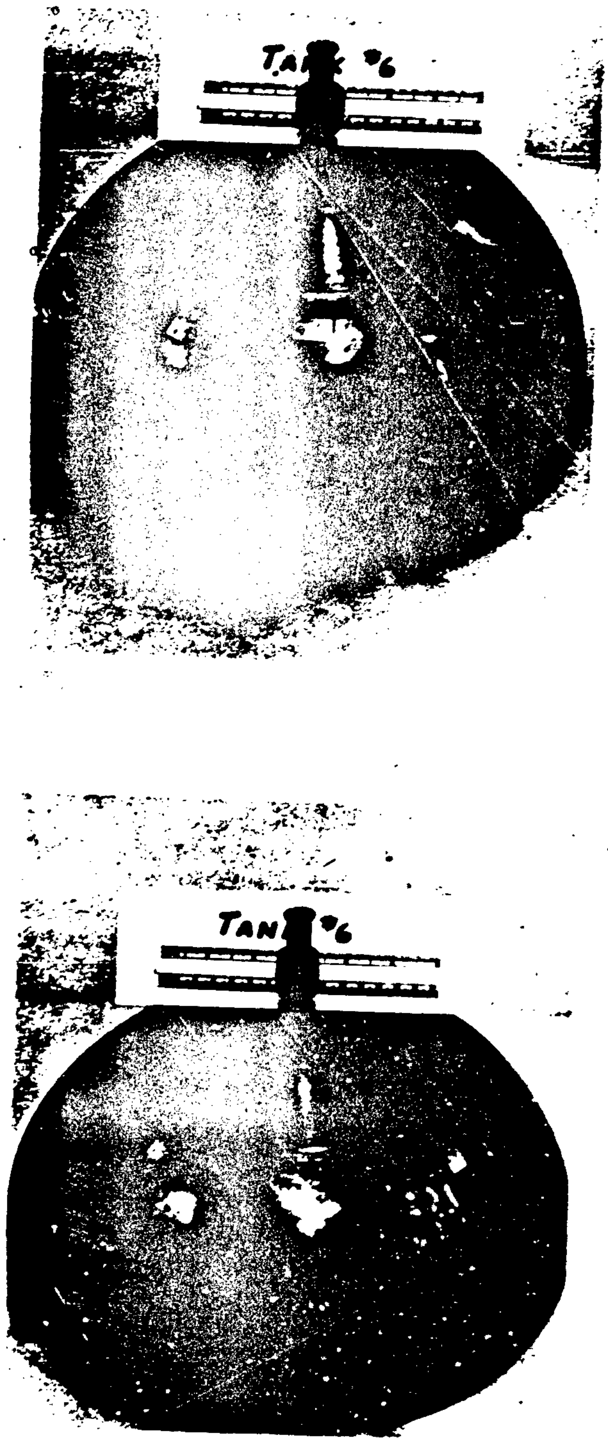


Figure 4. "Eeanie" End of Tank No. 6.

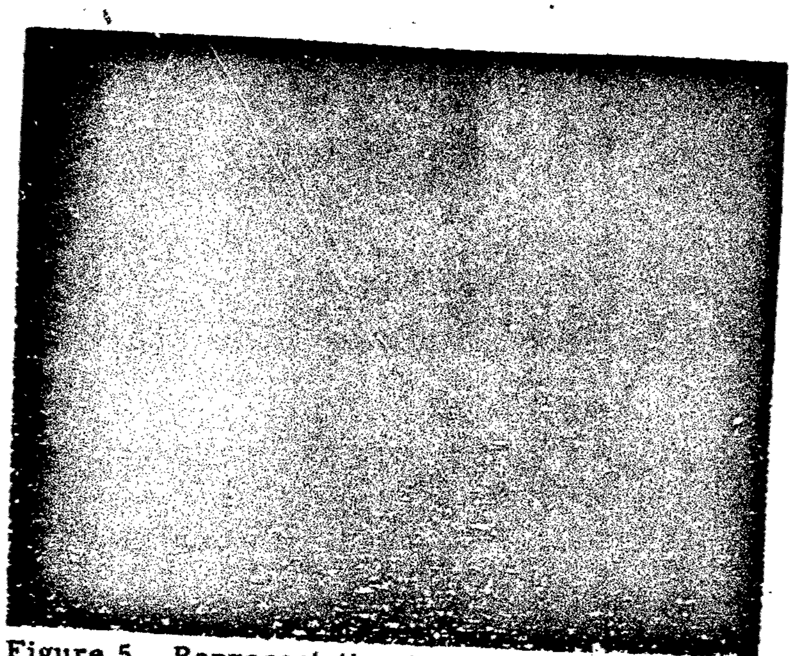


Figure 5. Representative Photomicrograph of Corrosion Pits in Tank No. 6. 100X

Figure 6. Photomicrograph of Hot-Short Crack in Dome Weld Area of Tank No. 6. 75X

Martin Marietta Corporation 16 May 1969

Materials Research and Engineering

Failure Analysis of Small Tank AFRPL S/N 7, 2014-T6 Aluminum Alloy

Report No. 69/20R

Author:____________________
Lawrence W. Loechel
Senior Engineer - Metals
Materials Research and Engineering

Approved:____________________
A. W. O'Brien, Jr.
Chief
Materials Research and Engineering

Author:____________________
Howard J. Brown
Head - Metals Unit
Materials Research and Engineering

Reference: (1) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, "Failure Analysis of Small Tank AFRPL S/N 2, Ti-6Al-4V Titanium Alloy," 31 March 1969, Materials Research and Engineering Report No. 69/14R.

(2) Aluminum Standards and Data 1968-69, Aluminum Association.

(3) DMIC Review of Recent Developments, "Corrosion and Compatibility," W. E. Berry, February 28, 1968.

(4) "Stress-Corrosion Cracking of Aluminum Alloys," DMIC Memo No. 231, August 1967.

INTRODUCTION

Tank S/N 7 is a 2014 aluminum alloy tank that had been exposed to N_2O_4 for 5 to 9 days when the tank failed by leaking in the end-boss weld area.

OBJECTIVE

The objective of this analysis was to determine the metallurgical cause of failure of tank number 7.

CONCLUSIONS

1. The origin of failure of small tank AFRPL S/N 7 was pitting and stress corrosion cracking in the fusion zone (weld bead edge) of the End Boss Weld.

2. The pitting and stress corrosion cracking occurred from external attack by nitric acid which formed on the tank as a result of humid atmosphere and N_2O_4 leaking from some other vessel in the test storage system.

RECOMMENDATIONS

1. In this case, the one recommendation is that no propellant tanks should be exposed to oxidizer fumes from leaking vessels while in a humid environment. HNO_3 formed (as occurred in this instance) can cause pitting and stress corrosion of propellant tankage.

2. Provisions should be made in design such that the exposure of short transverse grain direction to corrosive environments is avoided. Plate stock would have been better in this case for a welded-in outlet fitting since on longitudinal and long transverse grains would be exposed.

3. The material should always be in the fully aged -T6 condition for best corrosion resistance.

RESULTS AND DISCUSSION

1. Macroexamination - The tank had been lightly etched over its whole external surface, Figures 1 and 2. Numerous stress-corrosion cracks were found in the HAZ of the boss weld on one end of the tank, and severe corrosion pits were found in the weld, Figure 3.

2. Leak Test - The tank was baked at 250°F for one hour. It was then pressurized with 100% helium for 20 hours. The tank was then leak checked by the hand probe method, using a CEC helium mass spectrometer.

   Three leaks were found in the end boss area. One leak through a stress-corrosion crack had a magnitude of 2.2×10^{-5} acc/sec. The other two leaks were through corrosion pits and had a magnitude of 5.7×10^{-7} acc/sec and the other had a magnitude of 4.9×10^{-8} acc/sec.

3. Metallographic Examination - Microsections were made through the leak areas, Figures 4 and 5. It was apparent that leakage was due to external corrosion and stress-corrosion cracking along short transverse grain direction of the bar stock from which the outlet (boss) was machined, see Figure 6.

4. Corrosion Product Identification - The major element of the corrosion products taken from the tank were Al, Si, Cu, Mg, and Mn. These are the expected decomposition products of 2014. Tests for nitrates and oxides were positive.

   The corrosion product, as analyzed by wet chemical methods, was a mixture of nitrate salts and hydrated oxides of the alloying constituents which indicated the corrosive attack occurred by contact with nitric acid.

5. Chemical Analysis - The tank material was identified as 2014 aluminum alloy as determined by spectrographic analysis.

6. Mechanical Tests - Tensile specimens were taken longitudinally from the barrel section of the tank. The following results were obtained.

Ftu(ksi)	Fty(ksi)	%Elongation (in/in)
61,800	57,300	10.0
63,300	54,400	10.0

Requirements Ref. (2).

The hardness was determined to be R_B 80 which is slightly low in the T6 range. The normal range for T6 is R_B 80-86 for 2014 aluminum alloy. The hardness of the Boss was R_H 100 which indicated -T4 conditions.

7. X-Ray Inspection - All welds were radiographically examined. No defects other than the expected corrosion pits, stress-corrosion cracks and slight porosity were found.

8. Dimensional Checks - The tank was measured and determined to be 0.060 inches in barrel wall thickness and 185 inches in boss wall thickness. With drawings not available for reference, it was not known if these dimensions were acceptable.

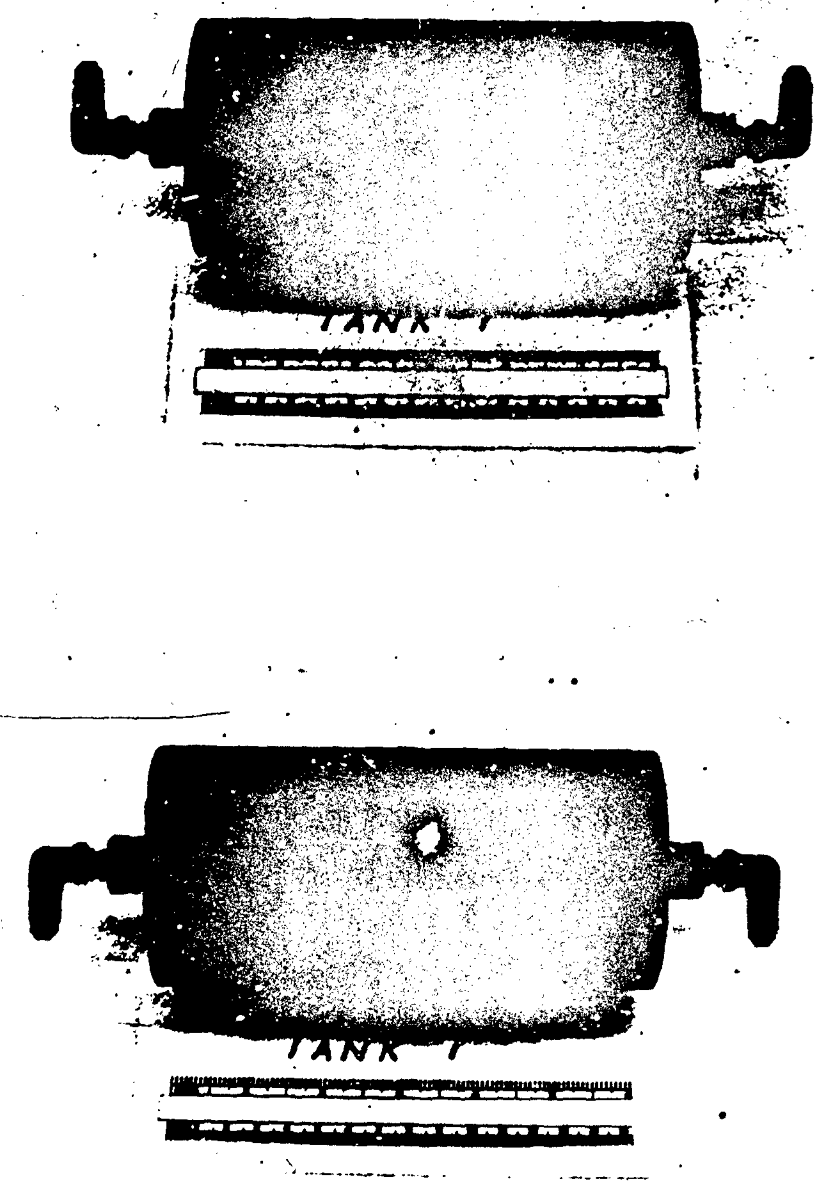


Figure 1. Sideviews of Tank Number 7. 1/2X
Note the Generally Etched Appearance
of the Tank.

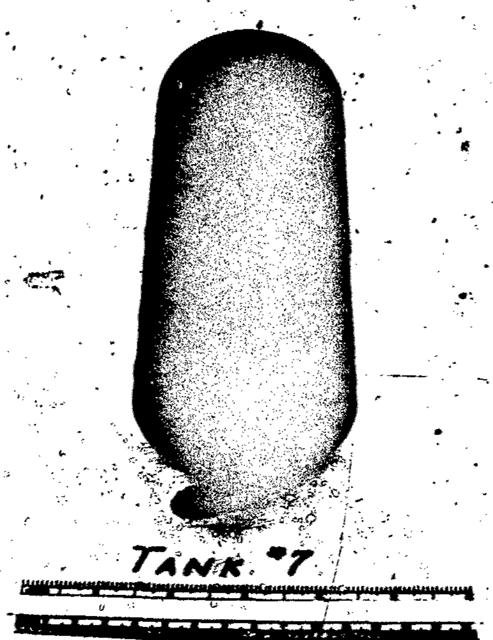


Figure 2. Endviews of Tank Number 7. 1/2X

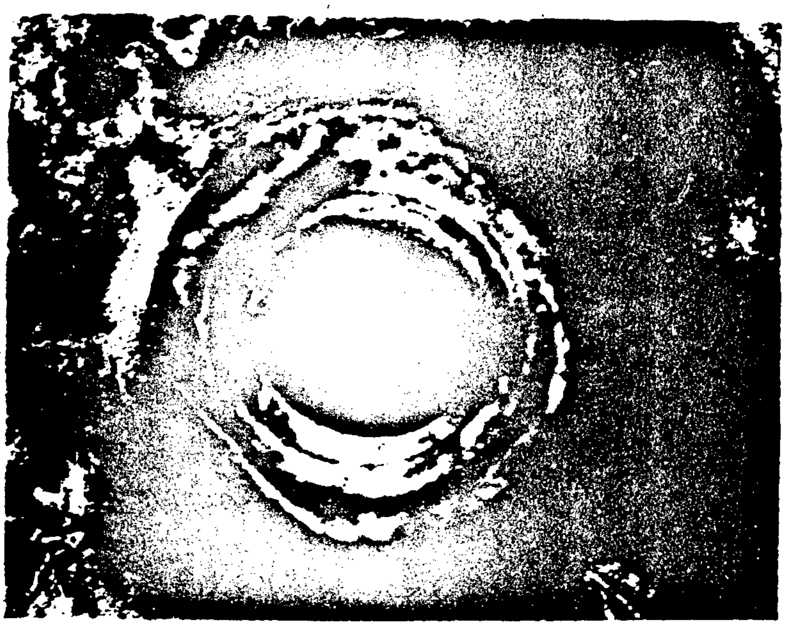


Figure 3. **Stress-Corrosion Cracks and Pitting in End Bond Weld of Tank Number 7. 2 1/2X**

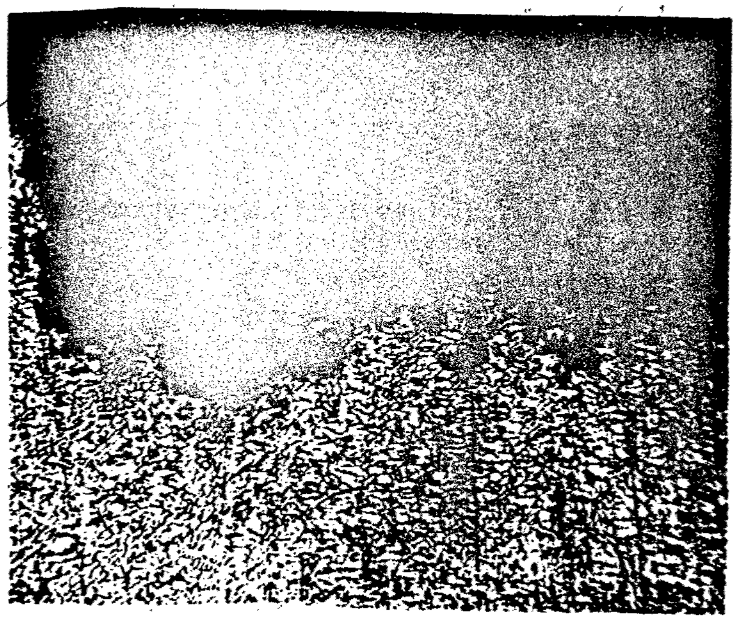


Figure 4. Photomicrograph of Corrosion Pit in Weld. (150X)

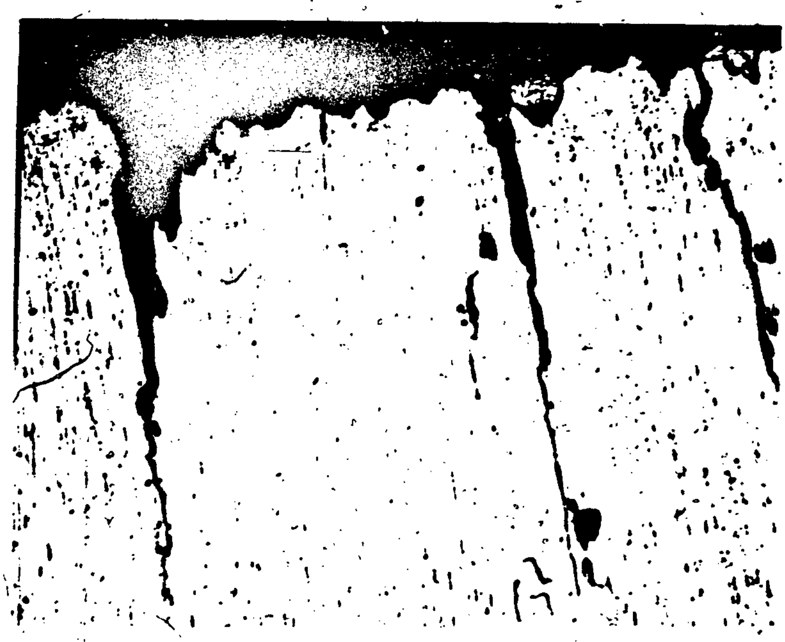


Figure 5. Photomicrograph of Stress-Corrosion Cracks in HAX (100X)

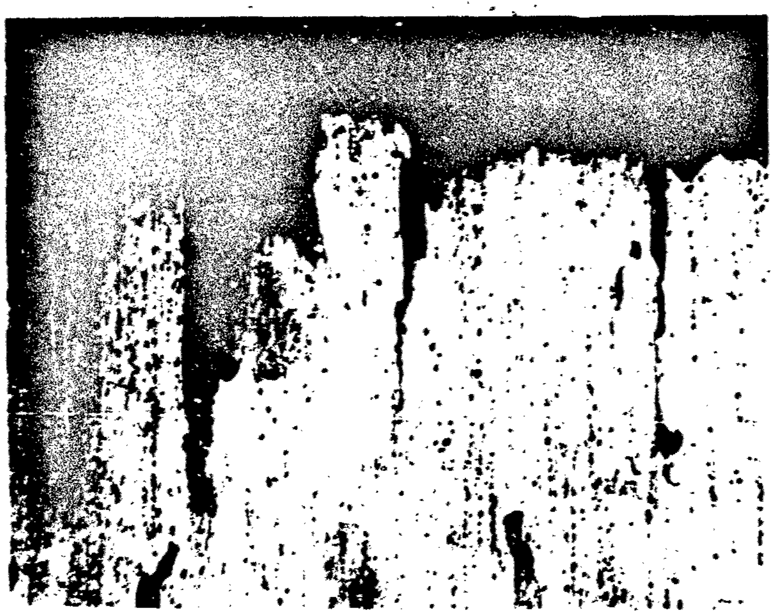


Figure 6. Photomicrograph of Area in Figure 5 in Etched Condition showing End Grain Exposure (75X)

Failure Analysis of Small Tank S/N 8, AM350 Precipitation Hardening Stainless Steel

Report No. 69/5R

Author:______________________
Lawrence W. Loechel
Senior Engineer-Metals
Materials and Process Technology

Approved:______________________
A. W. O'Brien, Jr.
Chief
Materials and Process Technology

Author:______________________
Howard J. Brown
Head - Metals Unit
Materials and Process Technology

INTRODUCTION

The second small tank to be failure analyzed as required by AF Contract No. F42600-68-A-2327 was Tank AFRPL S/N 8. This tank contained ClF5 for 295 days at Edwards AFB, California. Tank SN 8 was an AM350 Precipitation Hardening Stainless Steel Alloy and was badly pitted and rusted.

REFERENCES

(1) Martin Marietta Corporation-Materials and Process Technology report M.E. No. 68/77R "Failure Analysis of Small Tank S/N 4, AM350 Precipitation Hardening Stainless Steel", 3 January 1969.

OBJECTIVE

The objective of this failure analysis was to determine the metallurgical cause for the failure of S/N 8 AM350 Precipitation Hardening Stainless Steel Tank.

CONCLUSIONS

1. Small tank serial number 8 failed as a result of a corrosion through by nitric acid from the exterior surface of the tank.

2. The nitric acid apparently formed on the failed tank by condensation of water (85% relative humidity) and N_2O_4 from a nearby leaking N_2O_4 vessel.

RECOMMENDATIONS

Test conditions should be regulated so that when other test specimens fail, the by-products of that failure should not be allowed to interfere with another test in progress.

RESULTS AND DISCUSSION

The following procedures were followed during failure analysis of tank no. 8.

1. Macroexamination - The tank was examined with the unaided eye and with magnifications to 30X with a steromicroscope.

   The tank was severely corroded, particularly the bottom half, as shown in Figures 1 and 2. Numerous corrosion pits were found on the bottom portion of the tank, as shown in Figures 3 and 4.

2. Leak Test - The tank was baked at 250°F for 1 hour after cooling to room temperature, it was pressurized with 100% helium. The pressure dropped to zero in 16 hours. Since the leakage was so profuse it was neither possible, nor necessary, to chamber leak test the tank. Instead the tank was checked by the hand probe method using a Consolidated Electronics Corporation helium mass spectrometer.

   Two leaks were found as shown in Figure 3. An off-scale leak was found in the corrosion pit on the weld heat affected zone as shown in Figure 4. Another leak with a magnitude of 2.16×10^{-7} atm cc/sec was found in the pit shown in Figure 5.

3. Metallographic Examination - Microsections were cut, mounted, incrementally polished, and examined on a metallograph. Figures 6 and 7 are representative photomicrographs showing cross sections of both leaks.

The leaks were caused by external corrosion that extended through the wall of the tank.

4. Corrosion Product Analysis - Corrosion products taken from the external surface of the tank were identified as -FeOOH by x-ray diffraction. This would indicate the corrosion products were results of corrosion by a strong oxidizing acid such as HNO_3. X-ray fluoresence showed the corrosion products were strong in Fe and Cr which would be in the normal corrosion products if the AM350 precipitation hardening stainless steel were attacked by acid. Also shown by X-ray fluoresence in weaker concentration were the elements Ti, K, Si, and Ca.

   Note: -FeOOH (ferrous hydroxide) is the initial rusting stage of steels exposed to moist and/or oxidizing environments. Further oxidation yields $Fe(OH)_3$ (ferric hydroxide) which ultimately oxidizes to Fe_2O_3 (common rust).

5. Chemical Analysis

Parent Metal		Weld Metal	
Cr	16.41	N	0.0898
Ni	4.41		0.0944
Mn	0.96		
Si	0.49		
Mo	2.40		
N	0.0947		
	0.0964		

   This analysis indicated the material met the requirements of the drawing.

6. X-Ray Inspection - The leak areas were x-rayed prior to sectioning. No defects were visible in any of the welds.

7. Mechanical Tests - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained.

	Ftu ksi	Fty ksi	Percent Elongation Percent in 2 inch
	168	158	8
	163	157	6
	161	154	6.5
	164	159	2.5
Drawing Callout	185	150	

The hardness was determined to be R_a 70.

Although the mechanical properties did not enter into the reasons for failure of the tank, in this instance, the ultimate tensile strength was below the value required by drawing. The AM350 precipitation hardening stainless steel tank serial no. 4, reference (1) was similar.

8. Dimensional Checks - The barrel thickness was 0.030 inch. The dome thickness ranged from 0.026 to 0.028 inch. The thickness of the boss end plugs tapered from 0.059 to 0.099 inch. These dimensions were within the requirements of the drawing, GD/C-TSP-001.

9. Internal Tank Examination - The inside of the tank was discolored and appeared to have been slightly corroded, Figure 8. This amount of corrosion could have easily occurred after the tank was depressurized and stored under ambient conditions and apparently was not a result of corrosion during storage conditions.

10. The cause of leakage of this tank apparently was that under 85% relative humidity and close proximity of this tank to a leaking N_2O_4 vessel, HNO_3 was condensed on the top of the tank. The HNO_3 then drained down the sides of the tank and concentrated on the bottom. Corrosion occurred generally over the outer surfaces of the tank and heavy pitting occurred on the bottom of the tank with two pits penetrating the wall thickness of the tank. Actually, HNO_3 is the suspected oxidizing acid that caused corrosion in this case since there was no fluorides or chlorides present in the corrosion residue.

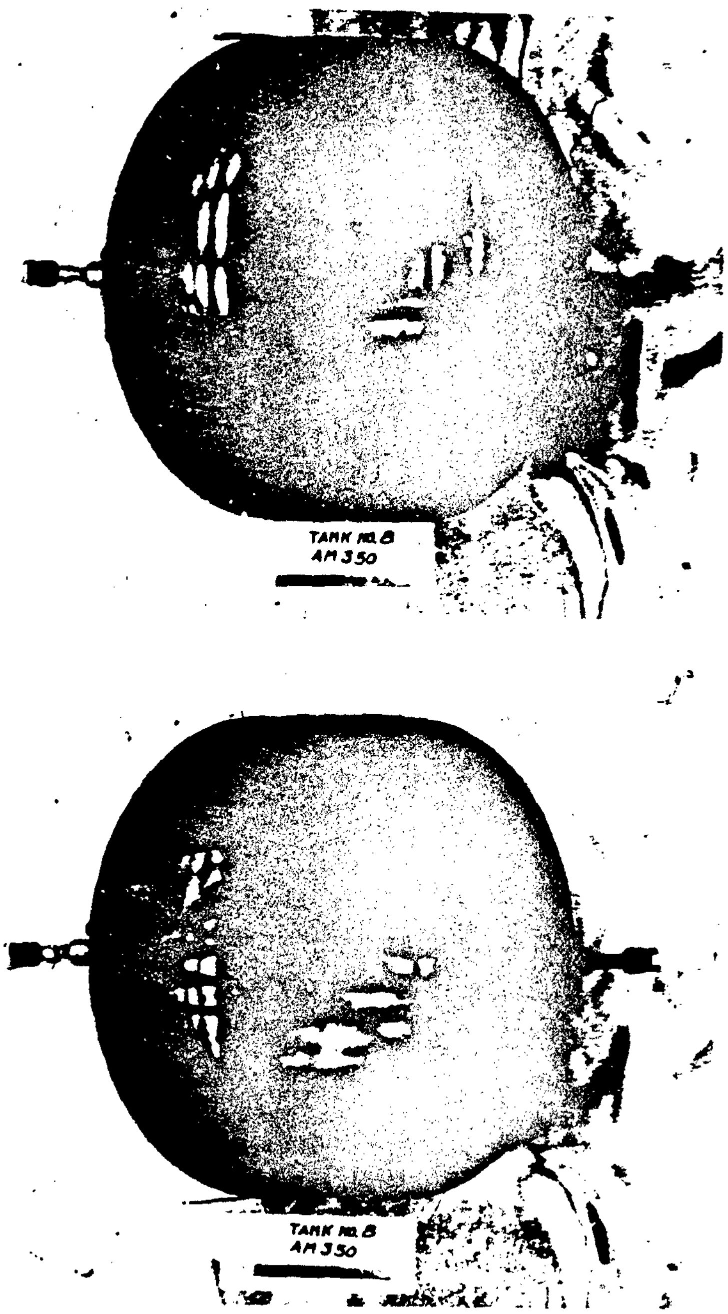


Figure 1. Sideview of Tank Serial No. 8. Representative Photomacrographs Showing General Corrosion. Top of Tank Is To The Left of The Photograph. Approximately 1/4X magnification.

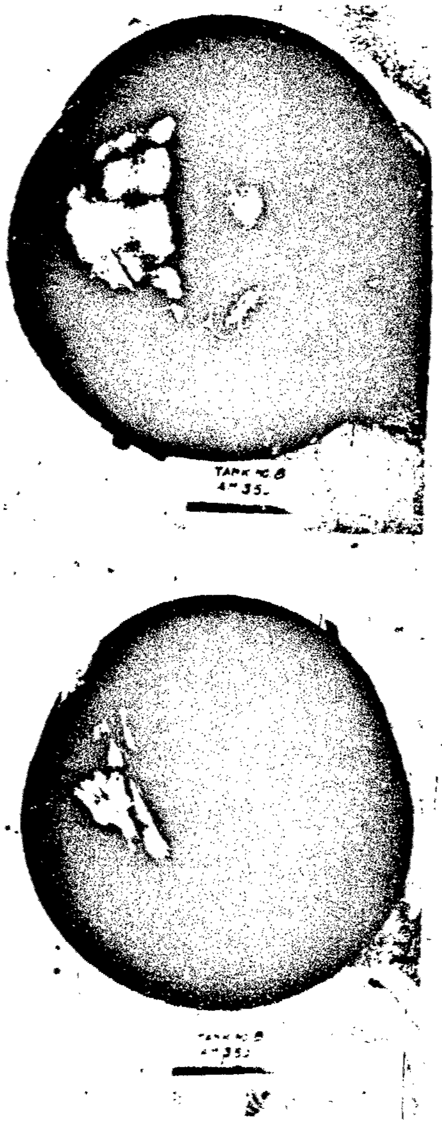


Figure 2. Top and Bottom View of Tank Serial No. 8. Representative Photomacrographs Showing General Corrosion. Approximately 1/4X Magnification.

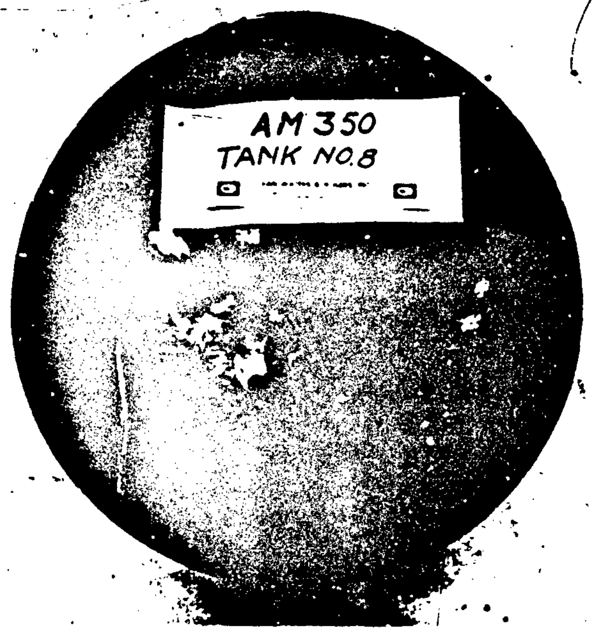


Figure 3. A Photomacrograph Showing The Two Leak Areas in Bottom of Tank Serial No. 8. Approximately 1/4X Magnification.

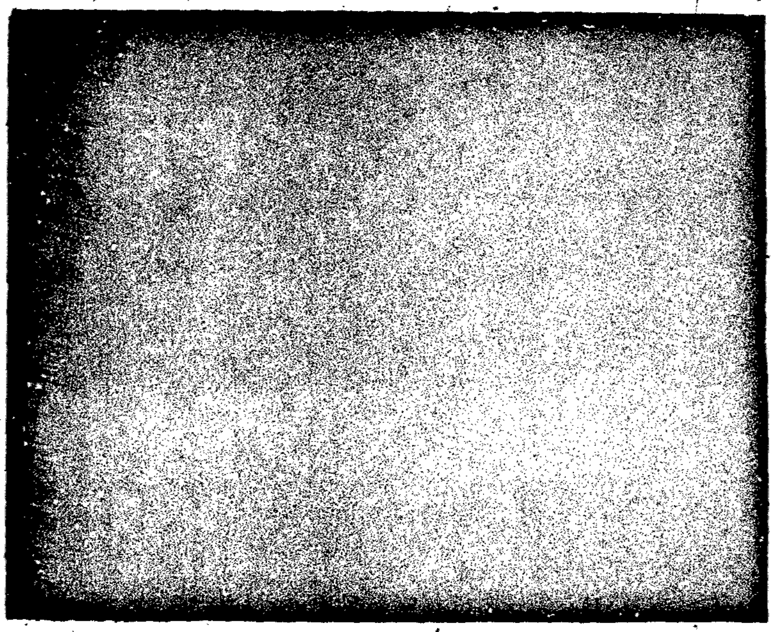


Figure 4. A Photomacrograph Showing the Pitting Corrosion In the Area of the "Off-Scale" Leak Area. 10X Magnification

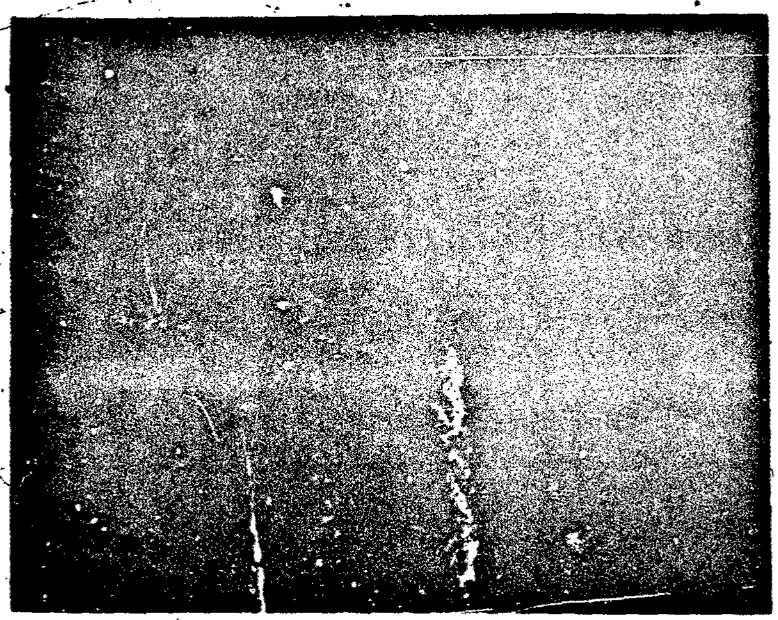


Figure 5. A Photomacrograph Showing the Pitting Corrosion In The Area of The 2.16×10^{-7} atm cc/sec Leak. 10X Magnification

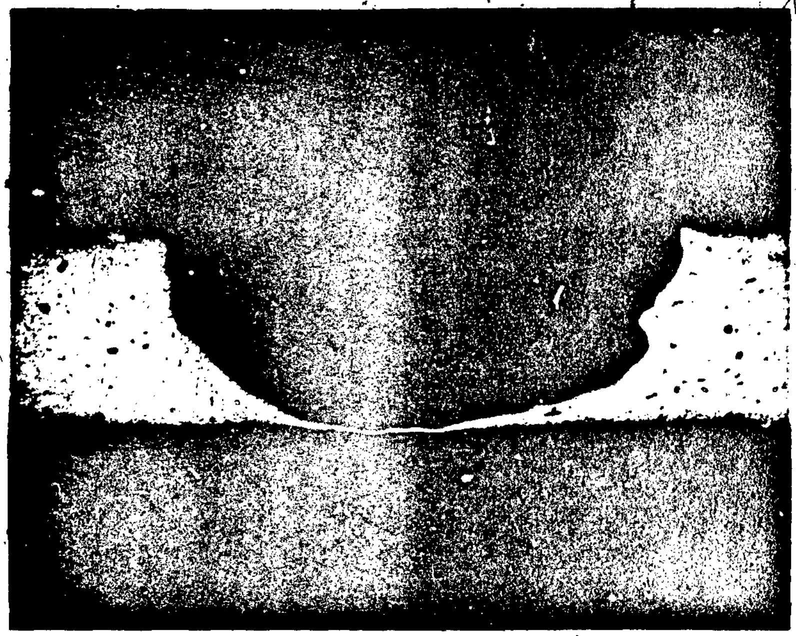


Figure 6. Photomicrograph Showing The Corrosion Pit In The "OFF-Scale" Leak. 50X Magnification

Figure 7. Photomicrograph Showing The Corrosion Pit In The 2.16×10^{-7} atm cc/sec Leak. 50X Magnification

Figure 8. Photomacrograph Showing The Appearance of The Inside and Outside of Leak Area of Tank Serial No. 8. 1/3X Magnification.

Failure Analysis of Small Tank S/N 9, AM350 Precipitation Hardening Stainless Steel

Report No. 69/13R

Author:

Lawrence W. Loechel
Senior Engineer-Metals
Materials and Process Technology

Approved:

A. W. O'Brien, Jr.
Chief
Materials and Process Technology

Author:

Howard J. Brown
Head - Metals Unit
Materials and Process Technology

INTRODUCTION

The third small tank to be failure analyzed as required by AF Contract No. F42600-68-A-2327 was Tank AFRPL S/N 9. This tank contained ClF_5 for 294 days at Edwards AFB, California. Tank S/N 8 was an AM350 Precipitation Hardening Stainless Steel Alloy and was badly pitted and rusted.

REFERENCES

(1) Martin Marietta Corporation-Materials and Process Technology report M.E. No. 68/77R "failure Analysis of Small Tank S/N 4, AM350 Precipitation Hardening Stainless Steel", 3 January 1969.

(2) Martin Marietta Corporation-Materials and Process Technology report M.E. No. 69/5R "Failure Analysis of Small Tank S/N 8, AM350 Precipitation Hardening Stainless Steel, 29 January 1969.

OBJECTIVE

The objective of this failure analysis was to determine the metallurgical cause for the failure of S/N 9 AM350 Precipitation Hardening Stainless Steel Tank.

CONCLUSIONS

1. Small tank serial number 9 failed as a result of corrosion through by nitric acid from the exterior surface of the tank.

2. The nitric acid apparently formed on the failed tank by condensation of water (85% relative humidity) and N_2O_4 from a nearby leaking N_2O_4 vessel.

RESULTS AND DISCUSSION

The following procedures were followed during failure analysis of tank no. 9.

1. Macroexamination - The tank was examined with the unaided eye and with magnifications to 30X with a stereomicroscope.

   The tank was the most severely corroded of the 3 AM350 tanks that have been examined during the program, Figures 1, 2, and 3. The bottom half was particularly bad. Several corrosion pits extending completely through the tank wall were found.

2. Leak Test - The tank was baked at 250 F for 1 hour after cooling to room temperature, it was pressurized with 100% helium. The pressure dropped to zero within 8 hours. Since the leakage was so profuse it was neither possible, nor necessary, to chamber leak test the tank. Instead the tank was checked by the hand probe method using a Consolidated Electronics Corporation helium mass spectrometer and by bubble testing with soapy water.

   A total of 16 leaks were found on the bottom and 1 leak was found on the top of the tank.

3. Metallographic Examination - Before sectioning and mounting the leak areas, each one was examined under the stereomicroscope. All of the leaks appeared to be the result of external corrosion. Representative photomicrographs of cross sections of the leaks are shown in Figures 4, 5, 6, 7, and 8.

4. Corrosion Product Analysis - Corrosion products taken from the external surface of the tank were identified as -FeOOH by x-ray diffraction. This would indicate the corrosion products were results of corrosion by a strong oxidizing acid such as HNO_3. X-ray fluoresence showed the corrosion products were strong in Fe and Cr which would be in the normal corrosion products if the AM350 precipitation hardening stainless steel were attacked by acid. Also shown by x-ray fluoresence in weaker concentration were the elements Ti, K, Si, Cl, and Ca.

The diffraction patterns and fluoresence patterns obtained were identical to those obtained from tank No. 8.

Note: -Fe00H (ferrous hydroxide) is the initial rusting stage of steels exposed to moist and/or oxidizing environments. Further oxidation yields $Fe(OH)_3$ (ferric hydroxide) which ultimately oxidizes to Fe_2O_3 (common rust).

5. Chemical Analysis

Parent Metal		Weld Metal	
Cr	16.41	N	0.0898
Ni	4.41		0.0944
Mn	0.96		
Si	0.49		
Mo	2.40		
N	0.0947		
	0.0964		

This analysis indicated the material met the requirements of the the drawing.

6. X-Ray Inspection - The leak areas were x-rayed prior to sectioning. No defects were visible in any of the welds.

7. Mechanical Tests - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained.

	Ftu ksi	Fty ksi	Percent Elongation Percent in 2 inch
	173	166	6
	162	154	8
	169	160	7
	168	161	11
Drawing Callout	185	150	

The hardness was determined to be R_a 70.

Although the mechanical properties did not enter into the reasons for failure of the tank, in this instance, the ultimate tensile strength was below the value required by drawing. The AM350 precipitation hardening stainless steel tanks serial no. 4, and no. 8 were similar.

8. Dimensional Checks - The barrel thickness was 0.029 inch. The dome thickness was 0.025 inch. The thickness of the boss end plugs tapered from 0.068 to 0.100 inch. These dimensions were within the requirements of the drawing, GD/C-TSP-001.

9. Internal Tank Examination - The inside of the tank was discolored and appeared to have been slightly corroded, Figure 9. This amount of corrosion could have easily occurred after the tank was depressurized and stored under ambient conditions and apparently was not a result of corrosion during storage conditions.

10. The 85% relative humidity and close proximity of this tank to a leaking N_2O_4 vessel, resulted in condensation of HNO_3 on the top of the tank, and caused tank S/N 9 to leak. The HNO_3 then drained down the sides of the tank and concentrated on the bottom. Corrosion occurred generally over the outer surfaces of the tank and heavy pitting occurred on the bottom of the tank with two pits penetrating the wall thickness of the tank. Actually, HNO_3 is the suspected oxidizing acid that caused corrosion in this case since there were no fluorides or significant amounts of chlorides present in the corrosion residue.

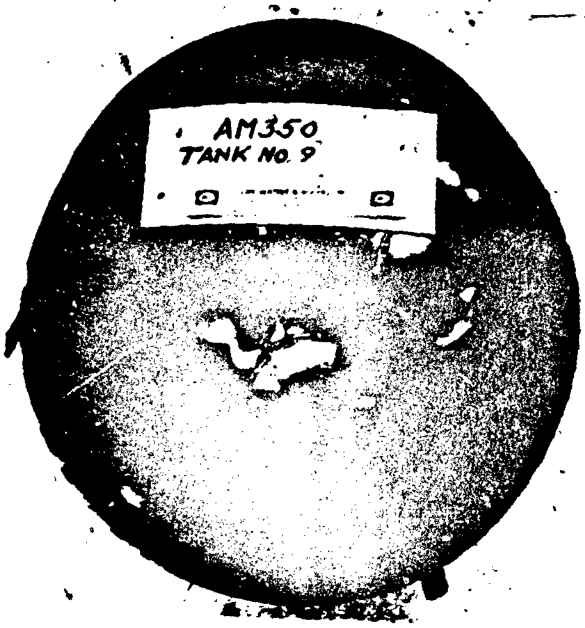


Figure 1. Top View of Tank No. 9.

Figure 2. Bottom View of Tank No. 9.
Circled areas are leaks.

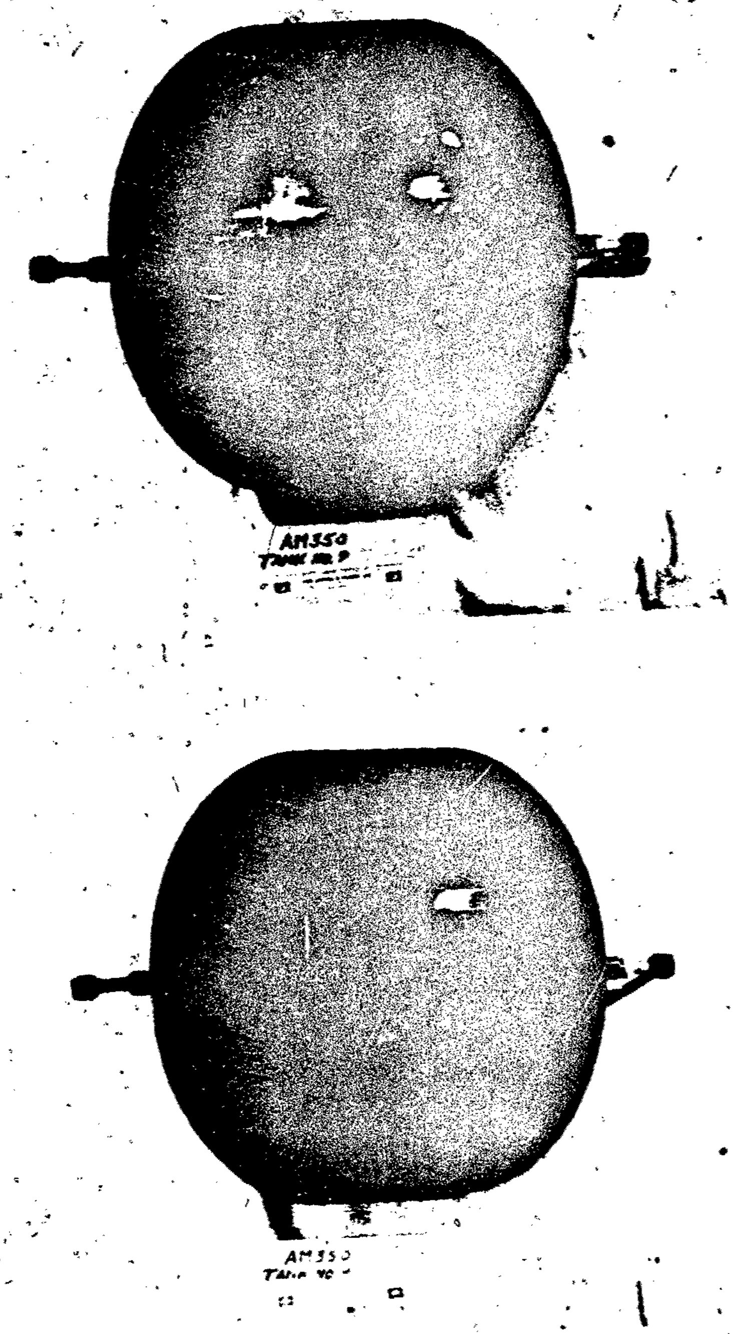


Figure 3. Side Views of Tank No. 9.

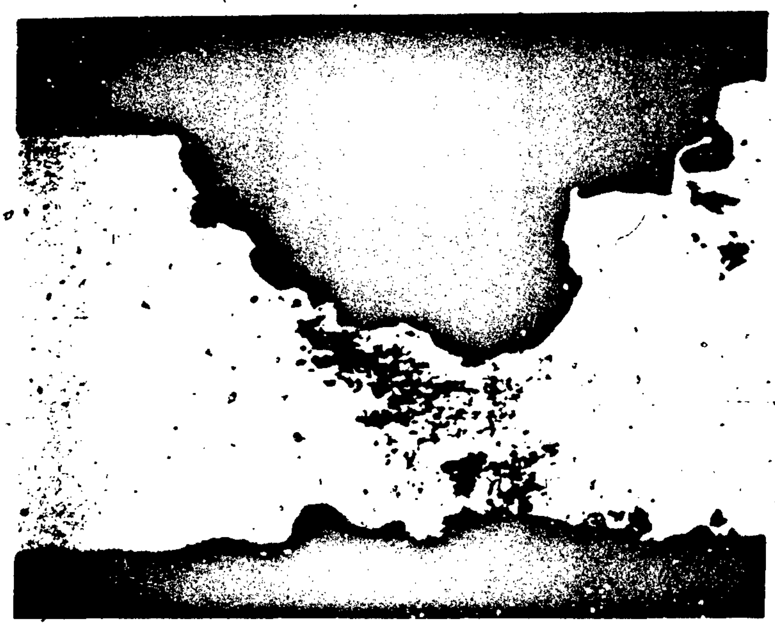


Figure 4. Photomicrograph Showing The microstructure in a leak area of the AM350 precipitation-hardening stainless steel tank No. 9. 100X

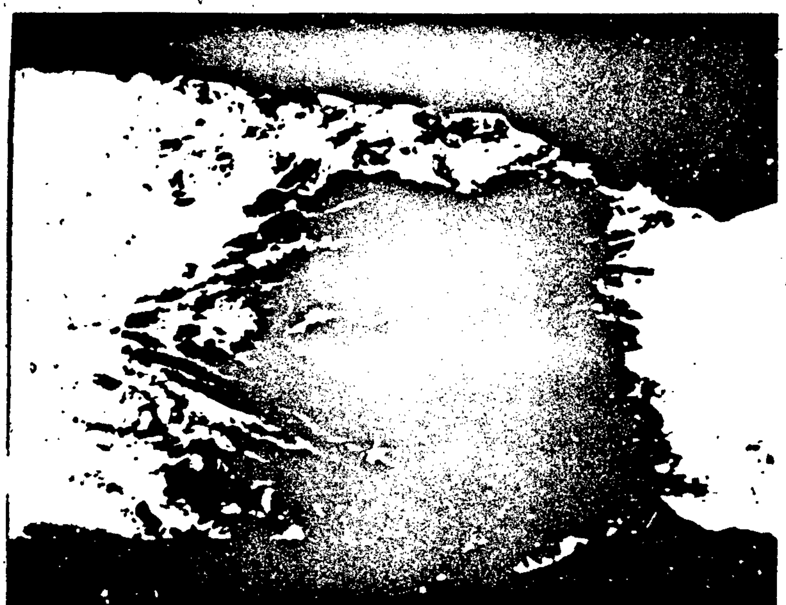


Figure 5. Photomicrograph Similar to That shown in Figure 4. 100X

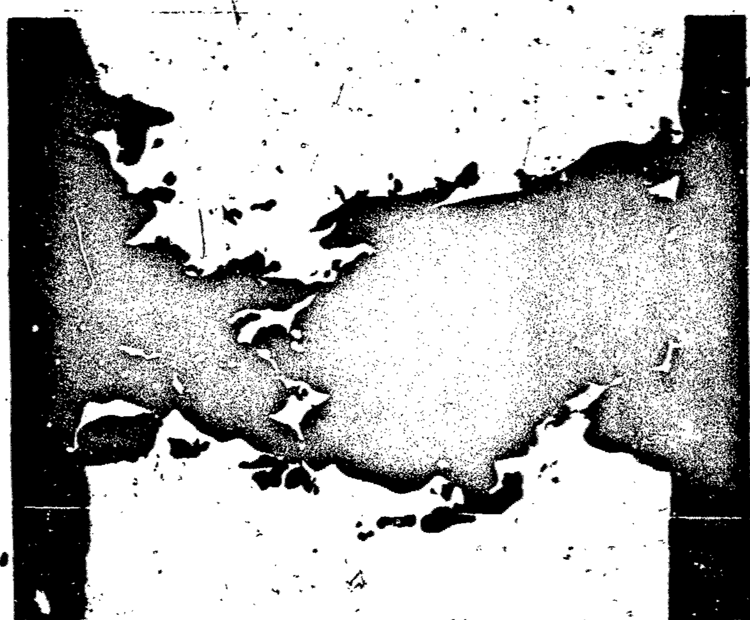


Figure 6. Photomicrograph Similar to Figures 4 and 5. 100X

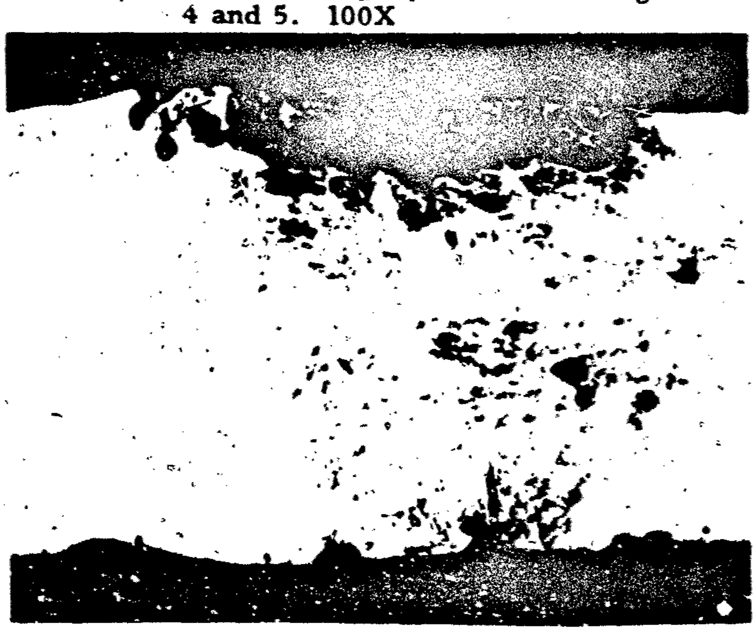


Figure 7. Photomicrograph Similar to Figures 4, 5 and 6. 100X

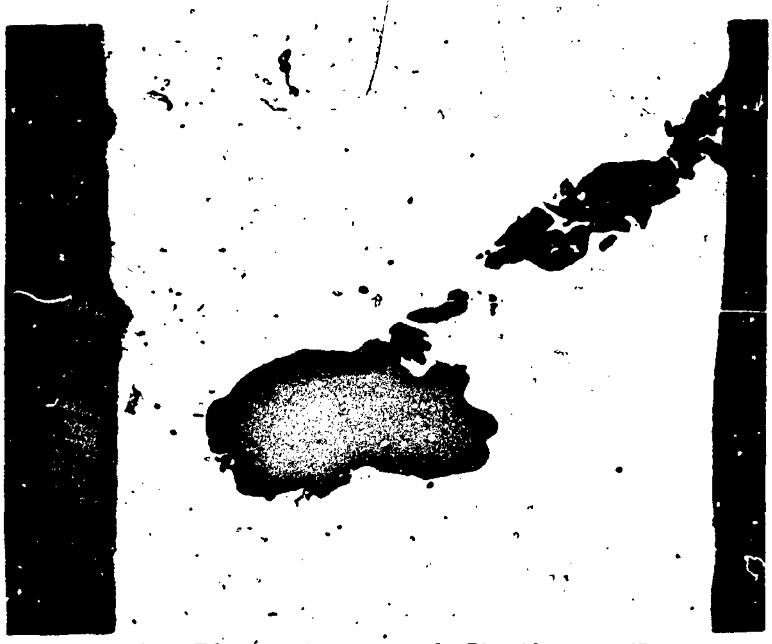


Figure 8. Photomicrograph Similar to Figures 4, 5, 6 and 7. 100X

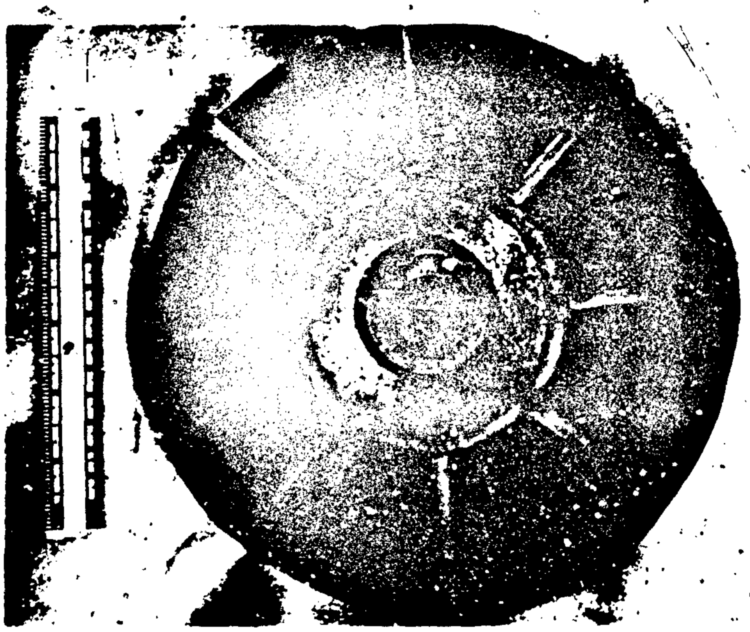


Figure 9. Photomacrograph Showing an Inside View of the Dome Area of Tank Serial No. 9. Approx. 1/3X

Failure Analysis of Small Tank AFRPL S/N 10, 6061 Aluminum Alloy

Report No. 69/34R

Author:______________________
Lawrence W. Loechel
Senior Engineer-Metals
Materials Research and Engineering

Approved:______________________
A. W. O'Brien, Jr.
Chief
Materials Research and Engineering

Author:______________________
Howard J. Brown
Unit Head - Metals
Materials Research and Engineering

Reference: (1) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 8, AM350 Precipitation Hardening Alloy", 2/3/69.

(2) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 9, AM350 Precipitation Hardening Alloy", 3/3/69.

(3) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 7, 2014 Aluminum Alloy", 5/19/69.

(4) Unpublished data relative to the corrosion rates of various aluminum alloys, parent and welds in various concentrations of HNO_3.

INTRODUCTION

Tank S/N 10 was a 6061 aluminum alloy tank that had been exposed to ClF_5 441 days when the tank failed by leaking through a weld area in the pressurant fittings.

OBJECTIVE

The objective of this analysis was to determine the metallurgical cause of failure of tank AFRPL S/N 10.

CONCLUSIONS

1. The failure was caused by external pitting and intergranular corrosion occurring in welds of the fitting-to-end segment welds in each end of the tank.

2. The external corrosion was caused by leakage of ClF_5 from some adjacent leaking vessel resulting in acid formation on the tank S/N 10.

RECOMMENDATIONS

As has been recommended previously in references (1), (2), and (3), vessels containing hygroscopic propellants should not be stored adjacent to similar vessels in case leaks do occur since these materials are not sufficiently resistant to acid environments.

RESULTS AND DISCUSSION

1. Macroexamination - The tank was lightly etched over its entire surface, Figures 1 and 2. The tank was severely corroded in the area of the fitting welds, Figures 3 and 4. The weld cross-over areas in the main tank body were not attacked, but areas of weld stops and starts were corroded, Figure 5.

2. Leak Test - The tank was baked at 250° F for one hour. It was then pressurized with 100% helium and allowed to soak for 16 hours. The tank was then leak checked by the hand probe method, using a CEC helium mass spectrometer. Three leaks were found in the fitting weld on one end of the tank. The leaks had a magnitude of 2.6×10^{-7}, 7.2×10^{-6}, and 2.3×10^{-5} atm. cc/sec. Two leaks having a magnitude of 2.4×10^{-5} atm. cc/sec were found in the other tank fitting.

3. X-Ray Inspection - The tank welds were x-rayed. No defects other than those attributable to corrosive attack were found.

4. Metallographic Examination - The leak areas shown in Figure 2 were cross-sectioned for metallographic examination. As shown in Figures 7, 8, and 9, the leakage failures were caused by corrosive attack. The leaks appeared to have originated on the external surface of the tank and so were probably caused by ClF_5 that had leaked from another test system in the same area as tank #10.

5. Electron Microscopy - Replicas of a cracked area of a weld were made and examined. The replicated surfaces were typical of corrosive attack, Figure 6.

6. Chemical Analysis - The tank was identified as having been made from 6061 aluminum alloy.

7. Mechanical Properties - Tensile specimens were taken longitudinally from the barrel section of the tank. The following properties were obtained:

Specimen	Ftu (ksi)	Fty (ksi)	Percent Elongation 2" gage, in/in
1	39.7	33.7	14
2	34.5	30.5	14
Minimum requirements per aluminum association			
-T4	30.0	16.0	16
-T6	42.0	35.0	10

Since there were no drawings available for the 6061 aluminum alloy tank, it was not determined if the properties were as originally intended, but they are listed for reference.

8. Dimensions - The tank thicknesses were as follows:

   a. Dome end segments - 0.065"
   b. Barrel panels - 0.076"

The above dimensions were presented for information and reference since no drawings were available.

9. Corrosion Product Analysis - The corrosion product obtained from the external surfaces of the tank was identified as aluminum fluoride hydroxide hydrate. This is the corrosion product that would be likely to form as the result of ClF_5 attack.

As shown previously in tests at Martin Marietta Corporation, welds areas are attacked by acid environments as much as twenty to thirty times faster than parent metal depending on the amount of weld heat applied to the weldments in aluminum alloys. Starts and stops in welds are particularly susceptible. Therefore, if an oxidizer such as ClF_5 or N_2O_4 should leak near weld areas and acids form as a result of hydrolysis of these propellants, the weld zones will start showing severe attack within 48 hours. (Ref. 4)

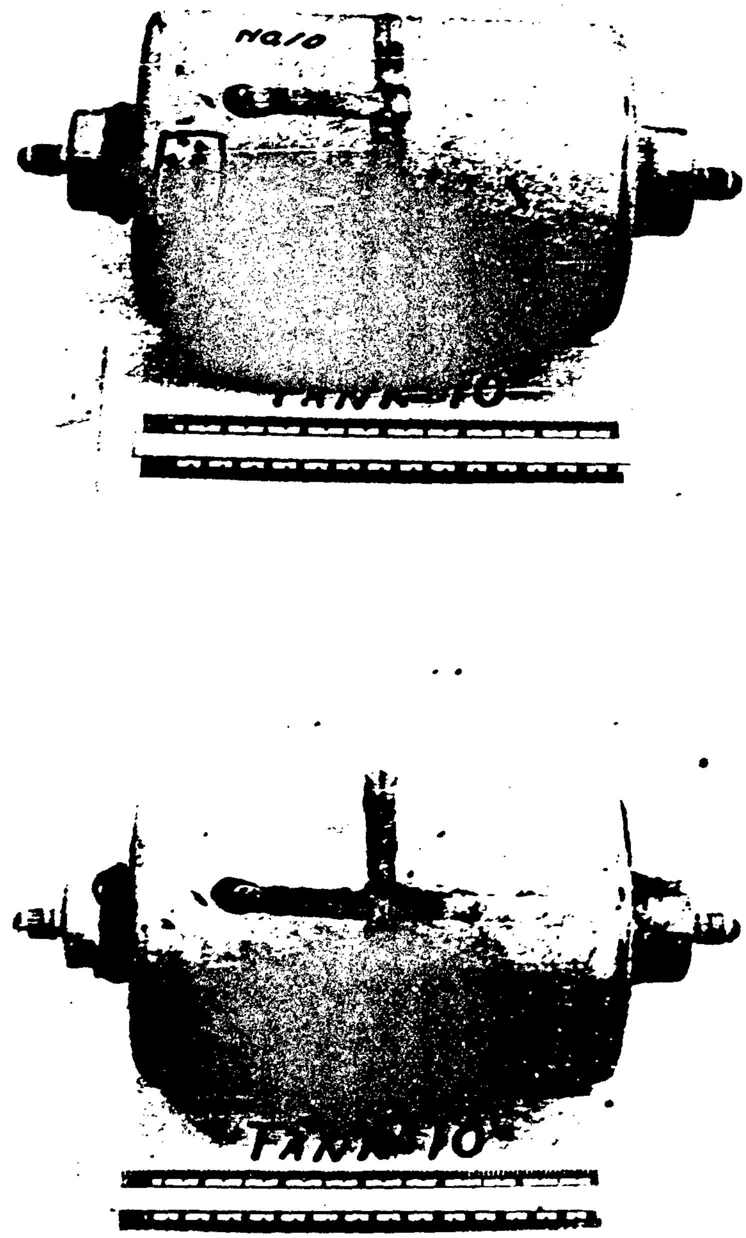


Figure 1. Sideviews of Tank No. 10. 1/2X

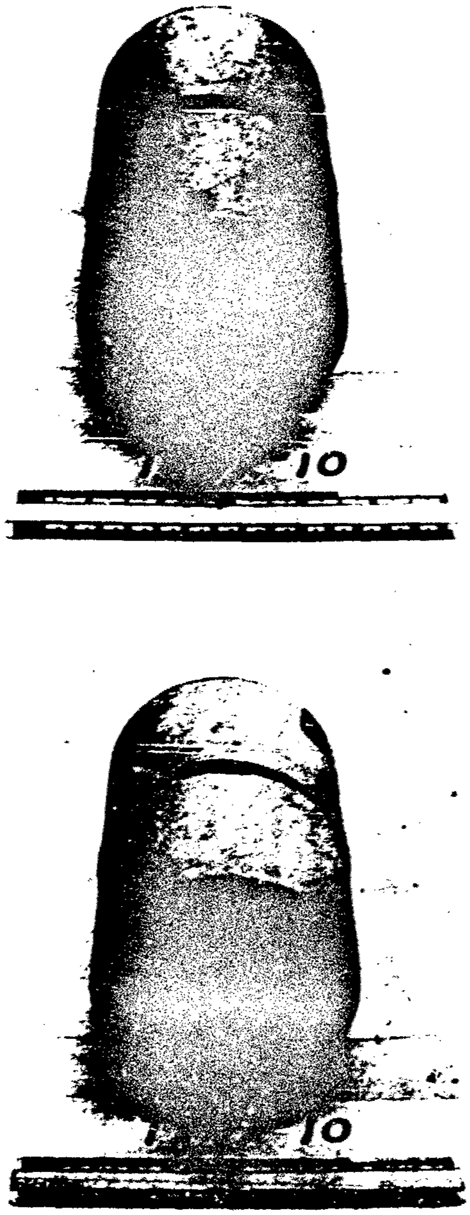


Figure 2. Endviews of Tank No. 10. 1/2X

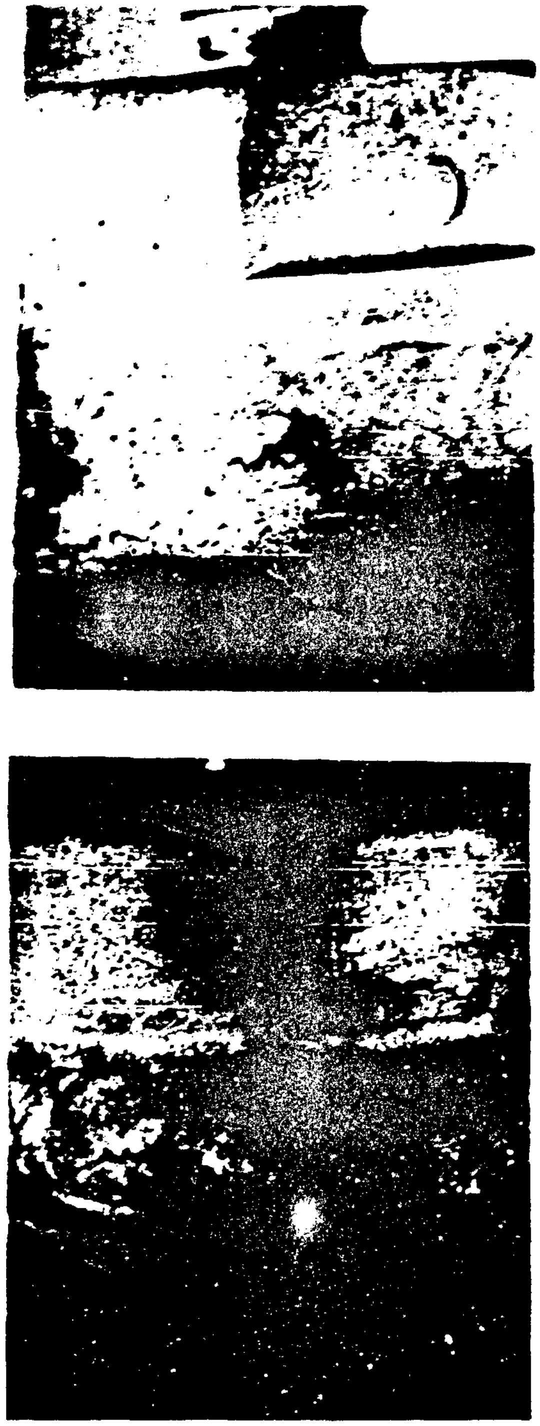


Figure 3. Corrosion attack in fitting weld on End "A" of Tank No. 10. 3X

Figure 4. Large corrosion pit in HAX of fitting of end "B" of Tank No. 10. 3X

Figure 5. Corrosive attack in weld stop areas of Tank No. 10.

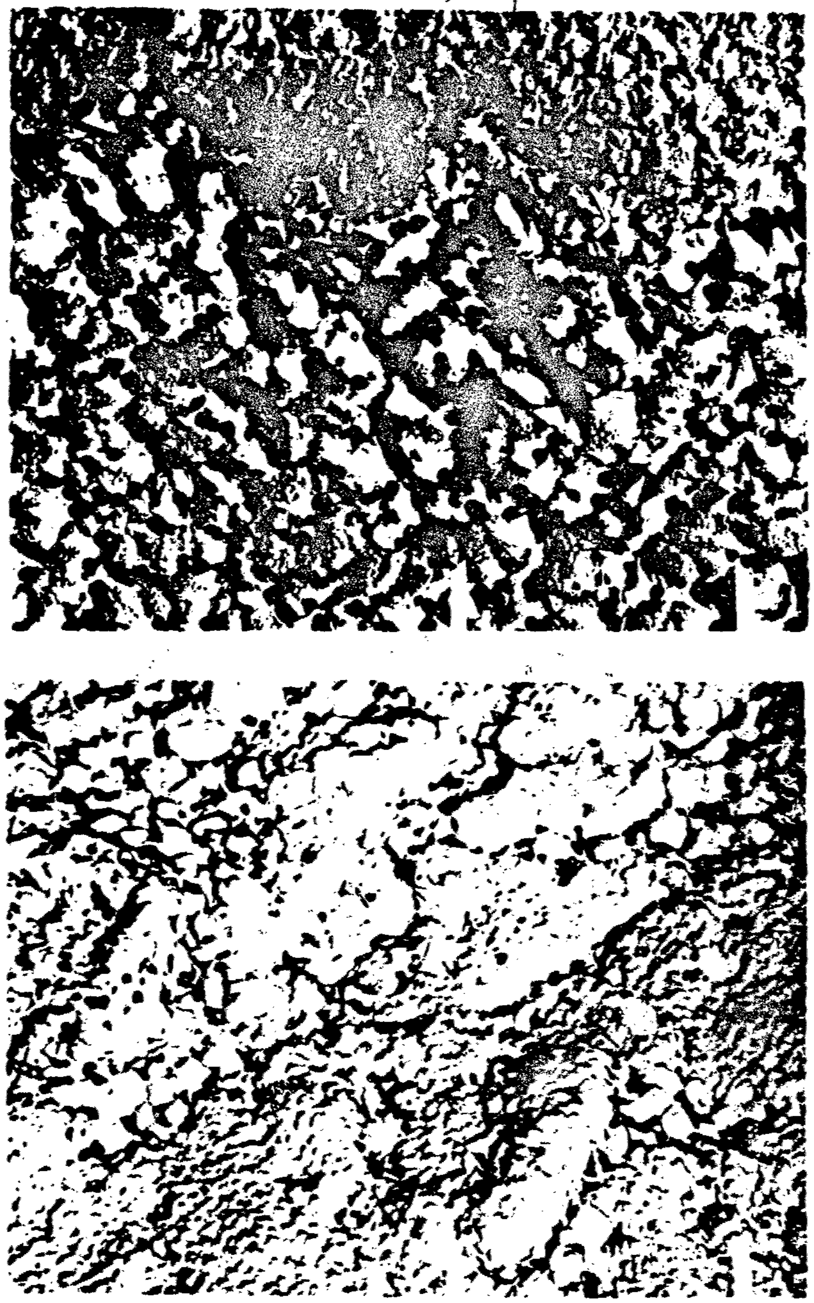


Figure 6. Electron Photomicrograph of Corrosion Failure in Tank No. 10. 7000x

Figure 7. Leak Area in Fitting of Tank No. 10.
75X

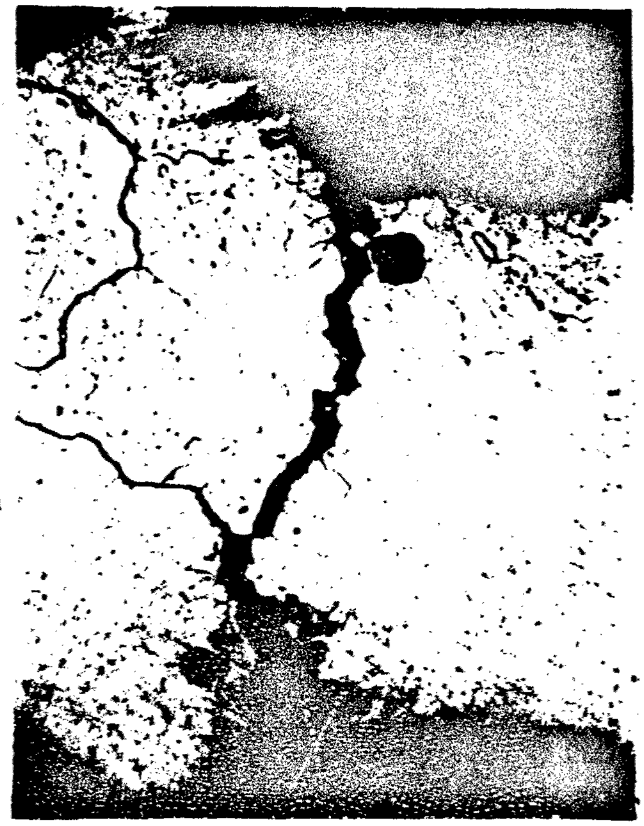


Figure 8. Leak Area Shown in Figure 7 at 200X.

Figure 9. Corroded Area of Weld Stop.
50X

Failure Analysis of Small Tank AFRPL S/N 11, 6061 Aluminum Alloy

Report No. 69/39R

Author: ____________________
Lawrence W. Loechel
Senior Engineer - Metals
Materials Research and Engineering

Approved: ____________________
A. W. O'Brien, Jr.
Chief
Materials Research and Engineering

Author: ____________________
Howard J. Brown
Unit Head - Metals
Materials Research and Engineering

Reference: (1) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 8, AM350 Precipitation Hardening Alloy", 2/3/69.

(2) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 9, AM350 Precipitation Hardening Alloy", 3/3/69.

(3) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 7, 2014 Aluminum Alloy," 5/19/69

(4) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 10, 6061 Aluminum Alloy,"8/8/69.

(5) Quality Control Laboratories Report #69M1121, 8/11/69.

(6) Unpublished data relative to the corrosion rates of various aluminum alloys, parent and welds in various concentrations of HNO_3.

INTRODUCTION

Tank S/N 11 was a 6061 aluminum alloy that had been exposed to ClF_5, when the tank failed by leaking through a weld in the pressurant fittings.

OBJECTIVE

The objective of this analysis was to determine the metallurgical cause of failure of tank AFRPL S/N 11.

CONCLUSIONS

1. The failure was caused by external pitting and intergranular corrosion occurring in welds of the fitting-to-end segment welds in each end of the tank.

2. The external corrosion was caused by leakage of ClF_5 from some adjacent leaking vessel or fitting resulting in acid formation on the tank S/N 11.

RECOMMENDATIONS

As has been recommended previously in references (1), (2), (3), and (4), vessels containing hygroscopic propellants should not be stored adjacent to similar vessels in case leaks do occur since these materials are not sufficiently resistant to acid environments.

RESULTS AND DISCUSSION

1. Macroexamination - The tank was lightly etched over its entire surface, Figures 1, 2, and 3. The tank was severely corroded in the area of the fitting welds, Figures 4 through 9. The weld cross-over areas in the main tank body were not attacked. Significant acid etching was observed on the top fitting weld as shown in Figures 6 through 8. Figure 9 shows cracking as a result of intergranular corrosion in the stop area of the bottom fitting weld.

2. Leak Test - The tank was baked at 250°F for one hour It was then pressurized with 100% helium and allowed to soak for 16 hours. The tank was then leak checked by the hand probe method, using a CEC helium mass spectrometer. Two leaks were found in the fitting weld on the top end of the tank. The leaks had a magnitude of 3.1×10^{-6} and 3.0×10^{-5} atm. cc/sec. One leak having a magnitude of 1.6×10^{-8} atm. cc/sec. was found in the other tank fitting weld.

3. X-Ray Inspection - The tank welds were x-rayed. No defects other than those attributable to corrosive attack were found.

4. Metallographic Examination - The leak areas shown in Figures 6, 7, 8, and 9, were cross-sectioned for metallographic examination. As shown in Figures 10, 11, and 12, the leakage failures were caused by corrosive attack. The leaks appeared to have originated on the external surface of the tank and so were probably caused by ClF_5 that had leaked from another test system in the same area as tank #11. The top hydraulic fitting of tank #11 could have caused the leak as evidenced by the rust on the threads (see Figure 6).

5. Electron Microscopy - Replicas of two cracked areas of welds were made and examined. The replicated surfaces were typical of corrosive attack, Figures 13 and 14.

6. Chemical Analysis - The tank was identified as having been made from 6061 aluminum alloy.

7. Mechanical Properties - Mechanical properties were not required by agreement with AFRPL. However, a hardness test was made and revealed the material was Rockwell H-99 which is equivalent to 6061-T4. Since there were no drawings available for the 6061 aluminum alloy tank, it was not determined if the hardness was as originally intended, but it is listed for reference.

8. Dimensions - The tank thicknesses were as follows:

   a. Dome end segments - 0.066"
   b. Barrel panels - 0.065"

   The above dimensions were presented for information and reference since no drawings were available.

9. Corrosion Product Analysis - The corrosion product obtained from the external surfaces of the tank was identified as aluminum fluoride hydroxide hydrate, Ref. 5. This is the corrosion product that would be likely to form as the result of ClF_5 attack.

As shown previously in tests at Martin Marietta Corporation, weld areas are attacked by acid environments as much as twenty to thirty times faster than parent metal depending on the amount of weld heat applied to the weldments in aluminum alloys. Starts and stops in welds are particularly susceptible. Therefore, if any oxidizer such as ClF_5 or N_2O_4 should leak near weld areas and acids form as a result of hydrolysis of these propellants, the weld zones will start showing severe attack within 48 hours. (Ref. 6)

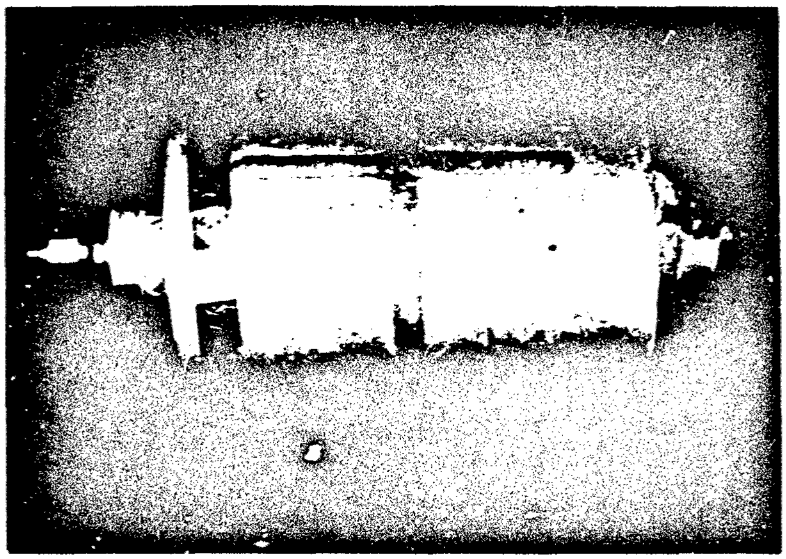


Figure 1. Photomacrograph showing overall sideview of small tank no. 11. Top of tank is shown to the right. 0.6X

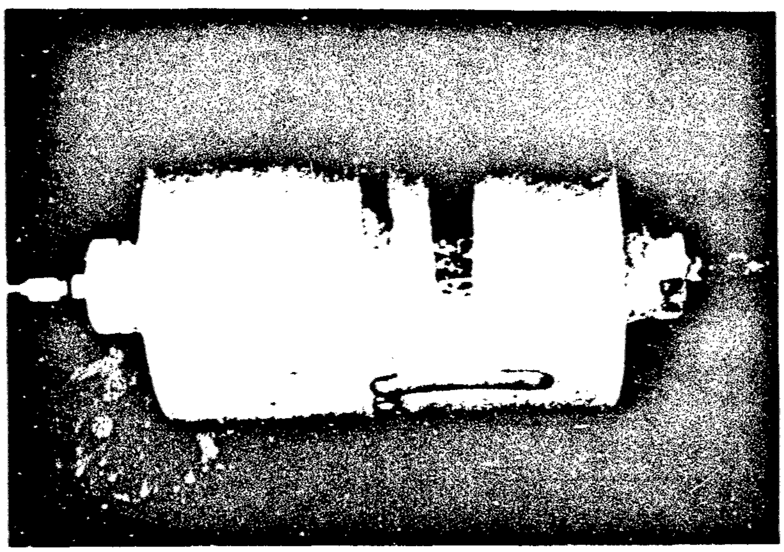


Figure 2. Photomacrograph showing overall sideview of small tank no. 11. Top of tank is shown to the right.

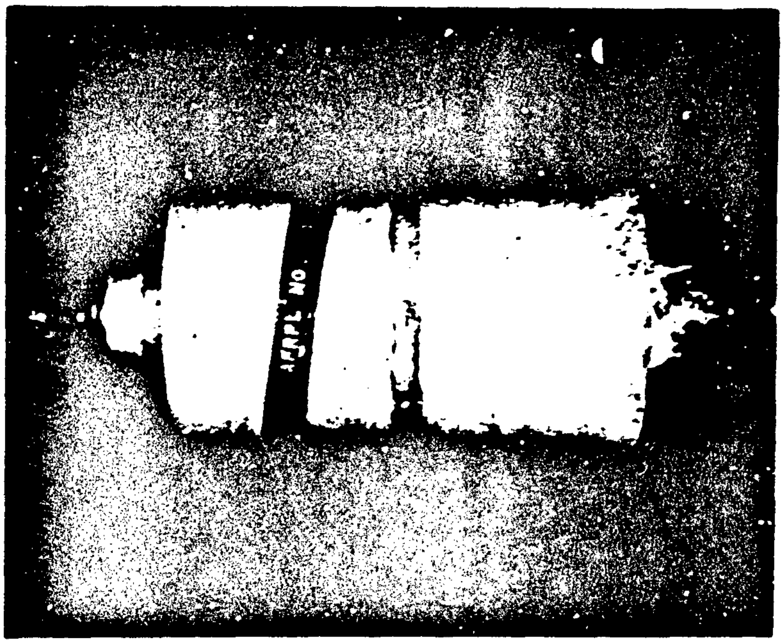


Figure 3. Photomacrograph showing overall sideview of small tank no. 11. Top of tank is shown to the right. 0.6X

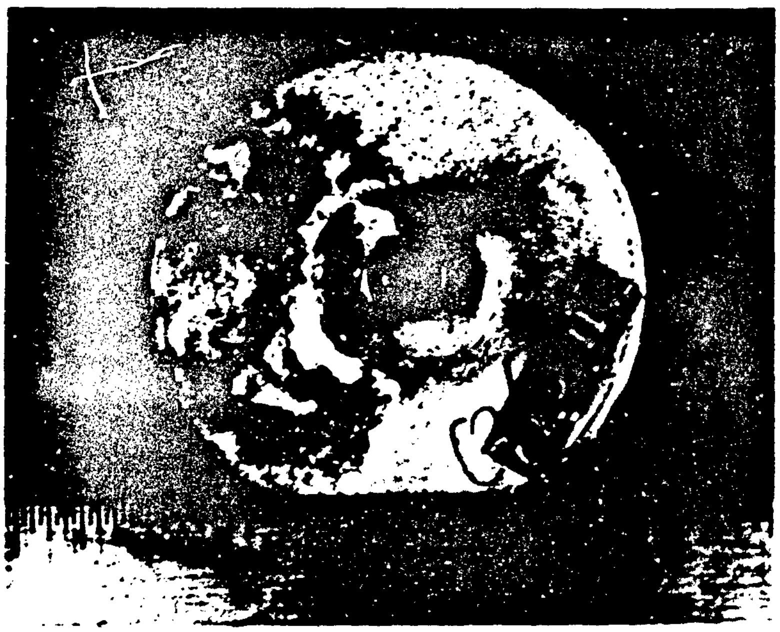


Figure 4. Photomacrograph showing overall view of the top end of small tank no. 11 0.75X

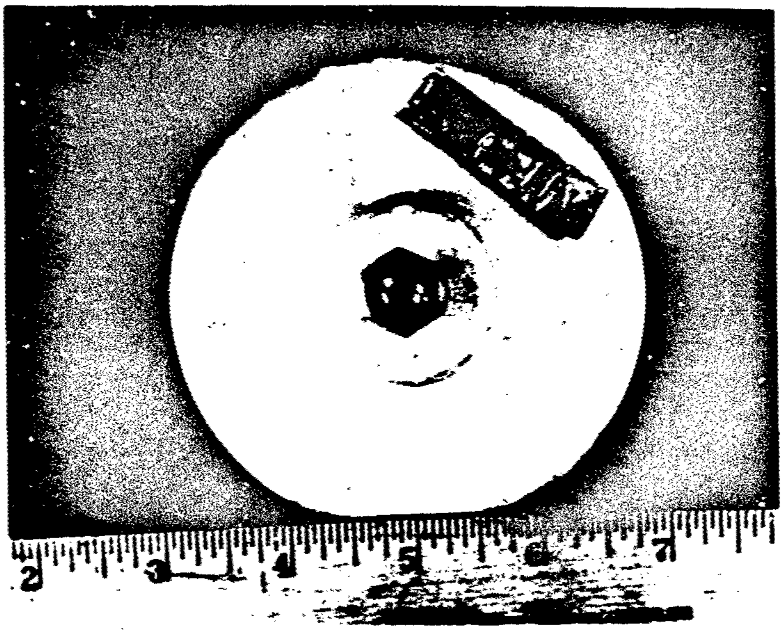


Figure 5. Photomacrograph showing an overall view of the bottom of small tank no. 11 0.75X

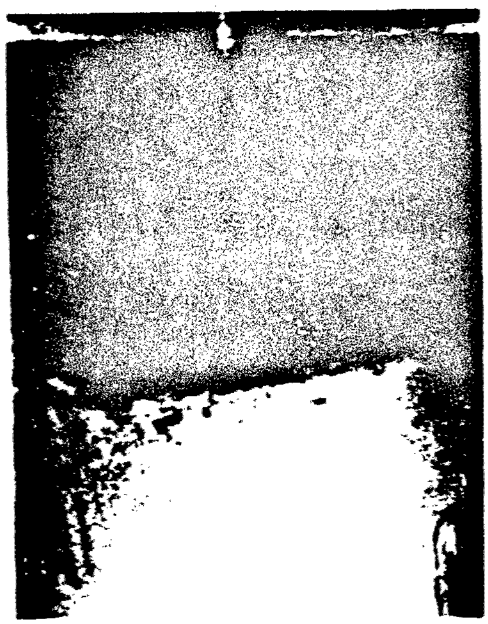


Figure 6. Photomacrograph showing the two leak areas in the weld of the top boss-to-end segment of small tank no. 11 1X

Figure 7. Photomacrograph showing at slightly higher magnification the 19X500 count leak area shown in Figure 6. 1.5X

Figure 8. Photomacrograph showing at slightly higher magnification the 92x1000 count leak area shown in Figure 6. 1.5X

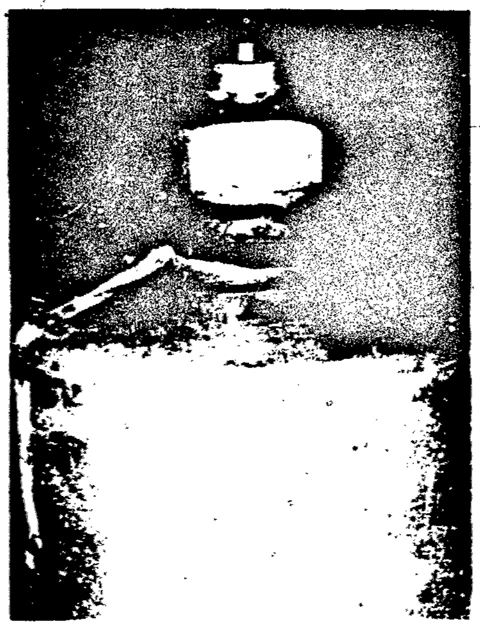


Figure 9. Photomacrograph showing the single leak area in the weld of the bottom boss-to-end segment of small tank no. 11. 1X

Figure 10. Photomicrograph showing intergranular corrosive attack in weld zone of tank no. 11, in the 92x1000 leak area. 10X

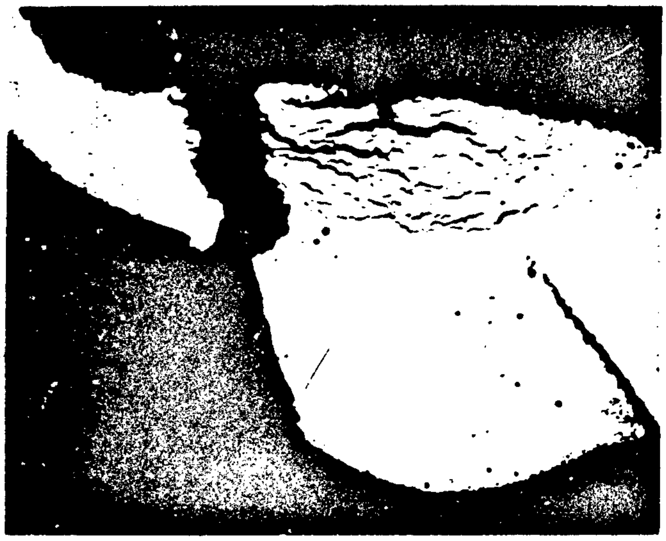


Figure 11. Photomicrograph showing intergranular corrosion in the heat affected zone and weld bead of small tank no. 11, in the 19x500 leak area. 10X

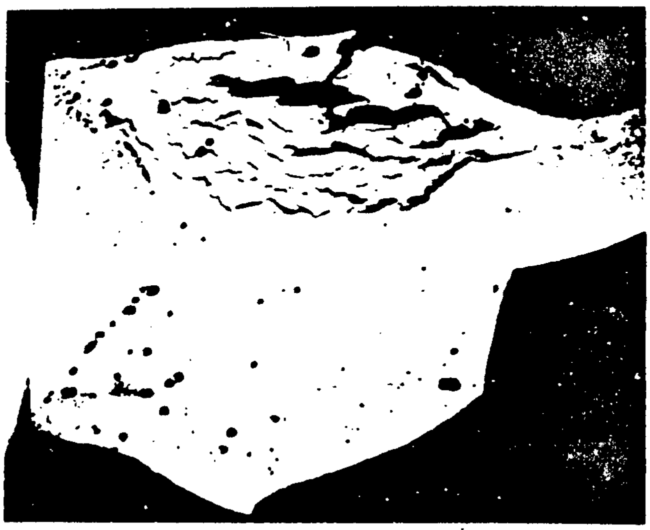


Figure 12. Photomicrograph showing intergranular corrosion in the weld stop area of small tank no. 11, in the 42x1 leak area. 10X

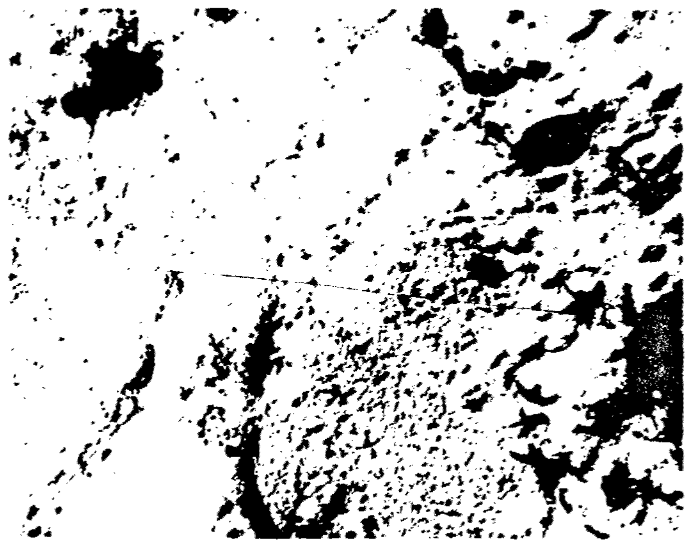


Figure 13. Electron photomicrograph showing representative evidence of intergranular corrosion attack observed on the surface of the fracture of leak area 92x1000 on small tank no. 11. 15,000X

Figure 14. Electron photomicrograph showing representative evidence of intergranular corrosion attack observed on the surface of the fracture of leak area 19x500 on small tank no. 11. 15,000X

Martin Marietta Corporation 13 October 1969

Materials Research and Engineering Page 1 of

Failure Analysis of Small Tank AFRPL S/N 12, 6061 Aluminum Alloy

Report No. 69/41R

Author:____________________
Lawrence W. Loechel
Senior Engineer - Metals
Materials Research and Engineering

Approved:____________________
A. W. O'Brien, Jr.
Chief
Materials Research and Engineering

Author:____________________
Howard J. Brown
Unit Head - Metals
Materials Research and Engineering

Reference: (1) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 8, AM350 Precipitation Hardening Alloy", 2/3/69.

(2) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 9, AM350 Precipitation Hardening Alloy", 3/3/69.

(3) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 7, 2014 Aluminum Alloy", 5/19/69.

(4) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 10, 6061 Aluminum Alloy", 8/8/69.

(5) Lawrence W. Loechel, Howard J. Brown, and A. W. O'Brien, Jr., "Failure Analysis of Small Tank AFRPL S/N 11, 6061 Aluminum Alloy", 9/25/69.

(6) Quality Control Laboratories Report #69M2172, 9/05/69.

(7) Quality Control Laboratories Report #69M1122, 8/11/69.

(8) Unpublished data relative to the corrosion rates of various aluminum alloys, parent and welds in various concentration of HNO_3.

INTRODUCTION

Tank S/N 12 was a 6061 aluminum alloy tank that had been exposed to ClF_5 when the tank failed by leaking through a weld area in the pressurant fittings and in a cross-over weld in mid-barrel section.

OBJECTIVE

The objective of this analysis was to determine the metallurgical cause of failure of tank AFRPL S/N 12.

CONCLUSIONS

1. The failure was caused by external pitting and intergranular corrosion occurring in welds in the fitting-to-ends segment welds in each end of the tank and at the start area of the barrel girth weld.

2. The external corrosion was caused by leakage of ClF_5 from some adjacent leaking vessel or fitting resulting in acid formation on the tank S/N 12.

RECOMMENDATIONS

As has been recommended previously in references (1), (2), (3), (4), and (5), vessels containing hygroscopic propellants should not be stored adjacent to similar vessels in case leaks do occur since these materials are not sufficiently resistant to acid environments.

RESULTS AND DISCUSSION

1. Macroexamination - The tank was lightly etched over its entire surface, Figures 1, 2, and 3. The tank was severely corroded in the area of the fitting welds, Figures 4, 5, and 7. The weld cross-over areas in the main tank body were not severely attacked, but the start area of the girth weld was cracked, see Figure 6. Significant acid etching was observed on the bottom fitting weld as shown in Figure 7. Figure 8 shows cracking as a result of intergranular corrosion in the stop area of the top fitting weld.

2. Leak Test - The tank was baked at 250 F for one hour It was then pressurized with 100% helium and allowed to soak for 16 hours. The tank was then leak checked by the hand probe method using a CEC helium mass spectrometer. One leak having a magnitude of 1.06×10^{-7} atm. cc/sec was found in the fitting weld on the top end of the tank. One leak having a magnitude of 2.05×10^{-8} atm. cc/sec. was found in the bottom tank fitting weld. One leak having a magnitude of 2.4×10^{-7} atm. cc/sec. was found in the weld start area of the girth weld.

3. X-Ray Inspection - The tank welds were x-rayed. No defects other than those attributable to corrosive attack were found.

4. Metallographic Examination - The leak areas shown in Figures 6, 7, and 8, were cross-sectioned for metallographic examination. As shown in Figures 9, 10, 11, 12, 13, and 14, the leakage failures were caused by corrosive attack. The leaks appeared to have originated on the external surface of the tank and so were probably caused by ClF_5 that had leaked from another test system in the same area as tank #12.

5. Electron Microscopy - Replicas of cracked areas of welds were made and examined. The replicated surfaces were typical of corrosive attack, Figure 15.

6. Chemical Analysis - The tank was identified as having been made from 6061 aluminum alloy, Ref. 6.

7. Mechanical Properties - Mechanical properties were not required by agreement with AFRPL. However, a hardness test was made and revealed the material was Rockwell H-99 to H-102 which is equivalent to 6061-T4. Since there were no drawings available for the 6061 aluminum alloy tank, it was not determined if the hardness was as originally intended, but it is listed for reference.

8. Dimensions - The tank thicknesses were as follows:

   a. Dome end segments - 0.066"
   b. Barrel panels - 0.070"

   The above dimensions were presented for information and reference since no drawings were available.

9. Corrosion Product Analysis - The corrosion product obtained from the external surfaces of the tank was identified as aluminum fluoride hydroxide hydrate, reference (7). This is the corrosion product that would be likely to form as the result of ClF_5 attack.

   As shown previously in tests at Martin Marietta Corporation, weld areas are attacked by acid environments as much as twenty to thirty times faster than parent metal depending on the amount of weld heat applied to the weldments in aluminum alloys. Starts and stops in welds are particularly susceptible. Therefore, if an oxidizer such as ClF_5 or N_2O_4 should leak near weld areas and acids form as a result of hydrolysis of these propellants, the weld zones will start showing severe attack within 48 hours. (Reference 8).

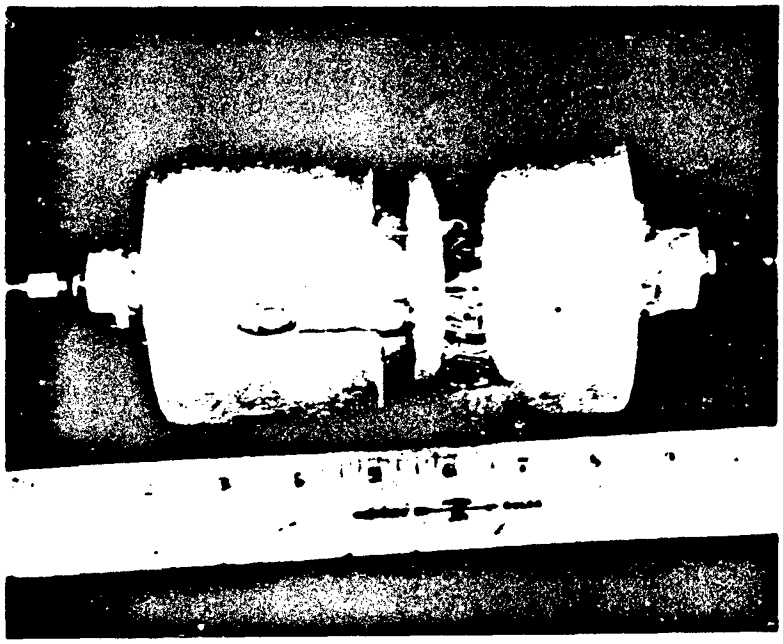


Figure 1. Photomacrograph showing overall sideview of small tank no. 12. Top of tank is shown to the right. 0.6X

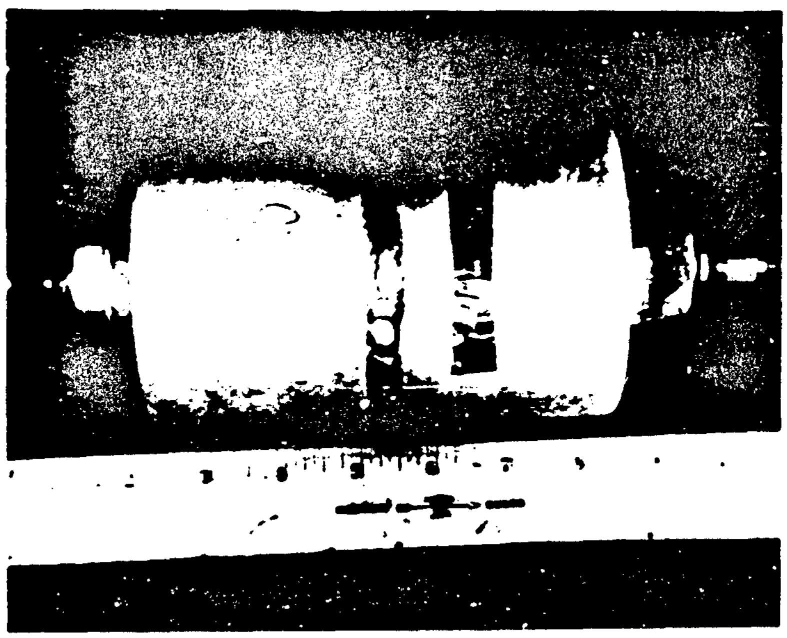


Figure 2. Photomacrograph showing overall view of small tank no. 12. Top of tank is shown to the right. 0.6X

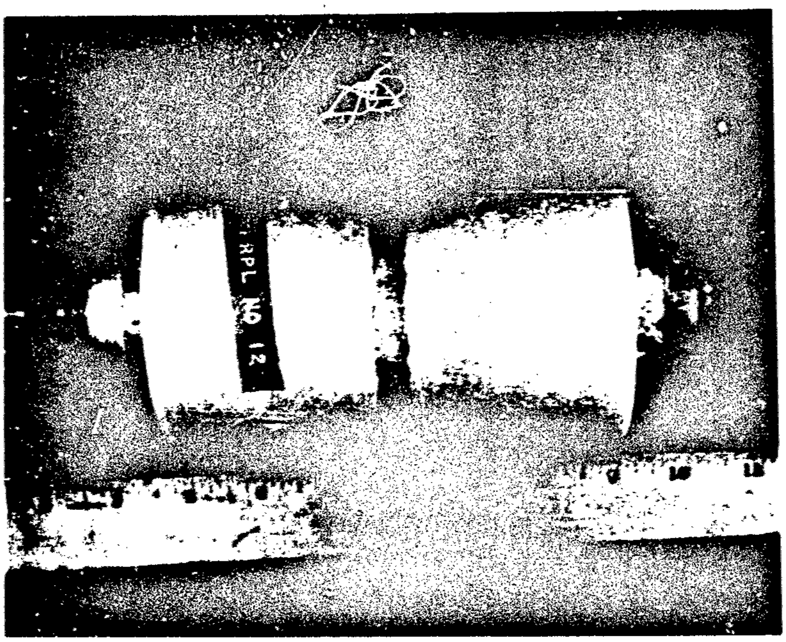


Figure 3. Photomacrograph showing overall sideview of small tank no. 12. Top of tank is shown to the right. 0.6X

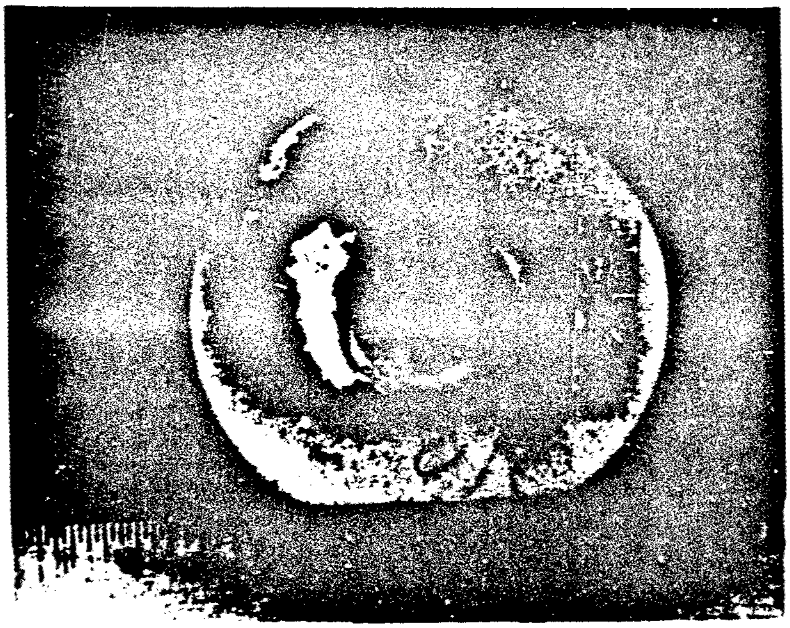


Figure 4. Photomacrograph **showing and overall** view of the top end of small **tank no. 12.** 0.75X

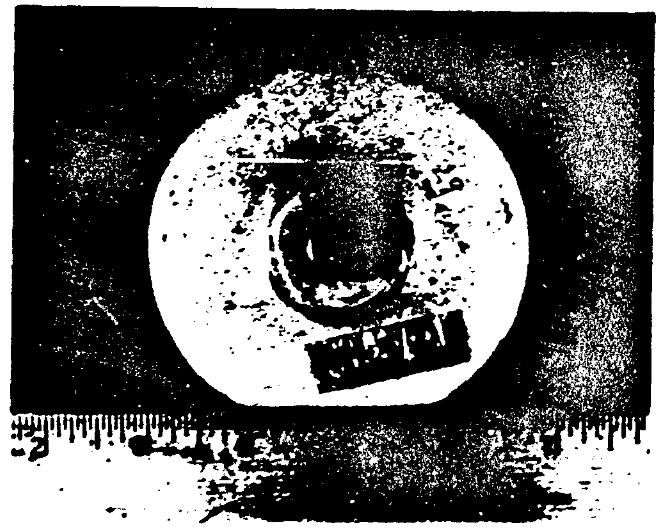


Figure 5. Photomacrographs showing an overall view of the bottom of small tank no. 12. 0.75X

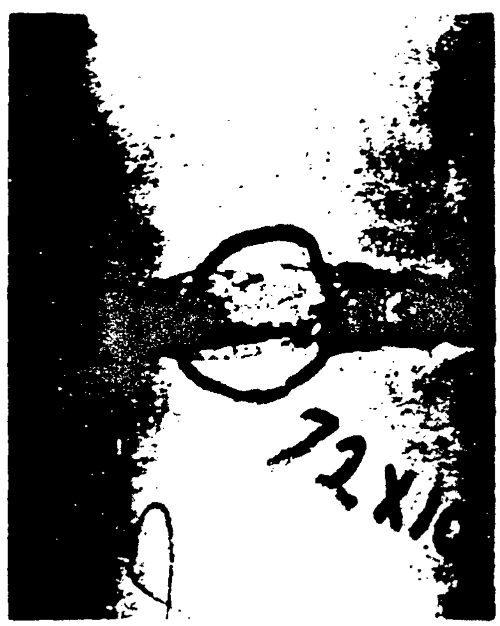


Figure 6. Photomacrograph showing the leak in the weld start area of the girth weld of small tank no. 12. 1X

Figure 7. Photomacrograph showing the leak area in the fitting-to-end cap weld in the top of small tank no. 12. 1.5X

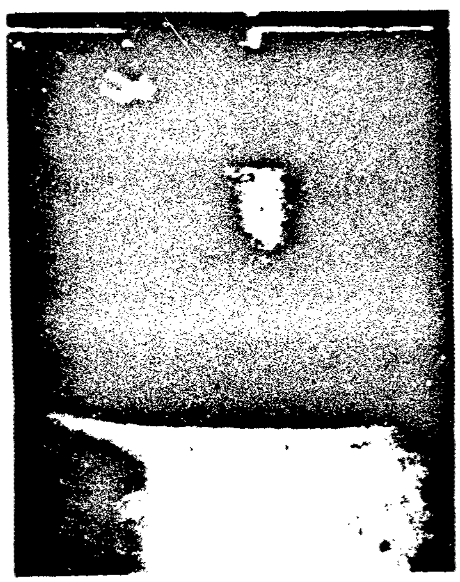


Figure 8. Photomacrograph showing the leak area in the fitting-to-end cap weld in the bottom of small tank no. 12. 1.5X

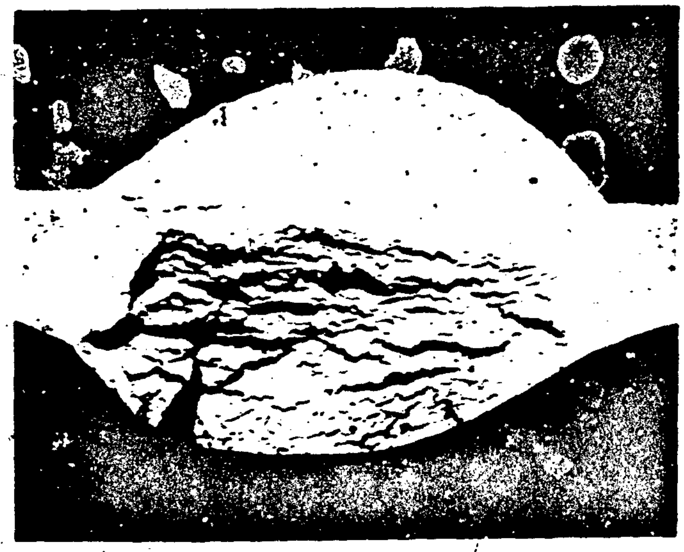


Figure 9. Photomicrograph showing heavy intergranular corrosion attack in the weld zone of small tank no. 12, in the 72 x 10 leak area. 10X

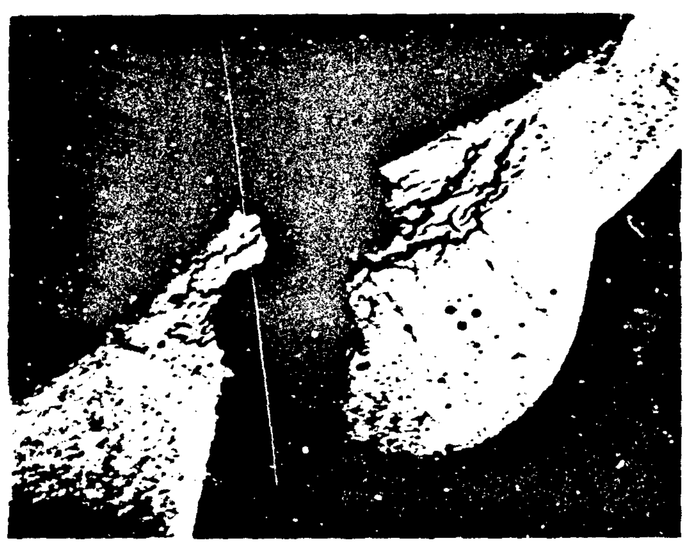


Figure 10. Photomicrograph showing a through crack and heavy intergranular corrosion attack in the weld zone of small tank no. 12, in the 62 x 1 leak area. 10X

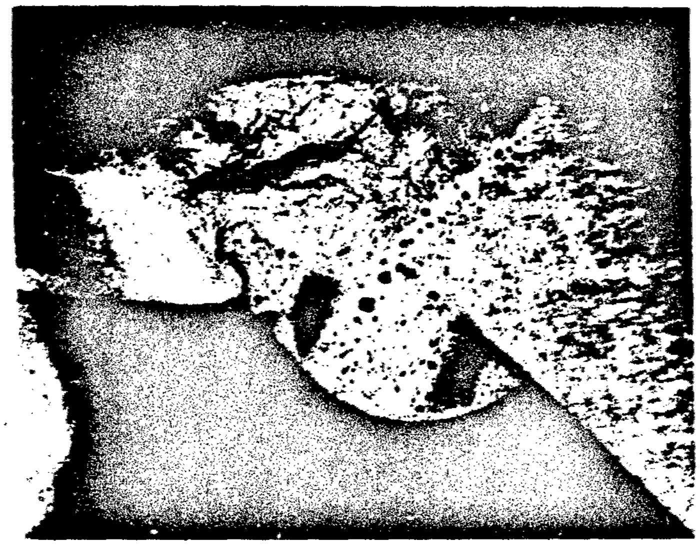


Figure 11. Photomicrograph showing intergranular corrosion in the weld and heat affected zone of small tank no. 12 in the 32 x 10 leak area. 10X

Figure 12. Photomicrograph showing the same relative area as Figure 11 after further polishing to expose the leakpath. 10X

Figure 13. Photomicrograph showing representative intergranular corrosion through the weld area of the 32 x 10 leak area in small tank no. 12. 200X

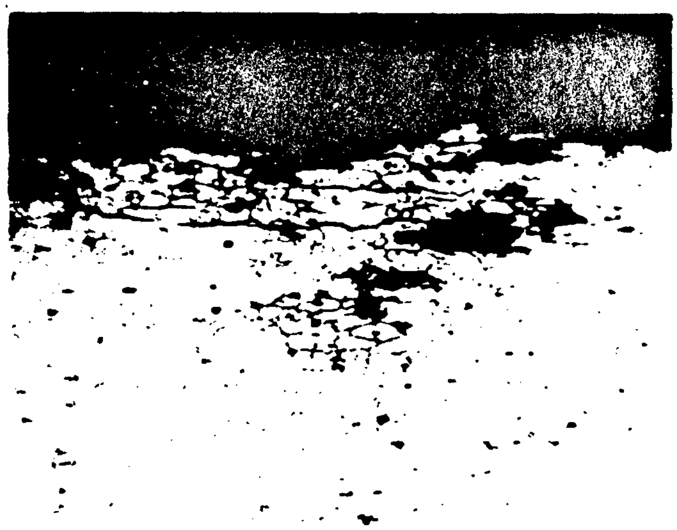


Figure 14. Photomicrograph showing representative intergranular corrosion in the weld bead area in the 32 x 10 leak area in small tank no. 12. 200X

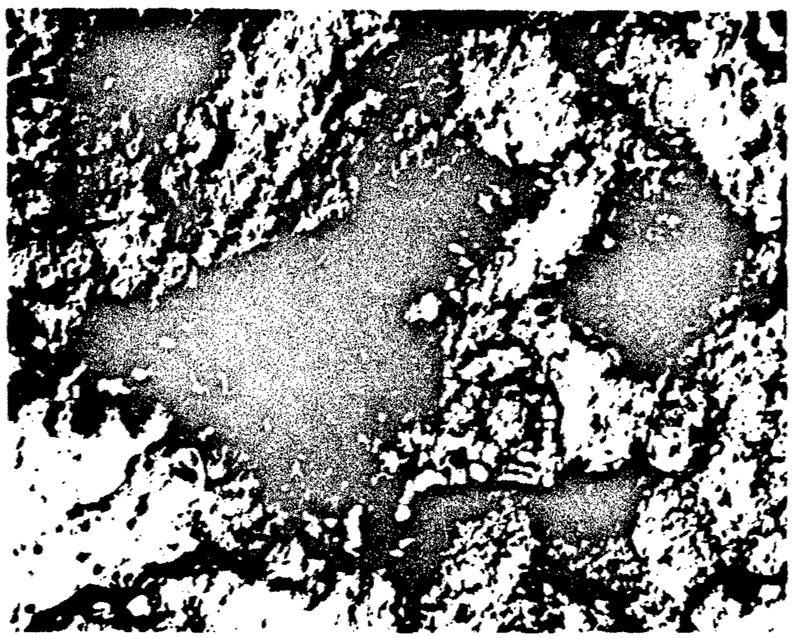


Figure 15. Electron photomicrograph showing representative evidence of intergranular corrosion observed on the surface of the fractures of leak areas 62 x 1 and 32 x 10. 15,000X

APPENDIX NO. II

AFRPL LABORATORY TEST REPORTS

LABORATORY TEST REPORT	Report Nr. -936	Date 20 Oct 69
Requesting Organization (Symbol and/or Name) RPPO RPRO	Name of Requestor Lt Mears	Phone Number 32515

Sample, Test or Project

305805 FRJ

Work Required

Failure Analysis on Aluminum Alloy Tank

TEST DATA

I. MATERIALS:

1. 7007 Al alloy tank - 6.5 Zn, 1.8 Mg., 0.25 Mn., 0.15 Cr., 0.15 Zr., and Al (bal).

2. 5180 Al alloy filler weld metal - 2.0 Zn., 4.0 Mg., 0.45 Mn., 0.15 Zr., 0.15 Ti., and Al (bal).

II. BACKGROUND:

The tank contained ClF_3 for 479 days and ClF_5 for 156 days before a leak was detected on a Monday. The tank was checked on a daily basis excluding week-ends. There had been no major buildup of corrosion products on the tank prior to the leak.

III. CONCLUSIONS:

The tank failed as a result of environmentally induced stress corrosion cracking. The primary leak occurred at the cross-over weld bead (Fig. 1). A second leak was located at the boss-to-tank weld bead (Fig. 2).

IV. RECOMMENDATIONS:

1. Since all the evidence indicates that this tank failed primarily as a

It is certified that this is an accurate report of test or analysis performed by the Chemical & Materials Branch.

Performed By		Signature of Approving Official
Name H. REDE, CAPT	Name R. A. SCIALOY, MAJOR	Name JOHN T. NAKAMURA
Name	Name	Title Chief Analytical Section
		Chemical & Materials Branch mcb

RPL Form 31

result of a corrosive environment, it is recommended that test tanks be isolated from each other. Fumes from other leaking vessels greatly enhance failure of this particular type of storage vessel, as well as others undergoing tests presently.

V. RESULTS AND DISCUSSION:

1. Macroexamination - The tank had been lightly etched over its entire external surface with a major build-up of corrosion products at the primary leak area (Fig. 1). The internal surface had maintained a metallic luster (Fig. 3). Examination of the internal surface also revealed several minor defects attributed to the welding operation. None showed any evidence of leaks during the leak-check operation. Figures 4 to 6 show these defects.

2. Leak Check - The tank was leak checked by the hand probe method using a CEC helium mass spectrometer. Other than the primary leak at the cross-over welds, a second leak was found at the base of the boss-to-tank weld bead. A crack could be seen in this area by use of a stereo-zoom microscope (Fig. 2). No other leaks were detected.

3. Metallographic Examination - Specimens were cut from the leak areas, Figs. 1 and 2. Separation of the crack in Fig. 2 occurred while cutting and it could be seen that corrosion progressed from the outside towards the inside of the tank (Fig. 7).

Two types of corrosion were found in the leak area of Fig. 1. A stress corrosion crack (Figs. 8 & 9) which is believed to have caused the primary leak and a type of intergranular attack due to exfoliation corrosion common to Al-Zn-Mg alloys (Fig. 10). The stress corrosion crack probably developed due to residual stresses, since the design limit of 15% of yield stress during testing is not usually considered sufficient to induce stress corrosion cracking. The chemical agent responsible for the stress corrosion cracking and exfoliation attack is unknown. The finding of aluminum fluorides in the corrosion products taken from the area in Fig. 1 suggests that hydrofluoric and/or hydrochloric acids are distinct possibilities. The hydrolysis of ClF_5 in the humid environment (85°F & 85% relative humidity) could account for the presence of these acids.

It is speculated that the corrosive environment which etched the surface of the tank was enough to have caused the stress corrosion cracking. The massive build-up of corrosion products seen in Fig. 1 and the exfoliation attack is attributed to the action of the acids formed by the hydrolysis mentioned above.

4. Corrosion Product Identification - Qualitative analysis by emission spectrography and x-ray fluorescence revealed major constituents of 7007 and 5180 aluminum alloys, i.e., zinc and magnesium plus minor traces of iron, silicon, chromium, manganese, titanium, and copper. X-ray diffraction analysis showed hydrated aluminum fluoride compounds as the main corrosion product formed.

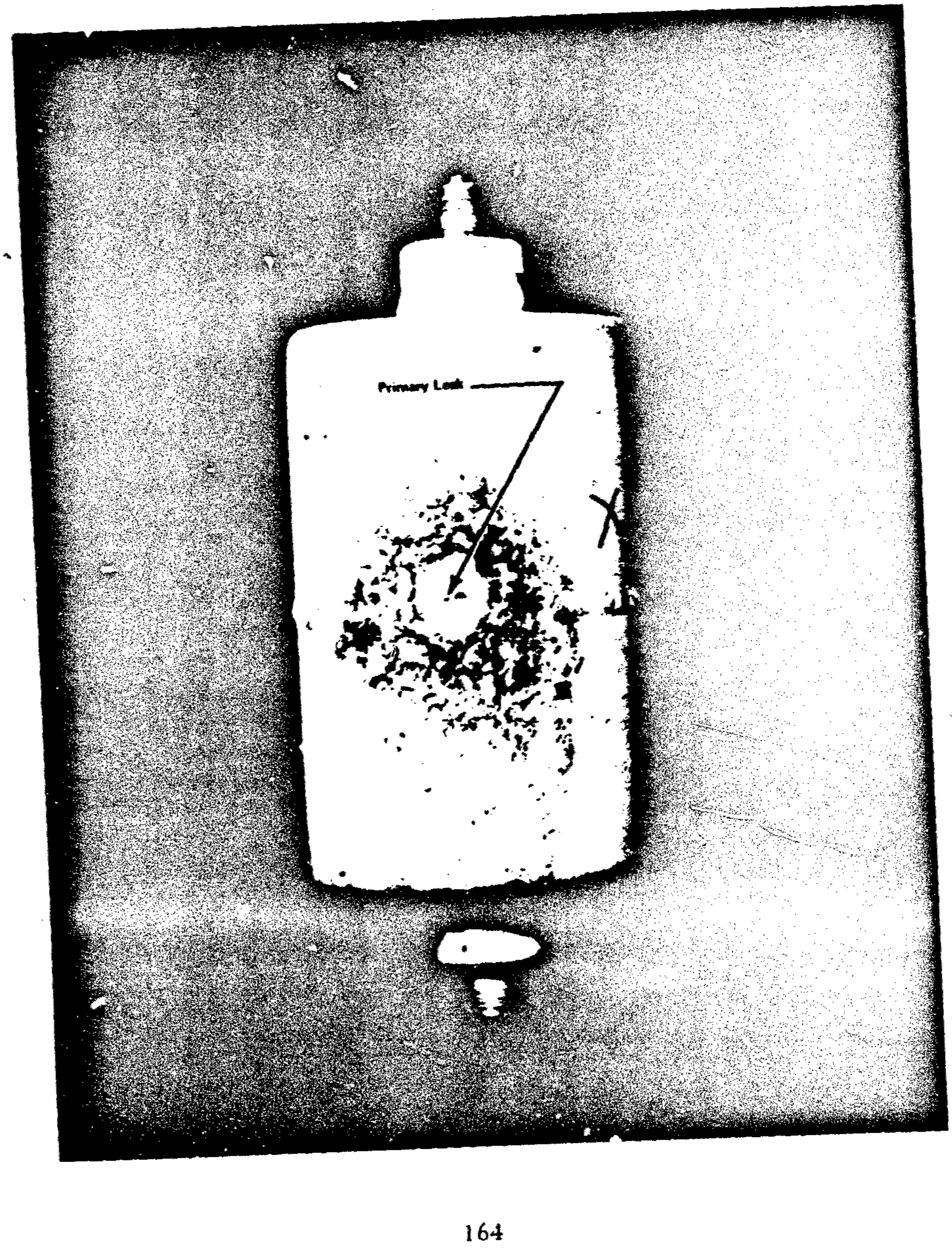

Primary Leak

Figure 2. External View of Crack at Base of Boss to Tank Weld Bead

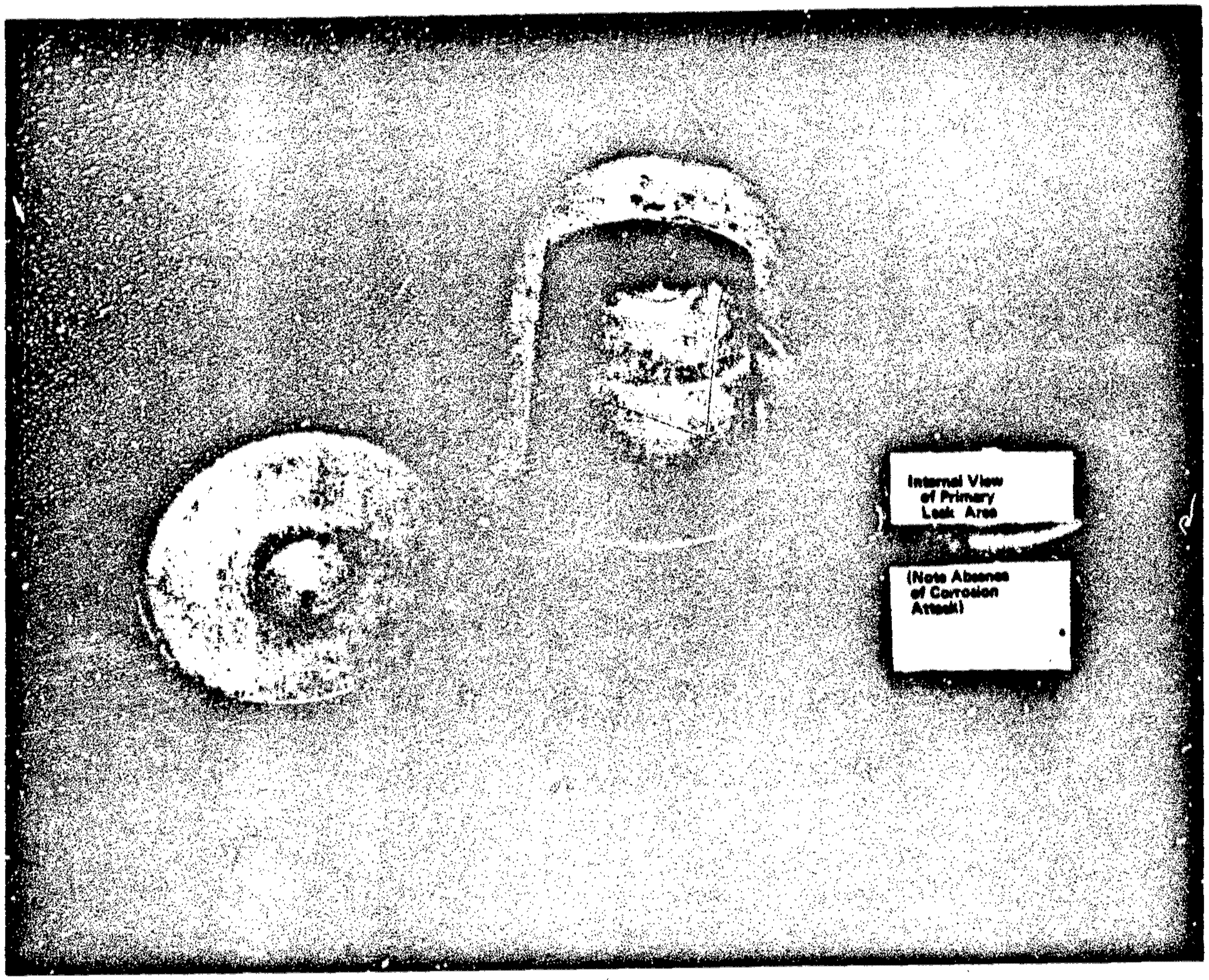


Figure 3. Internal View of Primary Leak Area
(Note Absence of Corrosion Attack)

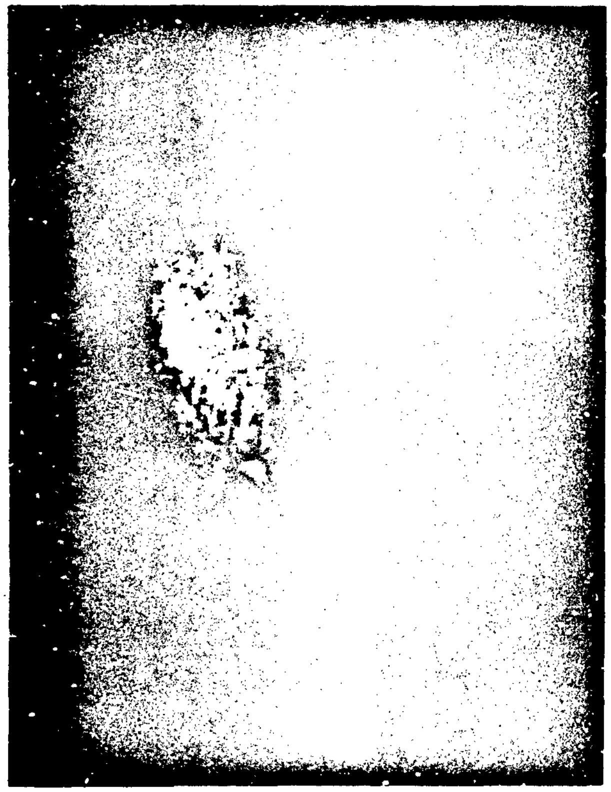


Figure 4. Internal View of Crack at Base of Vertical Weld Bead

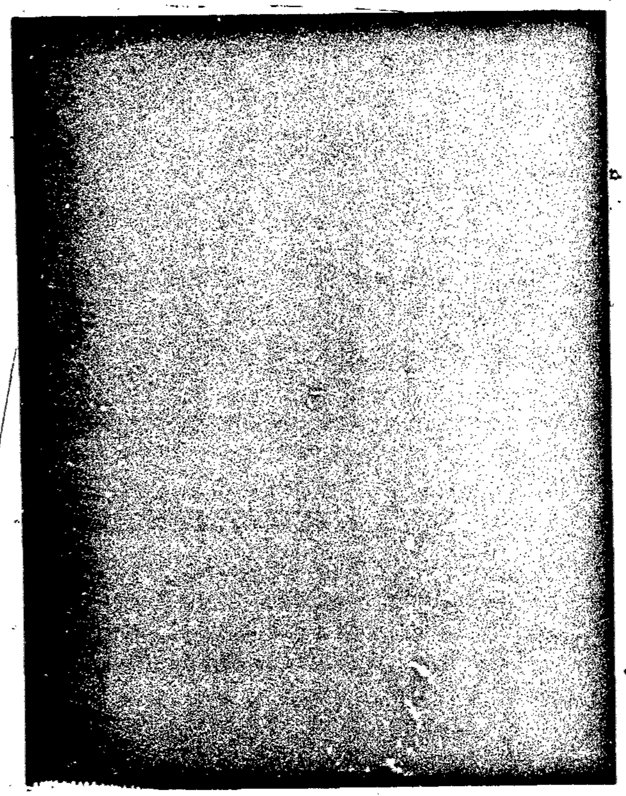


Figure 5. Internal View of Holes in HAZ of Vertical Weld Bead

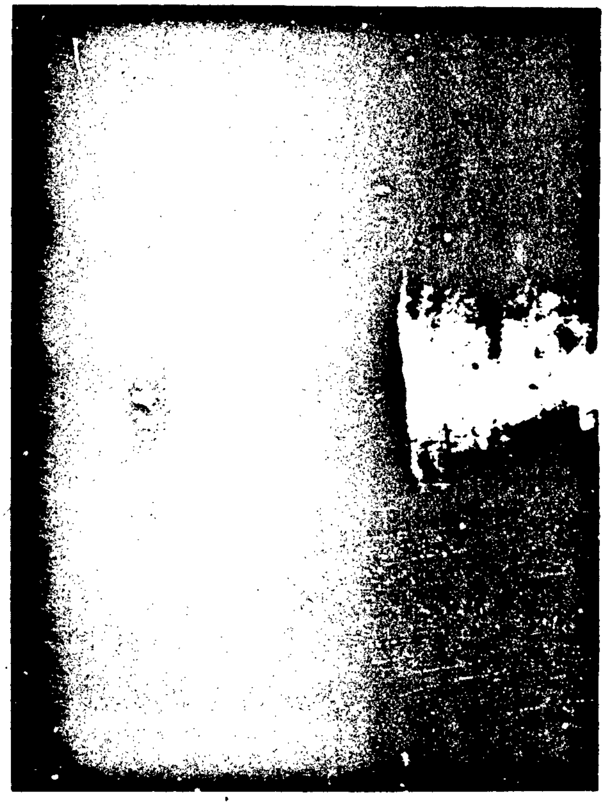


Figure 6. Internal View of Seam Formed in Boss to Tank Weld Bead

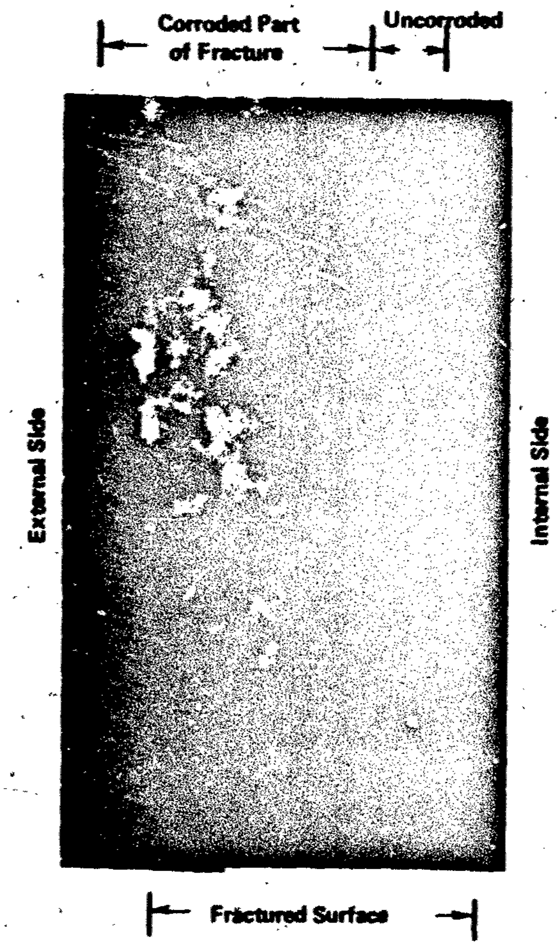


Figure 7. Edge View of Crack Through Thickness of Material Showing Corrosion Progressing from External (Left Side) to Internal (Right Side) Surface.

Figure 8. Stress Corrosion Crack of Primary Leak Area (ref Fig. 1).

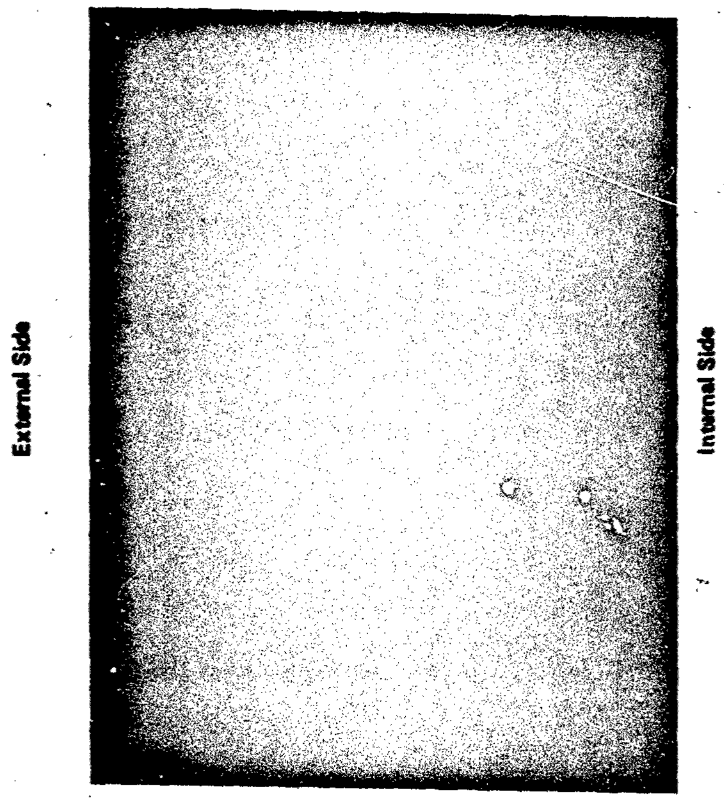


Figure 9. Same crack as in Figure 8.

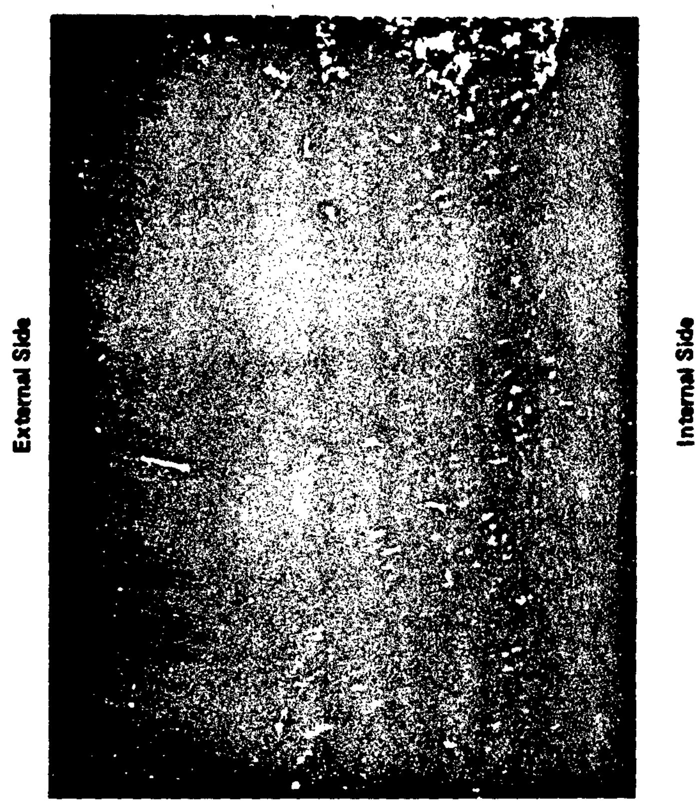


Figure 10. Exfoliation Corrosion

LABORATORY TEST REPORT	Report Nr. -1170	Date 10 Dec 69
Requesting Organization (Symbol and/or Name) RPRO	Name of Requestor Lt Mears	Phone Number 32515

Sample, Test or Project

305805FRJ

Work Required

Failure Analysis on 301 SS Tank

TEST DATA

I. MATERIAL: 301 SS - 0.08% C(max), 1.4-1.85% Mn, 0.03% P, 0.02% S, 0.55% Si, 16-19% Cr, 7-8.5% Ni, Fe (bal). The material was cryogenically-stretch formed and left ~~in the~~ unaged condition.

II. BACKGROUND: The tank was loaded with ClF_5 on 23 Aug 67 and developed a leak on 15 Sept 69.

III. CONCLUSIONS: The ~~tank failed~~ as a result of an environmentally induced stress corrosion crack. (Fig. 2).

IV. RESULTS AND DISCUSSION:

1. Macroexamination - The tank was lightly etched over its entire external surface. There was one crack slightly to the left of the vertical weld bead. (Figs. 1 & 2). It can be seen in Fig. 3 that the crack extends through the wall of the tank. In addition, there was no evidence of corrosion attack by the ClF_5 on the inside walls of the tank. (Figs. 3 & 4). However, the slight corrosive etching at the outside surface was sufficient for the stress corrosion crack to form.

2. Leak Check - The tank was leak checked by the hand probe method using

It is certified that this is an accurate report of test or analysis performed by the Chemical & Materials Branch.

Performed By		Signature of Approving Official
Name [illegible], CAPT	Name R. SCHALOW, MAJOR	Name JOHN T. NAKAMURA
Name	Name	Title Chief Analytical Section, Chemical & Materials Branch

mcb

FORM 31

a CEC helium mass spectrometer. The only leak found was from the crack shown in Figure 2.

3. Metallographic Examination - Figure 5 shows the major crack extending through the wall of the tank. Figure 6 shows cracks in the same vicinity of the major crack revealing crack growth is from the external towards the internal surface. Figure 7 reveals the crack to be of a transgranular nature which is typical of a stress corrosion crack in stainless steel.

V. REMARKS: It is apparent from the exterior surface etching that the test chamber atmosphere is highly corrosive. This atmosphere combined with the residual stresses generated during forming and welding was sufficient to induce stress corrosion cracking.

The absence of failures in tanks made from this material in the aged condition would seem to indicate that aging increases the resistance to stress corrosion cracking.

If the benefits of the proprietary heat treatment are substantiated by further tests, use of the unaged material in future tanks is not recommended.

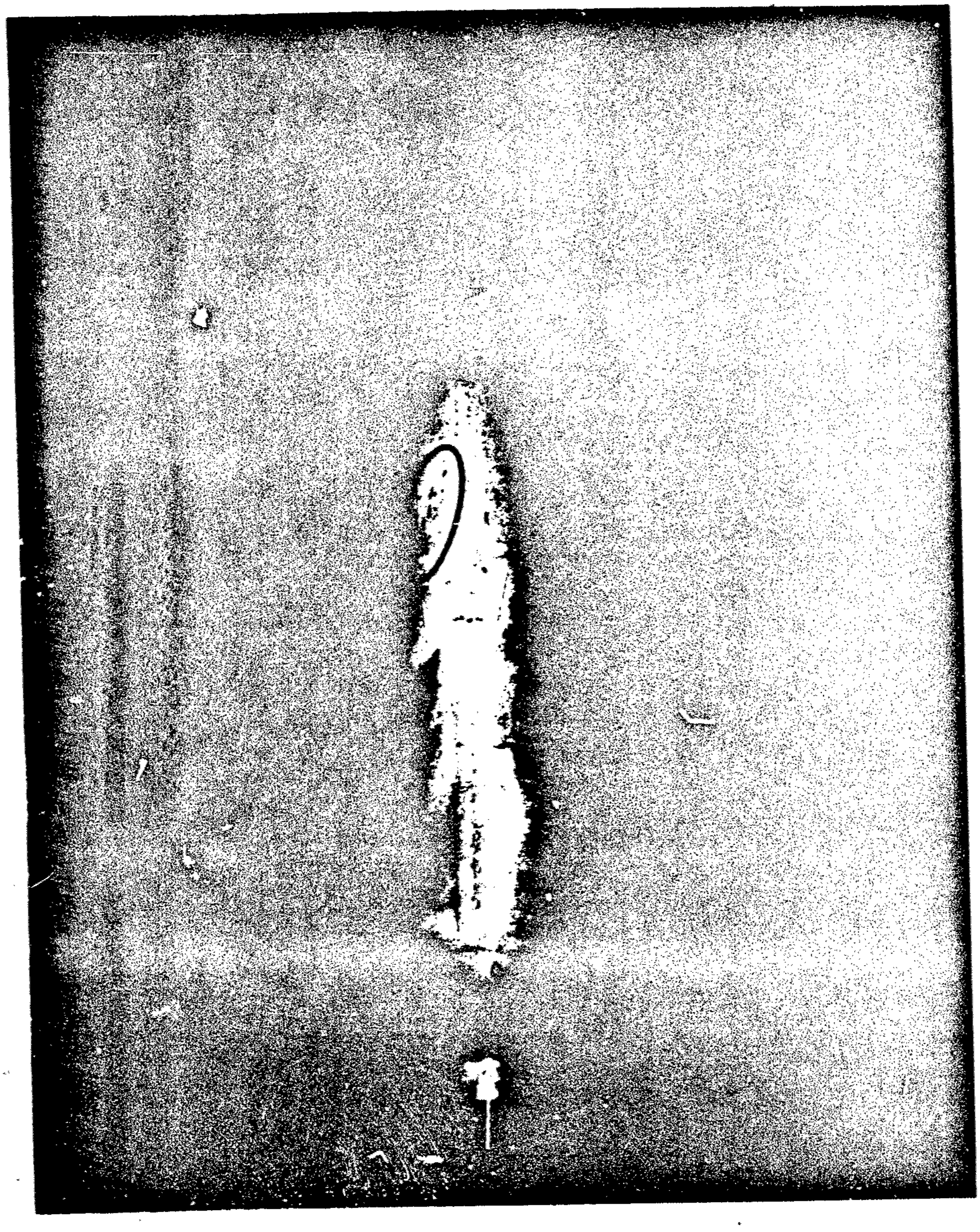


Figure 1

Figure 2

Figure 3.

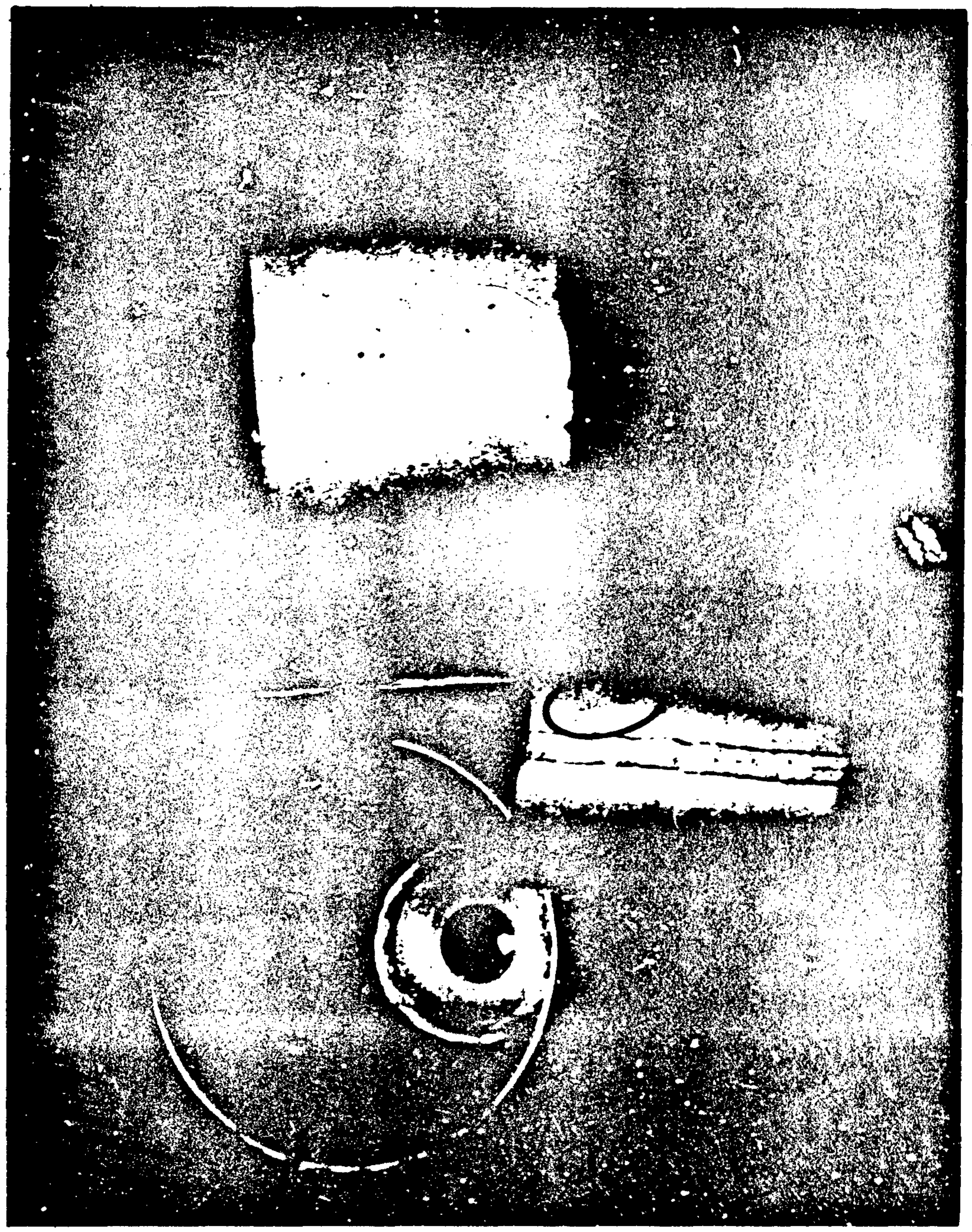


Figure 4

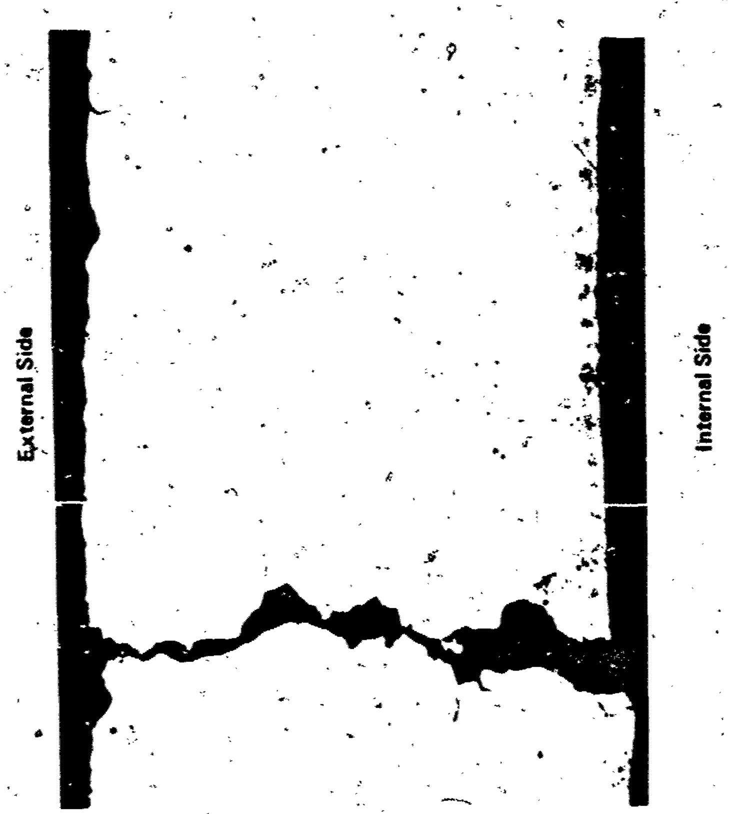


Figure 5. 301 SS (Unetched)
100X

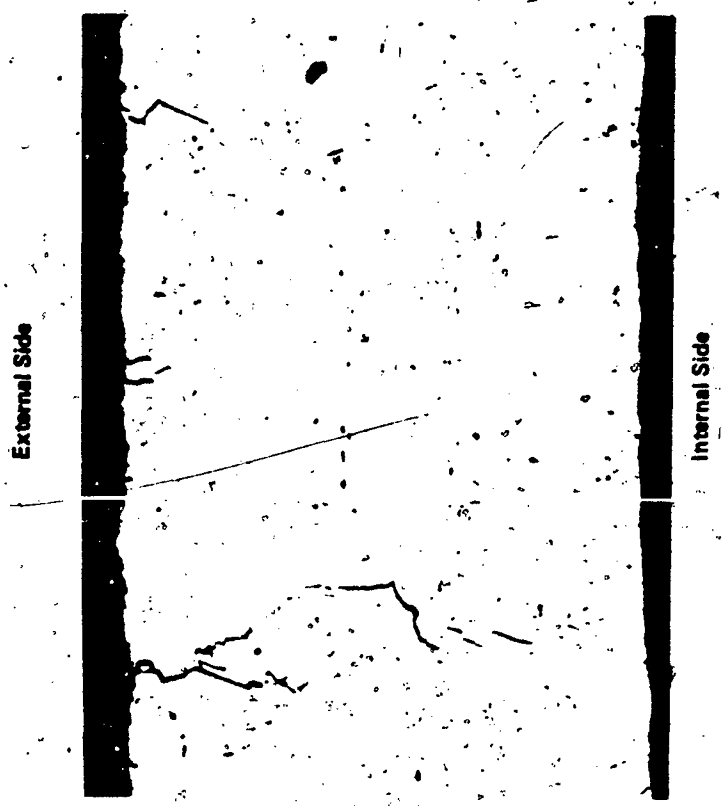


Figure 6. Unetched. 100X.

External Side

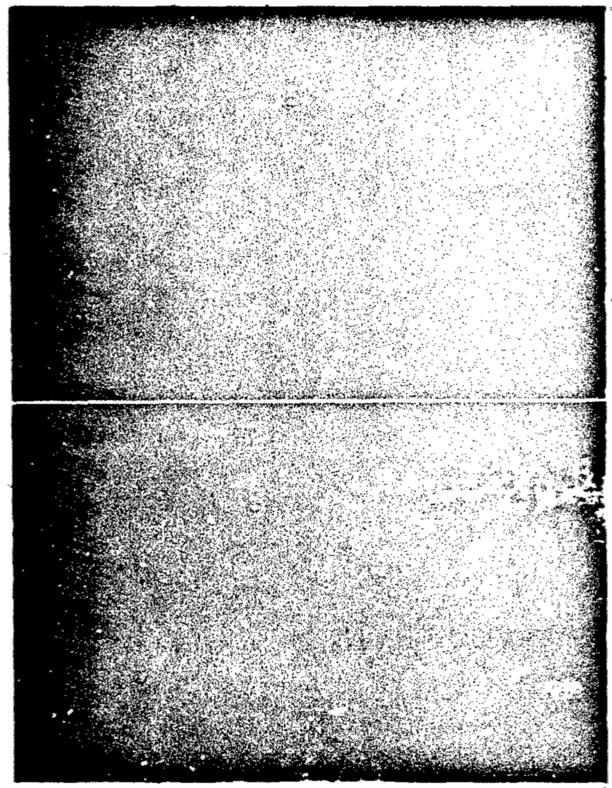


Figure 7. 301 SS (Etched). 200X

LABORATORY TEST REPORT	Report Nr. -10	Date 26 Jan 70
Requesting Organization (Symbol and/or Name) RPRO	Name of Requester Lt Mears	Phone Number 32515

Sample, Test or Project

305805FRJ

Work Required

Failure analysis of 15-gallon tank (No. 11) and connected aluminum tubing

TEST DATA

I. MATERIAL: (a) AM-350 stainless steel tank

(b) 6061-T6 aluminum alloy tubing with 4043 aluminum alloy weld filler (manually TIG welded).

II. BACKGROUND: The tank was loaded with chlorine pentafluoride (CPF) on 13 November 1968.

CPF leaked from the tank at the close-out weld near the top burst disc assembly on 3 April 1969 (Figs. 10 & 15)

The leak was repaired and checked.

The tank was loaded half full with CPF on 14 August 1969.

CPF leaked again at the close-out weld near the top burst disc assembly on 15 September 1969, so the tank was removed from the test program.

III. CONCLUSIONS: CPF escaped through the close-out weld leak and virtually emptied the tank. The CPF combined with the test chamber atmospheric moisture (79% relative humidity) to form HF. The HF corroded the tank exterior and etched the aluminum tubing on top of the tank. Corrosion pitting progressed through the wall from the outside to the inside of the tank.

It is certified that this is an accurate report of test or analysis performed by the Chemical & Materials Branch.

Performed By		Signature of Approving Official
Name GENE WHITING, AMN	Name R. SCHALOW, Major	Name JOHN T. NAKAMURA
Name	Name	Title Chief Analytical Section
		Chemical & Materials Branch mcb

RPL Form 31

IV. TESTS AND RESULTS:

A. AM-350 stainless steel tank: The tank was leak checked with helium at 25 psi. Two tiny holes were found on the side of the tank. (Figs. 1, 3, 7, 8, and 9) The exterior surface of the tank was pitted and generally covered with light-orange to brown corrosion products. (Figs. 1, 3, 5, 7, 8, & 9). X-ray analyses identified these products to be primarily $CrF_3 \cdot 3H_2O$. The larger of the two holes in the tank wall had a drip pattern stain on the inside. (See Fig. 2) This is an indication that corrosion took place from the outside toward the inside of the tank.

As noted by the relative cleanness, the interior surface of the tank was not pitted or otherwise corroded. (Figs 4 & 6). Corrosion products (elevated particulates) on the interior side near the two detected holes gave evidence of about ten additional sealed holes. (Figs. 4 & 6). X-ray methods of analysis did not clearly indicate the identity of these products.

B. Close-out weld: The close-out weld was oriented such that it faced downward onto the top of the tank. (Fig. 7). Corrosion of the close-out weld was localized. In figs. 10, 11, & 15 a "plug" of weld material appears missing. Two tongue-like protrusions can be seen directed toward the inside of the tube. The weld material could have been locally corroded away after a leak had developed in the weld region. The origin of this hypothetical leak is unknown. However, it is felt that the most probable cause was by pitting corrosion at a crack or crevice in the weld area of the interior surface of the tube. (Fig. 12)

Corrosion of the exterior wall of the aluminum tubing only occurred near the hole left by the close-out weld. The interior wall of the aluminum tube was not corroded. (Fig. 14)

The grain structure of the 6061-T6 tube is shown in Fig. 14. The grain structures of 6061 and 4043 in the close-out weld region are shown in Figs. 12 and 13. Note the accentuated laboratory etching of grain boundaries in the 6061-T6 tube near the weld. Diffusion to the grain boundaries probably occurred during welding. These diffusion aggregates have thus been eaten up by the lab etchant.

An entire cross-section of the tube at the hole of the close-out weld is shown in Fig. 11.

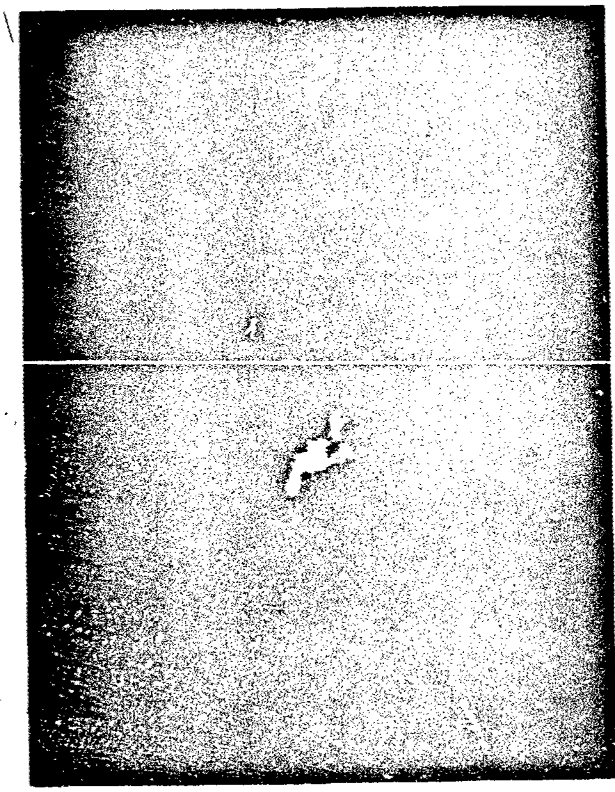


Figure 1. Hole in tank wall as seen from outside. 10X

Figure 2.

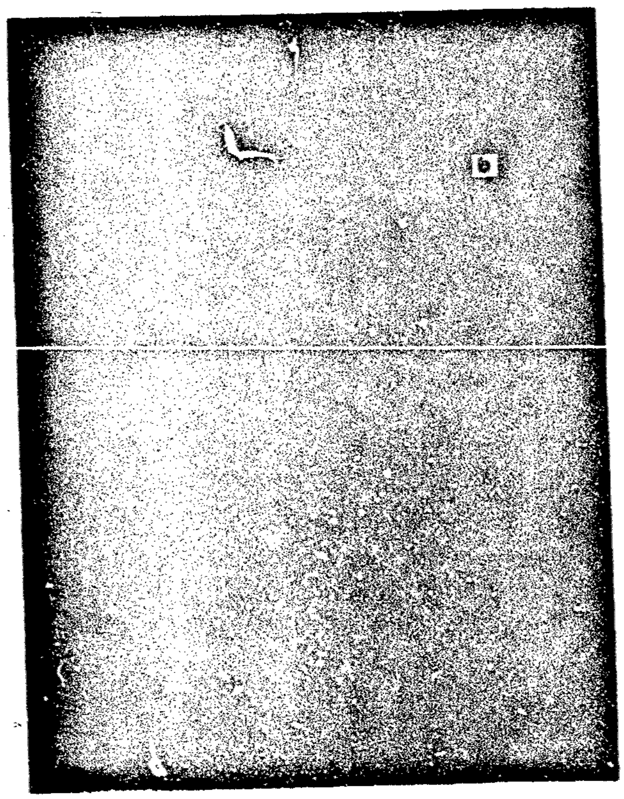


Figure 3. Holes in tank wall as seen
b. from outside. 10X

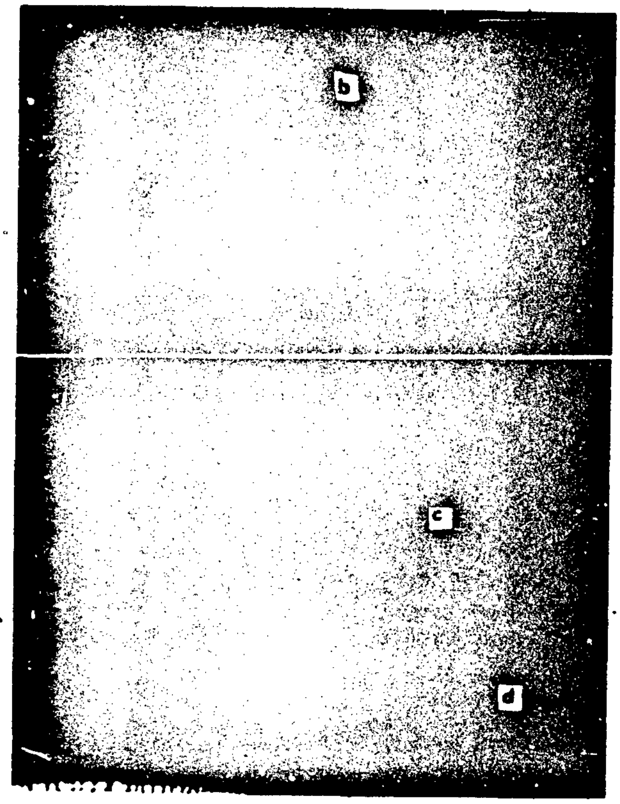


Figure 4. Holes in Figure 3 as seen from inside. 10X

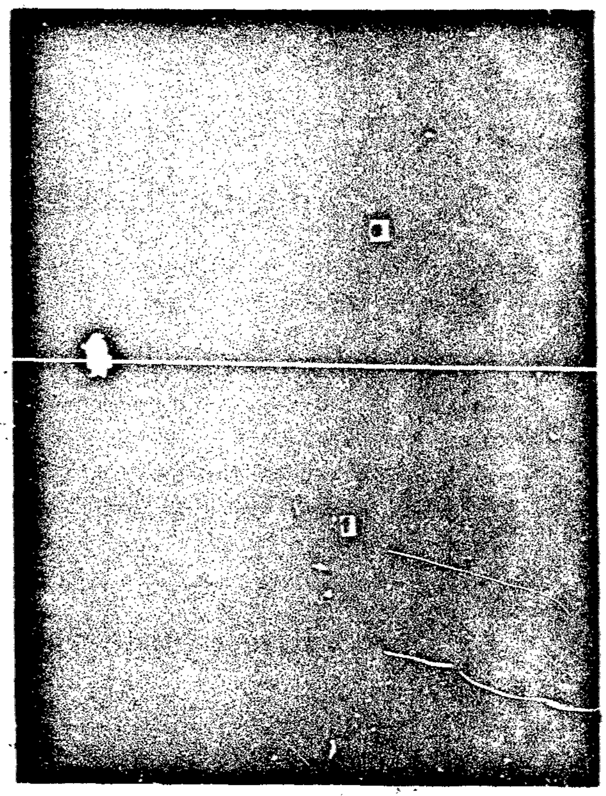


Figure 5. Holes in tank wall as seen from outside. 10X

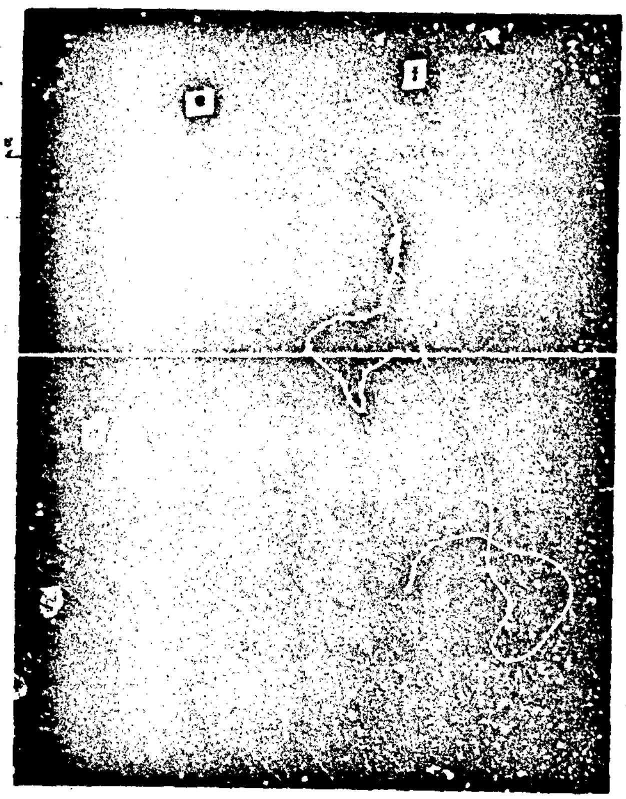


Figure 6. Holes in Figure 5 as seen from inside. 10X

Figure 7.

Figure 8.

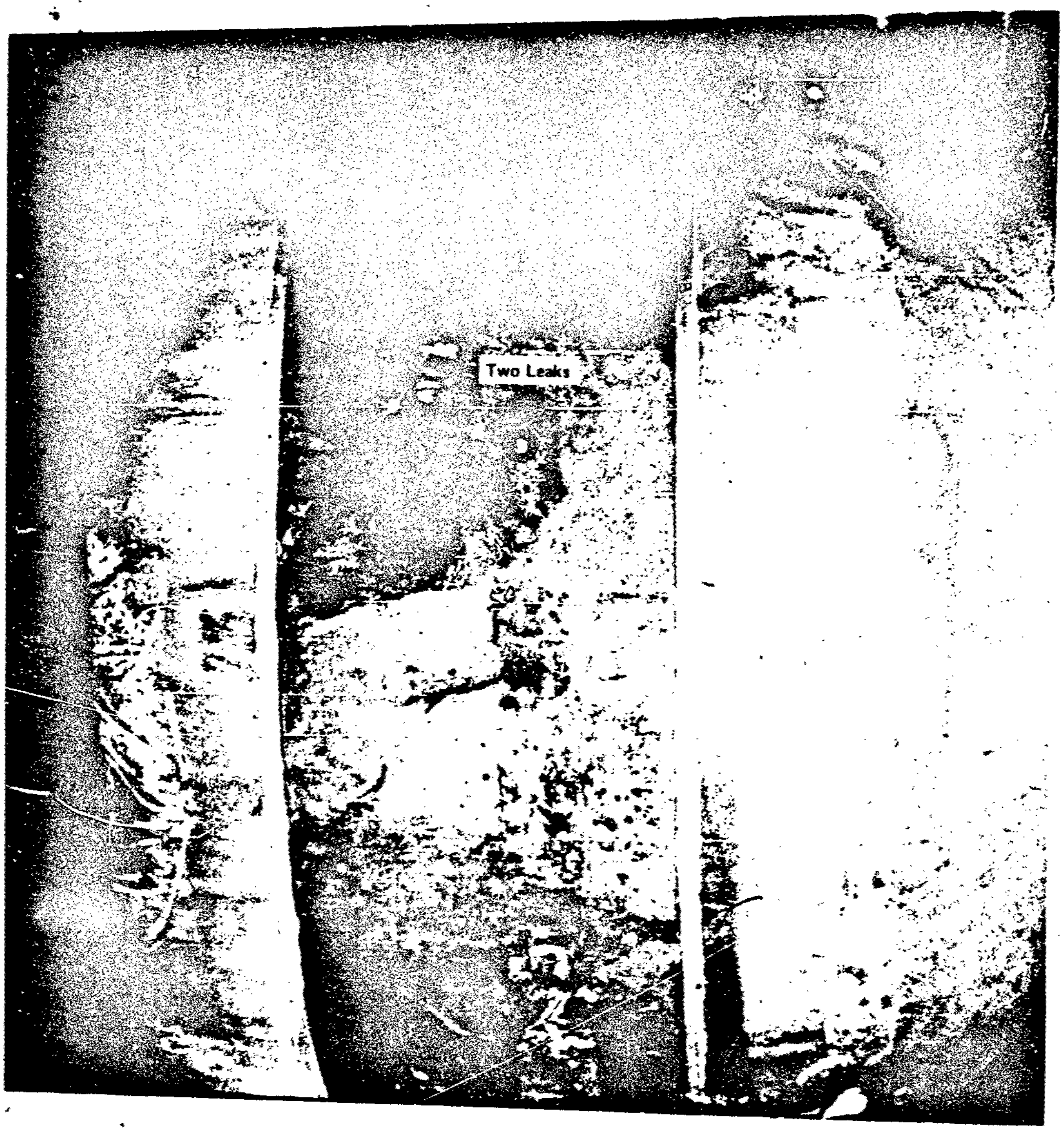


Figure 9.

Figure 10. Hole through close-out weld.

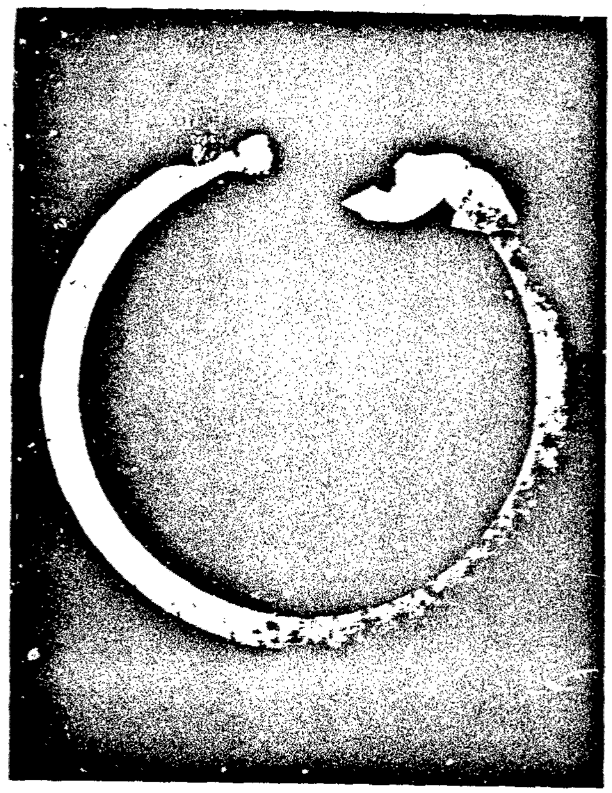


Figure 11. Cross-section of tube at close-out weld (Etched) 6X

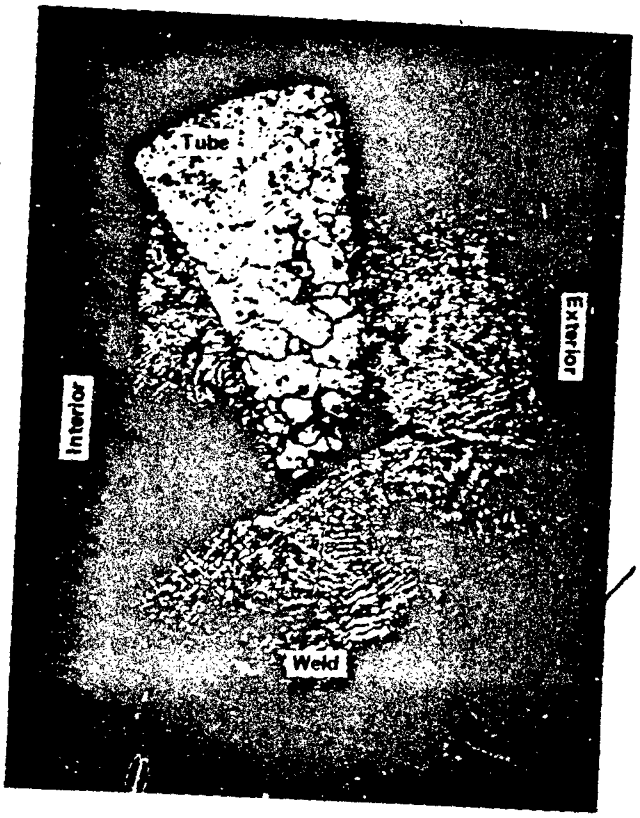


Figure 12. Weld Region of close-out showing grain structures (Etched) 41X

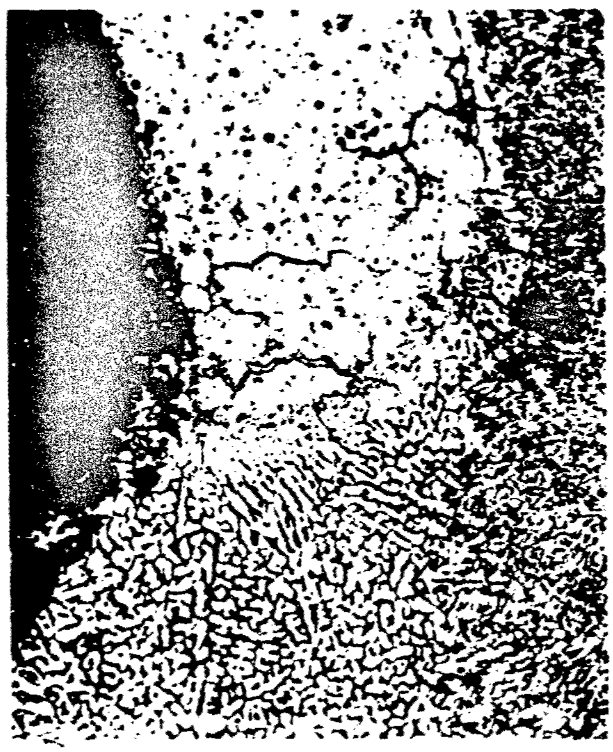


Figure 13. Weld region of close-out weld showing grain structures (Etched) 81X

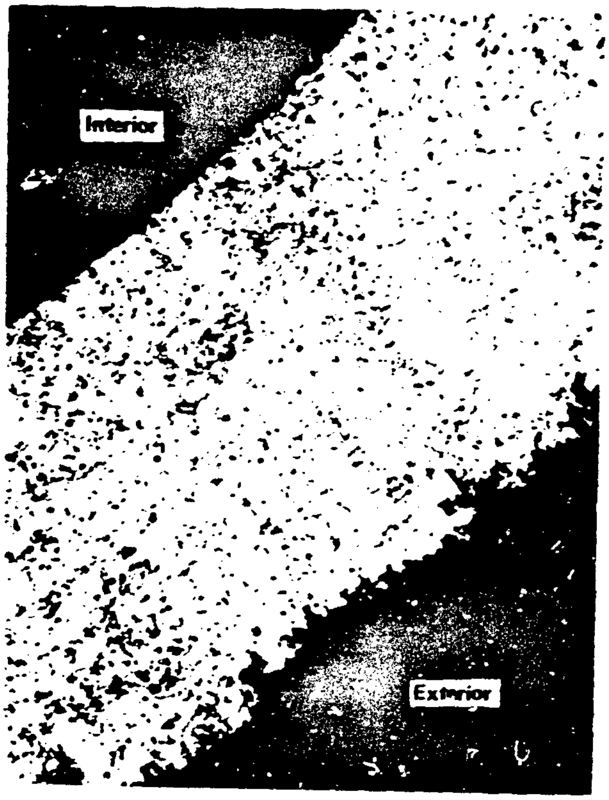


Figure 14. Aluminum tubing.
(Etched) 81X

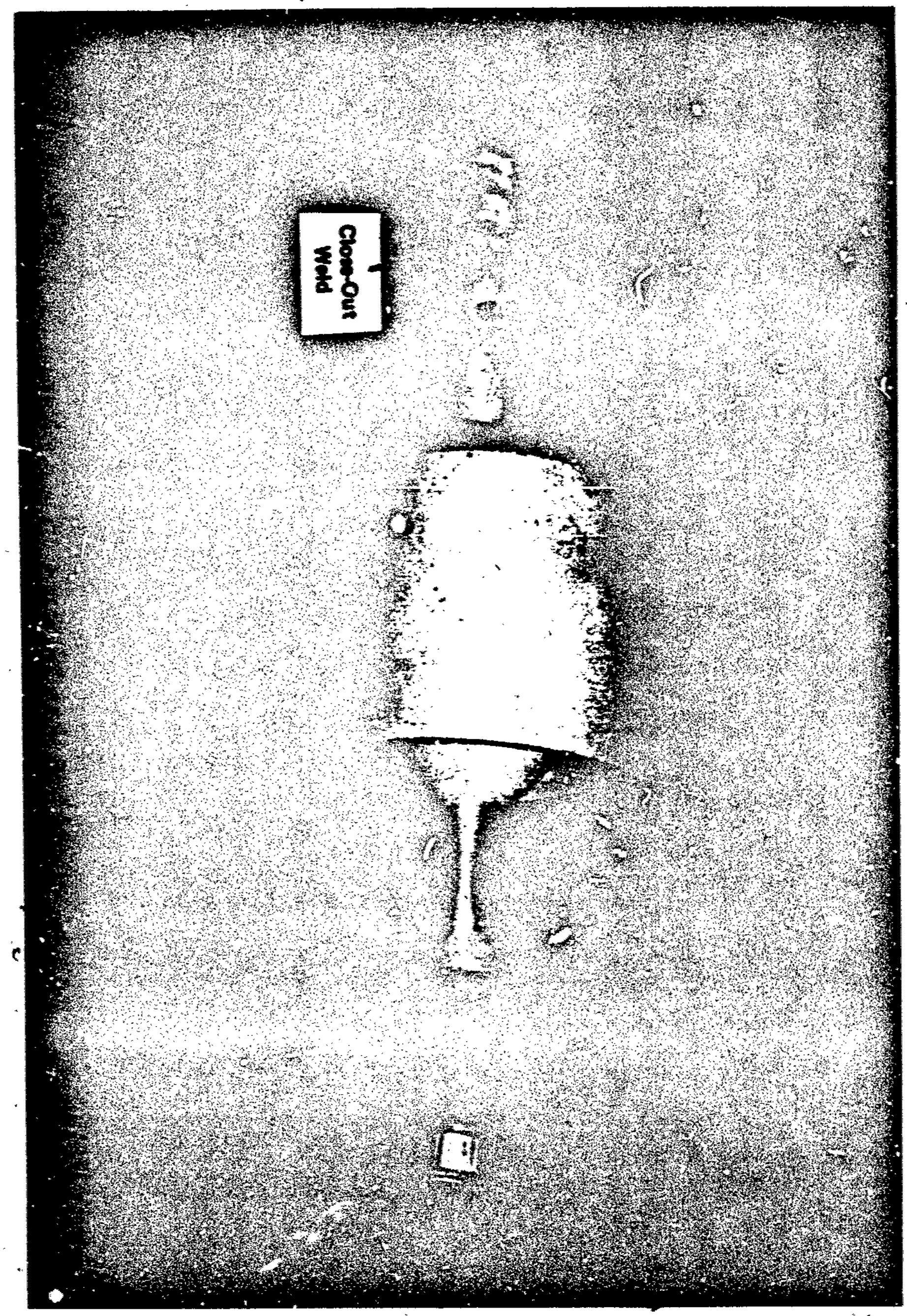


Figure 15. Burst Disc Assembly

LIQUID PROPELLANT TANK STORABILITY EVALUATION - INTEGRATED SYSTEM DESIGN AND BUILD-UP

The possible application of prepackaged liquid missile systems to current weapon system concepts stimulated a requirement to demonstrate the zero-maintenance storability of complete packaged liquid missile feed systems. Long periods of storage could affect the functional performance and reliability of each feed system element. Deteriorous effects include corrosion, fatigue, and chemical decay. Such effects would result in hazardous leakage, loss of pressurant or propellant, impaired pressurization device actuation, unsatisfactory expulsion of propellant, impairment of valves and pressure switches, and damage to other component operation.

To properly demonstrate the resistance of feed systems to deterioration, assembled packaged test systems were designed and fabricated. These systems were specifically designed from hardware which had established short-term reliability to determine if they could withstand typical service environments of temperature, humidity, vibration, and pressurization over representative periods of storage. The evaluation was restricted as to the variety of materials and fabrication processes for storable propellant tankage and components.

Demonstrating zero-maintenance storability and extended reliability of components typical of installation in ballistic missile propellant systems were designed on a small-scale basis using flight-type, off the shelf designed components modified to eliminate all non-metals, except in squibs and electrical actuators. The systems were assembled utilizing automatic tube welding equipment, separable connectors, and hand welds where necessary.

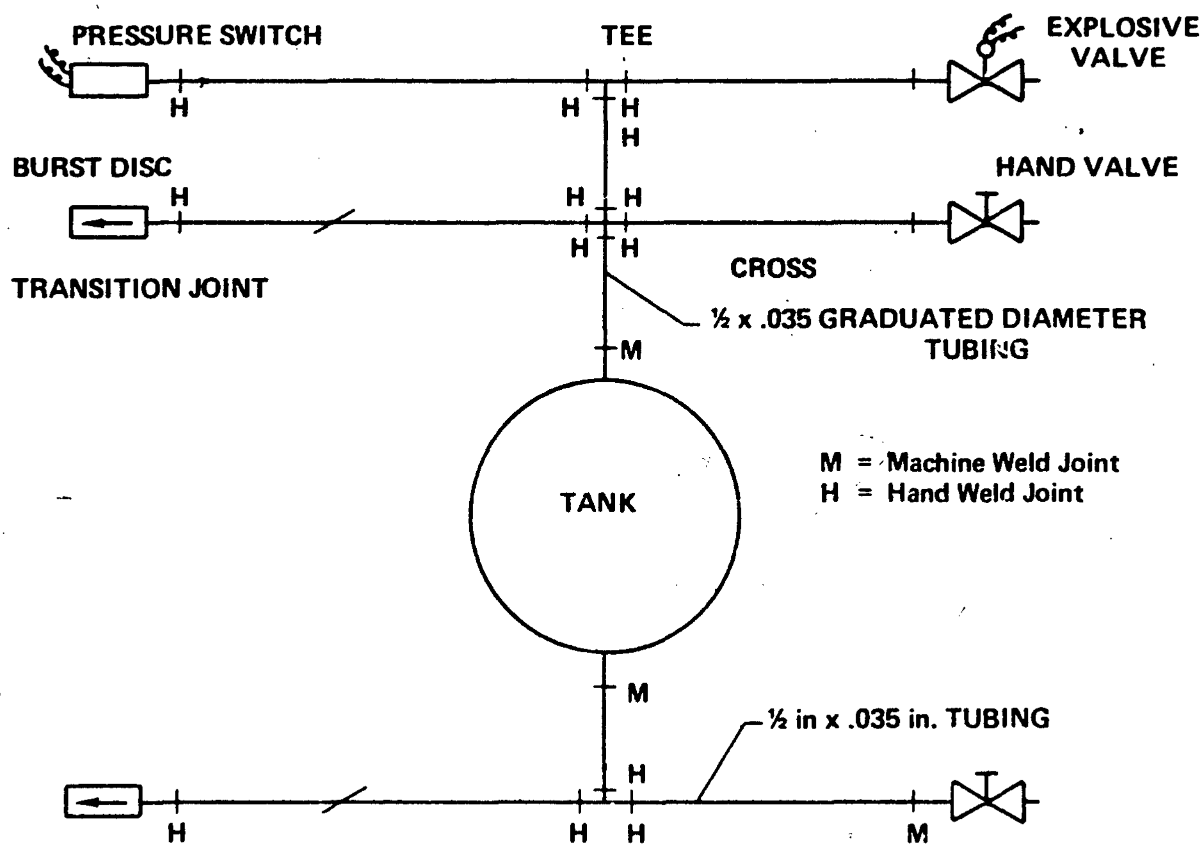
There were four basic types of system designs: all welded stainless steel, all welded aluminum, separable connector stainless steel, and separable connector aluminum assemblies.

APPENDIX NO. III

INTEGRATED SYSTEM DESIGN & BUILDUP

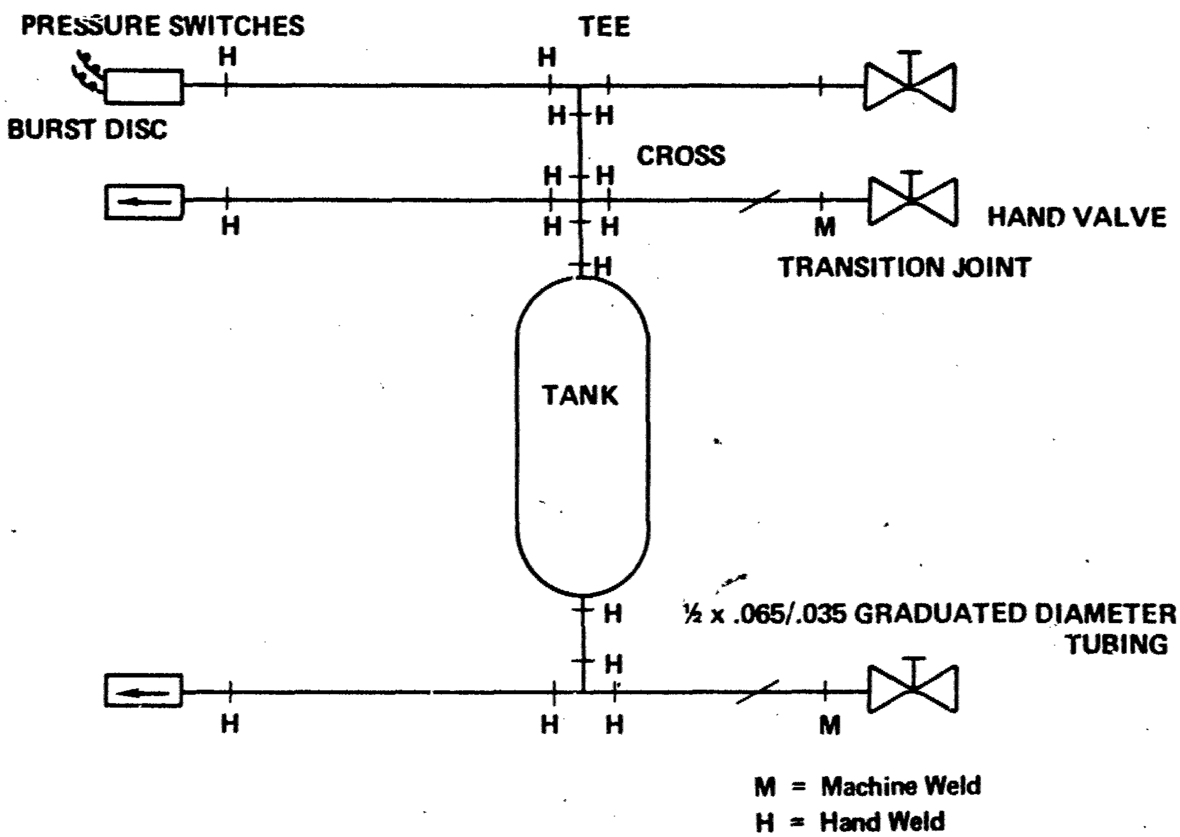
ALL WELDED STAINLESS STEEL SYSTEMS
ClF_5 & N_2O_4 APPLICATION

PART	MATERIAL
Tank	AM350
Transition Joint	347SST/6061-T6 Al
Pressure Switch	347 SST
Explosive Valve	347 SST
Burst Disc (100 psig)	6061-T651 Al
Burst Disc (120 psig)	6061-T651 Al
Hoke Hand Valve	347 SST
1/2 in x .035 in Tubing	347 SST
1/2 in x .035 in Cross	347 SST
1/2 in x .035 in Tee	347 SST
1/2 in x .065 in/,035 in Tubing	347 SST



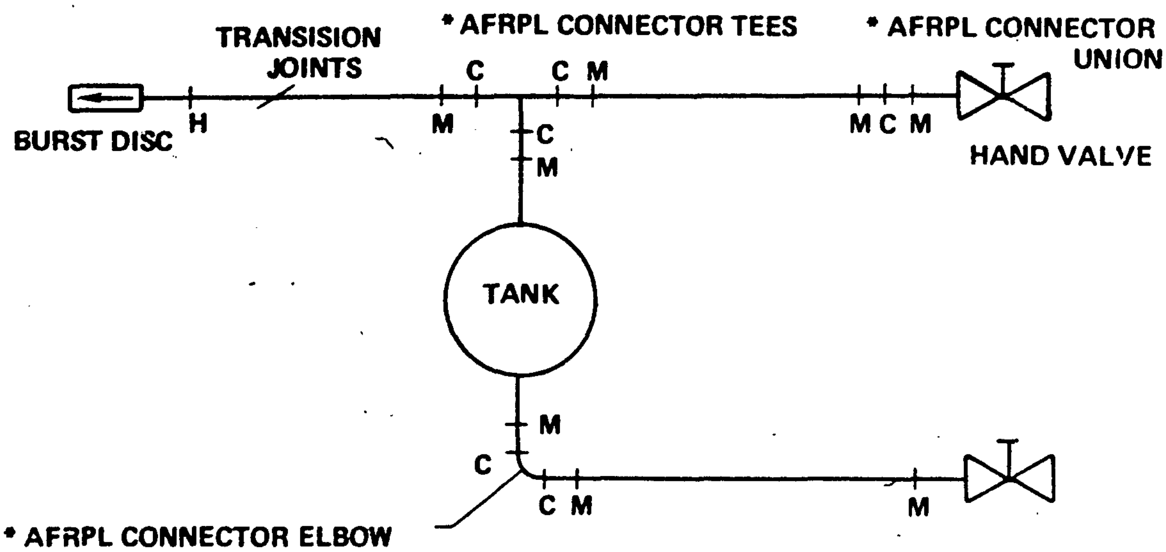
ALL WELDED ALUMINUM SYSTEMS
ClF_5 & N_2O_4 APPLICATION

PART	MATERIAL
Tank	6061-T6 Al
Transition Joint	347 SST/6061-T6 Al
Pressure Switch	347 SST
Explosive Valve	6061-T6 Al
Burst Disc (100 psig)	6061-T6 Al
Burst Disc (120 psig)	6061-T6 Al
Hoke Hand Valve	347 SST
1/2 in x .035 in Tubing	6061-T6 Al
1/2 in x .035 in Cross	6061-T6 Al
1/2 in x .035 in Tee	6061-T6 Al
1/2 in x .065 in Tubing	6061-T6 Al



SEPARABLE CONNECTOR STAINLESS STEEL SYSTEM
N_2O_4 APPLICATION

PART	MATERIAL
Tank	347 SST
Hoke Hand Valve	347 SST
Burst Disc	6061-T6 Al
Transition Joint	347 SST/6061-T6 Al
AFRPL (Connector Elbow (MS27866--8)	347 SST
Bobbin Seal (Unplated)	304-L SST
Plain Flange (MS27853-08)	CRES AMS5646
.035 Plain Flange (MS27853-08)	CRES AMS5646
Nut (MS27852-08)	A-286
AFRPL Connector Tee (MS27863-08)	AMS4127 Al Alloy
.065 in Plain Flange (MS27853-08)	CRES AMS5646
Plain Flange (MS27858-08)	AMS4127 Al Alloy
Bobbin Seal (MS27860-08)	AMS4127 Al Alloy
.035 in AFRPL Connector Union (MS27851-08)	

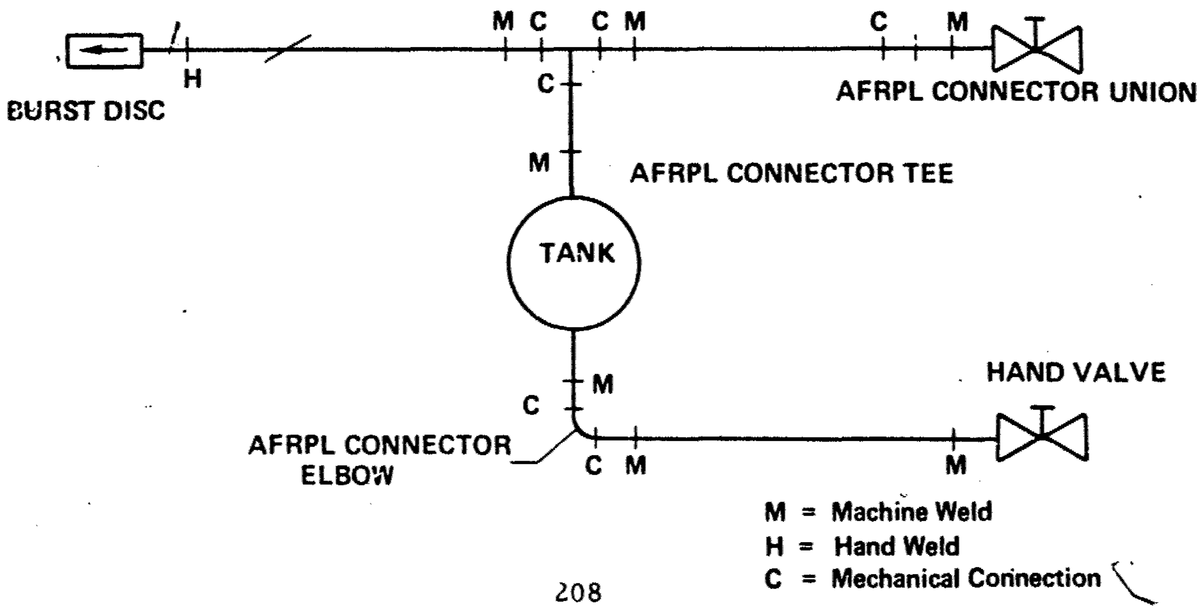


M = Machine Weld
H = Hand Weld
C = Mechanical Connection

* Used Unplated Bobbin Seal in Connectors

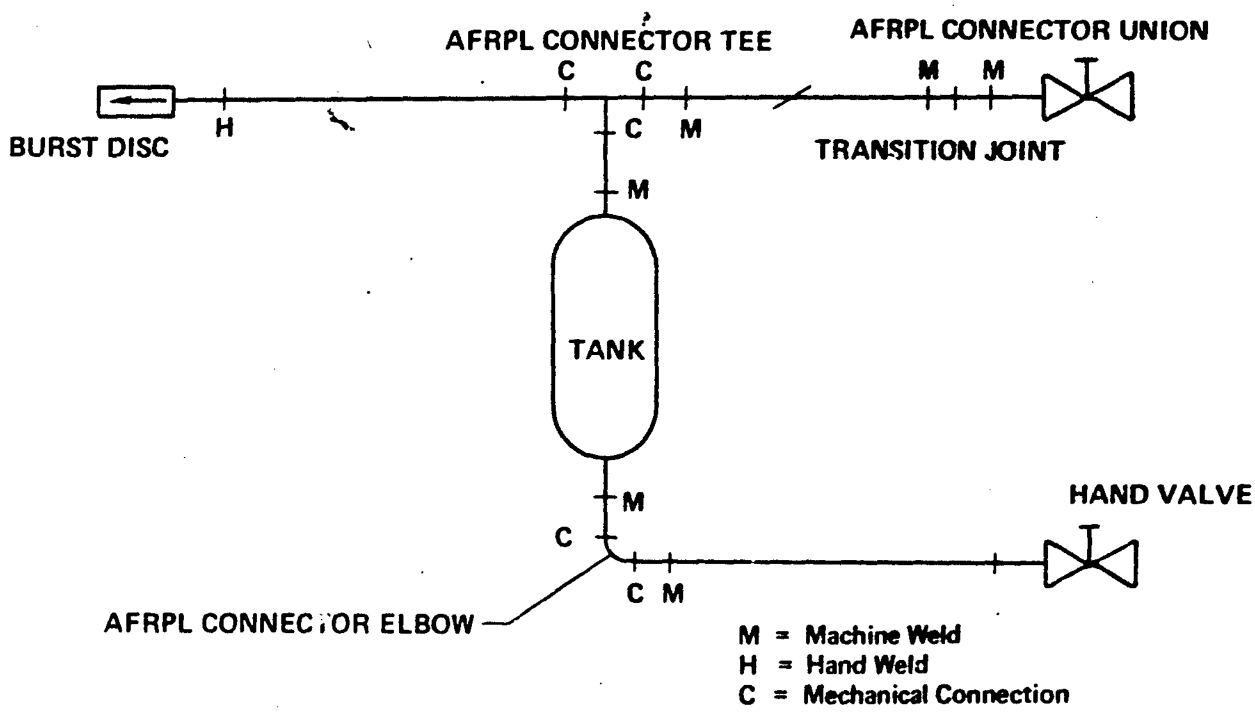
SEPARABLE CONNECTOR STAINLESS STEEL SYSTEM
ClF_5 APPLICATION

PART	MATERIAL
Tank	347 SST
Hoke Hand Valve	347 SST
Burst Disc	6061-T6 Al
Transition Joint	347 SST/6061-T6 Al
AFRPL Connector Elbow (MS27866-08)	347 SST
Bobbin Seal (Ni Plated - MS27855-08)	304 L
Plain Flange (MS27853-08)	CRES AMS5646
.035 Plain Flange (MS27853-08)	CRES AMS5646
Nut (MS27852-08)	A-286
AFRPL Connector Tee (MS27864-08)	AMS4127 Al
.065 in Plain Flange (MS27853-08)	CRES AMS5646
Plain Flange (MS27858-08)	AMS4117 Al Alloy
Bobbin Seal (MS27860-08)	AMS4127 Al Alloy
.035 in AFRPL Connector Union (MS27851-08)	



SEPARABLE CONNECTOR ALUMINUM SYSTEMS
ClF_5 & N_2O_4 APPLICATION

PART	MATERIAL
Tank	2219 Al
Hoke Hand Valve	347 SST
Burst Disc	6061-T6 Al
Transition Joint	347 SST/6061-T6 Al
AFRPL Connector Elbow (MS27862-08)	AMS4127 Al Alloy
Bobbin Seal (MS27860-08)	AMS4127 Al Alloy
Nut (MS27857-08)	AMS4117 Al Alloy
AFRPL Connector Tee (MS27863-08)	AMS4127 Al Alloy
.065 in Plain Flange (MS27858-08)	AMS4117 Al Alloy
.035 in Plain Flange (MS27858-08)	AMS4117 Al Alloy
.035 in AFRPL Connector Union (MS27856-08)	



The hardware which was procurred under contract was fabricated by the following manufacturers:

Tanks (Stainless Steel)	Convair
Tanks (Aluminum)	Martin
Hand Valve	Hoke
Burst Disc	Calmec
Transition Joint	Nuclear Metals, Inc.
Explosive Actuated Valves	Pyronetics, Inc.
Pressure Switches	Hydra-Electric Co.
AFRPL Connector Union	Scientific Advances, Inc.
AFRPL Connector Elbow	Scientific Advances, Inc.
AFRPL Connector Seals	Scientific Advances, Inc.

After the systems were assembled, they were LOX cleaned and leak checked with a helium mass spectrometer. All systems were leak tight with no leaks detected greater than 1×10^{-7} scc He/sec. All welds were X-rayed and found to be acceptable for the system's operating pressure of 80 psig and propellants.

AUTHOR BIOGRAPHY

Lt Mears was graduated from Virginia Polytechnic Institute in 1966 with a bachelor of science degree in Mechanical Engineering. Lt Mears has been a project engineer in the Subsystems Branch of the Liquid Rocket Division since April 1967. During his three years at the Air Force Rocket Propulsion Laboratory, Lt Mears has been project engineer on both in-house test programs and contractual efforts dealing with tankage, and expulsion and orientation devices for liquid propellants.

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Rocket Propulsion Laboratory Edwards, Calif. 93523	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP N/A

3. REPORT TITLE
Long-Term Storability of Propellant Tankage and Components.
Interim Report No. 1

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Interim Report, March 1969 through February 1970

5. AUTHOR(S) (First name, middle initial, last name)
Richard B. Mears, Lt, USAF

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
May 1970		2

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) AFRPL-TR-70-43
b. PROJECT NO. 305805 FRJ	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT
This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFRPL (RPOR-STINFO), Edwards, California 93523

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	See Block 1

13. ABSTRACT Air Force weapons systems require long-term maintenance-free storage, preferable under uncontrolled environmental conditions. Liquid propulsion system components must be capable of satisfactory operation after years of highly reactive propellants while retaining the propellant without leakage under severe ambient conditions of temperature and relative humidity. Oxidizer leakage caused by improper component design and severe ambient storage conditions has presented serious operational problems.

The Air Force Rocket Propulsion Laboratory (AFRPL) has initiated a program to investigate the storability of liquid system components and tankage under extreme conditions of relative humidity and temperature. A variety of system components and tankage materials are being evaluated for long-term storability with storable liquid rocket fuels and oxidizers. Storage conditions are 85°F temperature and 85% relative humidity for oxidizer systems and 70 to 150°F temperature for fuel systems. The propellants under test are N_2O_4, ClF_5, and MHF-5. Tankage materials under test are various alloys of aluminum, steel and titanium.

The results of almost 3 years of testing on a representative number of tankage materials have indicated that leakage of propellant can occur as a result of improper weld joint design, inadequate quality control in fabrication and inadequate acceptance leakage testing. Factors which can contribute to the development of oxidizer leakage are a high ambient relative humidity (>30%) and stress corrosion cracking susceptibility of the tank material in combination with the propellant and trace quantities of foreign compounds/elements in the propellant.

DD FORM 1473

Unclassified
Security Classification

Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Propellant storage						
Environmental effects						
Propellant leakage						
Corrosion						
Oxidizer Leakage						
Stress corrosion						
Intergranular corrosion						
Hydrazine blend storage						
Packaged propulsion system storability						
Stress corrosion cracking						
Rocket propellants						
Leak detection						
Propellant tank quality control						

Unclassified
Security Classification