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LONG-TERM STORABILITY OF PROPELLANT TANKAGE

H. M. WHITE, 2ND LT, USAF

TECHNICAL REPORT AFRPL-TR-71-20

MARCH 1971

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

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AFRPL-TR-71-20

LONG-TERM STORABILITY OF PROPELLANT TANKAGE

H.M. White, 2nd Lt, USAF

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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 areas 1-40 and 1-36. The project engineer is Lt Howard M. White and the time period covered by this report is from February 1970 through December 1970. This report supplements AFRPL-TR-69-82, "Long-Term Storability of Propellant Tankage and Components," and AFRPL-TR-70-43, " Long-Term Storability of Propellant Tankage and Components, Interim Report No. 2."

This technical report has been reviewed and is approved.

JERRY N. MASON, Capt, USAF
Chief, Subsystems Branch
Liquid Rocket Division

ABSTRACT

This report is the third in a series of progress reports for the Packaged Systems Storability Test Program conducted at the Air Force Rocket Propulsion Laboratory. Tentative conclusions regarding storability as affected by environment, propellant chemistry, weld procedures, and stress levels are presented.

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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. 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 leading fluid, dissipates into the atmosphere and does nothing to aggravate the leakage. If the relative humidity is on 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 storable fluorinated oxidizers such as ClF_3 and ClF_5, an analogous process would be expected with hydrogen fluoride as the hydrolysis product.

In the past, the selection of materials for system 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.

*Figures and tables are presented sequentially beginning on pages 12 and 15, respectively.

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. 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. No. 2014-T-6 aluminum is compatible with nitrogen tetroxide (N_2O_4 MIL-P-26539B); 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 testing), 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 presents 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. Coupons placed in propellant will demonstrate basic compatibility. Completely fabricated tanks must be loaded with propellant and tested to determine which tankage materials 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 "Package System Storability" to support 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.

The test systems are divided into three groups (Reference 2). The tanks discussed in this report are those which have been added during the period of time covered by this report.

Group I - Small Container Testing

There were no additions to this group during this reporting period.

Group II - Representative Tankage

Tanks added to this group are those reported in the first progress report as Phase II tankage (Reference 3). These tanks were reported in Group III in the previous progress report (Reference 2), but an examination of the fluid components associated with these tanks indicated that the components were not suitable for resumption of testing. The decision was made to test the tanks above as representative tankage in this group.

Group III - Expulsion and Feed System

Tanks added to this group are three 30-inch-diameter rolling diaphragm tanks (approximately 1100 pounds of N_2O_4) fabricated by the Reaction Motors Division of the Thiokol Chemical Corporation (Figure 2). Also added were two 28-inch-diameter, conospheroid tanks fabricated by Arde, Inc., (Figure 3). All tankage was loaded with N_2O_4 (MSC-PPC-2A specification).

SECTION III

TEST FACILITIES

The oxidizer facility reported in the first progress report (Reference 3) is presently being modified by the addition of an MSA "billionaire" toxic vapor detector and an automatic shutdown system for the environmental equipment. These modifications will prevent the extensive test article and facility damage encountered when large amounts of propellant are introduced into the humid environment of the oxidizer test facility (Reference 2).

The fuel facility (Reference 2) is also being modified by the installation of an MSA "billionaire"; however, no automatic shutdown for this facility is planned.

The fuel facility is presently inactive pending replacement of the present flammable insulation with a fire retardant variety. This facility is expected to be in operation by July 1971.

SECTION IV

PROCEDURES

The procedures established for testing of fuel and oxidizers (References 2 and 3) have remained essentially unchanged. The only change has been the purchase of MSA "billionaire" toxic vapor detectors to monitor the test facilities for a buildup in toxic vapor concentration. It is hoped that the addition of these instruments will prevent the type of damage that has resulted in the past when large amounts of propellant have been introduced into the test facility (Reference 2).

Also, the policy has been established that all cxidizer test articles added to the test program shall be painted to protect them from attack in the event of a leak in some other test article. This policy was initiated with the test articles removed as a result of the ClF_5 leak in September 1969.

SECTION V

DISCUSSION OF RESULTS
(FEBRUARY 1970-DECEMBER 1970)

During this period, a total of five tanks and one integrated tankage/expulsion system were subjected to post-test failure analysis. These reports are presented in the Appendix of this report.

The tanks that formally comprised Phase II (References 2 and 3) were returned to testing without the associated fluid components. It was determined that a large percentage of the components was damaged beyond repair, and since significant data could be obtained from the storage of the tankage alone, it was decided to return the tankage to testing. The components associated with the tankage are at present being salvaged or subjected to post-test analysis. A decision on whether to continue with storage testing of the components will be made at a later date.

A summary of results to date is presented in Tables I, II, and III.

SECTION VI

CONCLUSIONS

The Package Systems Storability Program has accumulated a significant amount of storage time, and sufficient data have been collected so that tentative conclusions and recommendations can be made. The conclusions and recommendations are based on failure analysis reported in earlier progress reports and general observations made during the program.

It has been observed that double heat welds which occur at start/stop points and at weld intersections or at weld repairs lead to a high incidence of hot short cracks. This condition is especially prevalent in manual repair welds because of poor control of heat input. This would lead to the conclusion that quality control criteria for acceptance of welds be made stringent enough, especially in the case of repair welds, to preclude the acceptance of defects.

This program has demonstrated the influence of propellant chemistry on storability. In five separate cases, tankage fabricated from titanium experienced failure due to stress corrosion cracking (at stress levels below the generally accepted threshold for stress corrosion cracking) in 1 month or less when loaded with "brown" N_2O_4 (MIL-P-26539 Specification Grade). At the present time, there are three titanium test articles with more than a year of storage time. These are loaded with "green" N_2O_4 (MSC-PPC-2A Specification Grade). The principal difference between the two is the presence of NO (0.4 to 0.8 percent) in the MSC-PPC-2A grade of N_2O_4. In one instance, it was noticed that because of poor tank design, excess stress levels existed in the short transverse direction of the material. This led to tank failure due to stress corrosion cracking, indicating that tank design must be carefully scrutinized to preclude significant stress levels along sensitive grain orientations.

The presence of trace amounts of tungsten resulted from inclusions produced by the tungsten inert gas (TIG) or heliarc, welding process. This in turn resulted in the rapid development of weld leakage in welded tube joints used with ClF_5. This is because the tungsten was removed in the form of gaseous tungsten fluoride, and it in turn resulted in a leak path. This process is somewhat analogous to intergranular corrosion. The problem of tungsten in fluoride service points up the need for strict quality control and the rejection of any weld showing traces of tungsten inclusions.

SECTION VII

RECOMMENDATIONS

In line with the conclusions presented in the preceding section of this report, tentative recommendations can be made with regard to improving the storability characteristics of liquid rocket propellants.

It is recommended that quality control systems be reviewed to preclude the possibility of the acceptance of tankage with poor design characteristics (i.e., excess stress along sensitive grain orientations) or questionable welds (i.e., hot short, cracks in double pass regions, or trace inclusions).

It is also recommended that in the case of titanium tankage loaded with N_2O_4, the propellant have sufficient NO content so as to prevent the initiation of stress corrosion cracking.

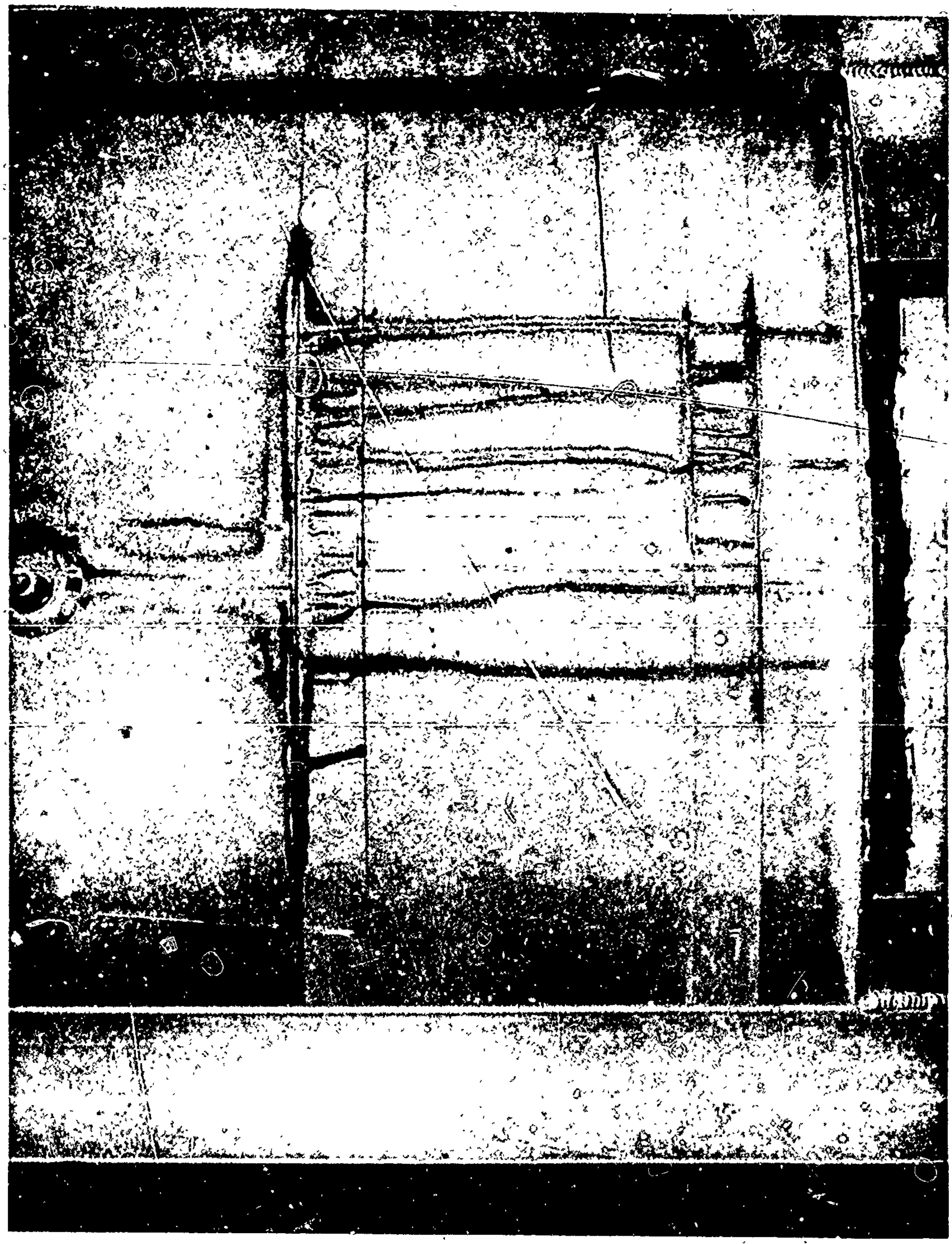

Figure 1. Hygroscopic Action of N_2O_4 Vapor

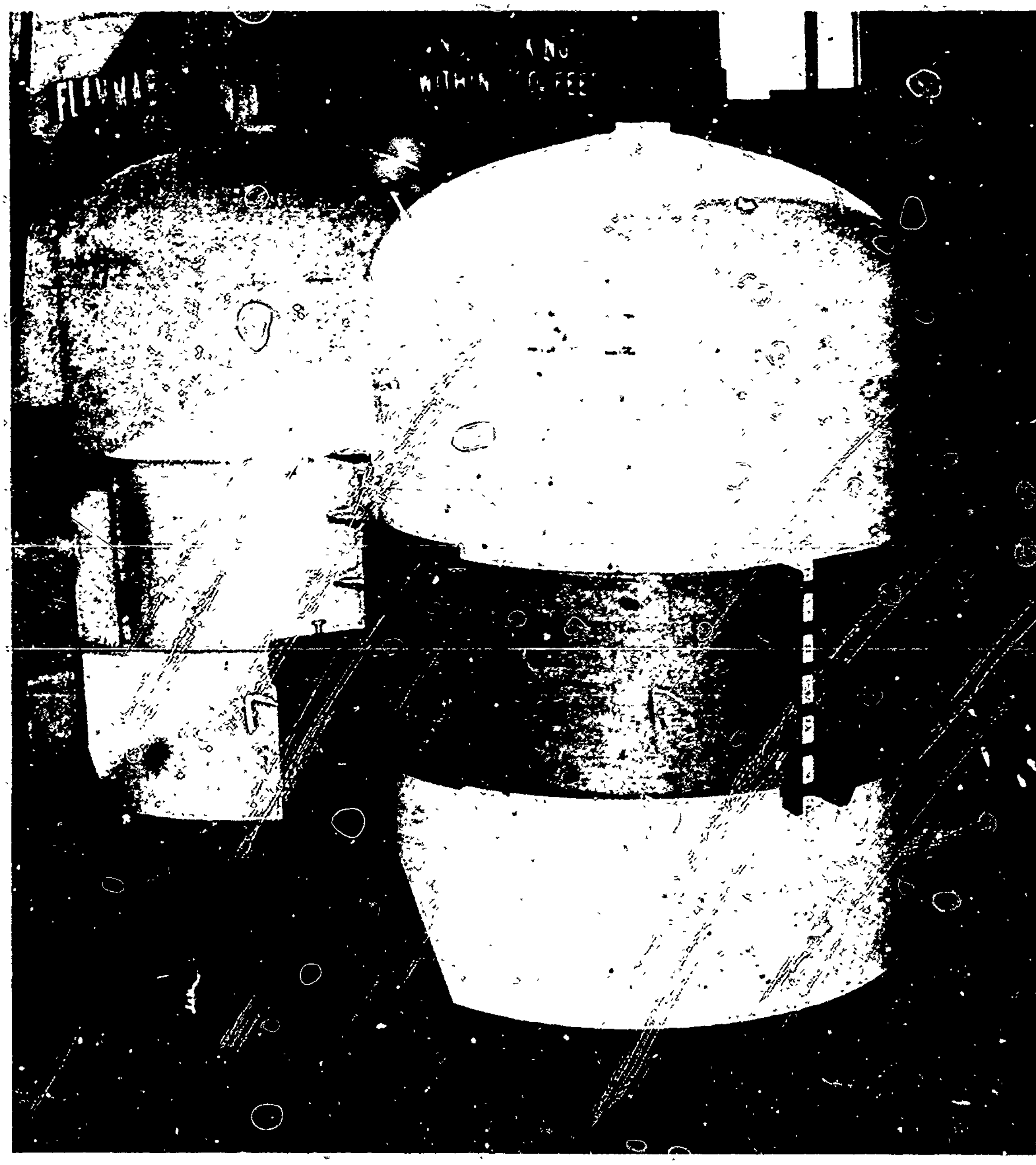

Figure 2. Thiokol 30-Inch Rolling Diaphragm Tanks

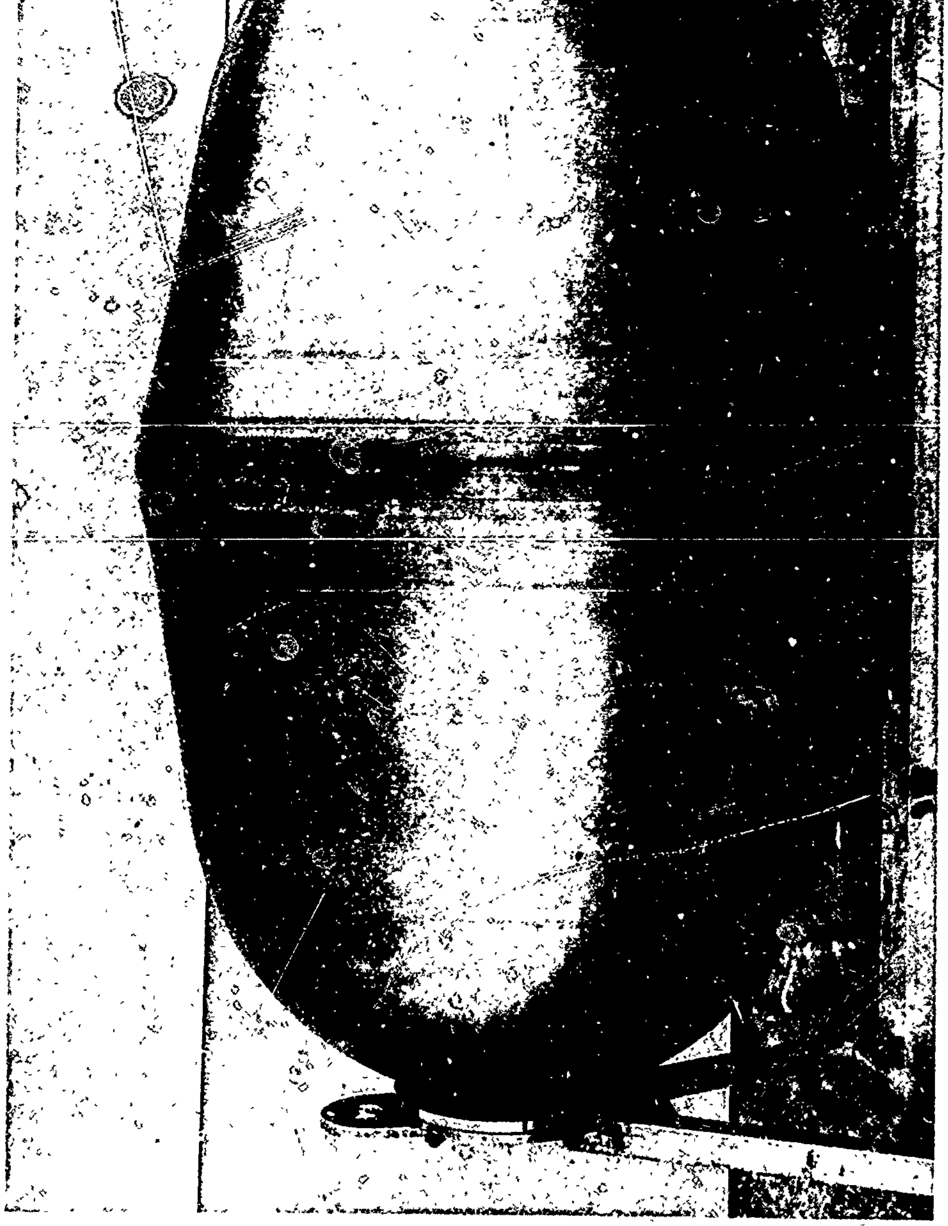

Figure 3. Arde Conospheriod Tank

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-inch	4	2014-T6	9-7-66	9-12-66	5
N_2O_4*	3- x 6-inch	1	2014-T6	1-3-67	1-5-67	2
N_2O_4*	3- x 6-inch	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	8	2014-T6	9-7-66		In test
ClF_5	Alcoa 1-qt	4	2014-T6	9-7-66	2-27-70	655
ClF_5	Alcoa 1-qt	1	2014-T6	9-7-66	5-22-67	57

*MIL-P-26539 Specification N_2O_4

TABLE I. GROUP I - SUMMARY OF RESULTS (Continued)

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	3	5456-T6	9-7 66		In test
ClF_5	Alcoa 1-qt	1	5456-T6	9-7-66	2-27-70	655
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		

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-T6	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

* MIL-P-26539 Specification N_2O_4

** MSC-PPC-2A Specification N_2O_4

TABLE II. GROUP II - SUMMARY OF RESULTS (Continued)

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	AM1350	1-3-67	10-24-67	294
ClF_5	GD/C	1	AM1350	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	11-28-68	12-29-70	460
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_2O_4**	Bullpup	3	2014	6-10-68		In test
N_2O_4**	ULPR	2	2219	5-21-68		In test

** MSC-PPC-2A Specification N_2O_4

TABLE IIIA. GROUP III - SUMMARY OF RESULTS

Propellant	Number	Pressure System	Expulsion System	Test Initiated	Test Terminated	Days In Test
MHF-5	2	LGG	RD	6-9-67		In test
MHF-5	2	SGG	RD	6-9-67		In test
MHF-5	1	H	RD	6-9-67		In test
MHF-5	2	LGG	ST	6-9-67		In test
MHF-5	2	SGG	ST	6-9-67		In test
MHF-5	2	H	ST	6-9-67		In test
N_2O_4	2	LGG	RD	5-22-67		In test
N_2O_4	2	SGG	RD	5-22-67		In test
N_2O_4	2	H	ST	5-22-67		In test
ClF_5	1	SGG	RD	6-20-67	10-7-67	20
ClF_5	1	H	ST	8-4-67	10-23-67	80
ClF_5	1	H	ST	8-4-67	8-18-70	1110
N_2O_4*	1	LGG	RD	5-10-67	12-20-70	941
N_2O_4*	1	LGG	RD	5-10-67		In test
N_2O_4*	1	SGG	RD	5-10-67		In test
N_2O_4*	1	H	RD	5-10-67		In test

* MSC-PPC-2A Specification N_2O_4

NOTE: LGG = liquid gas generator; SGG = solid gas generator; H = stored helium; ST = surface tension; RD = rolling diaphragm.

TABLE IIIB. GROUP III - SUMMARY OF RESULTS

Propellant	Tank	Quantity	Expulsion Device	Material	Test Initiated	Test Terminated	Days In Test
N_2O_4*	Arde	2	Ring-stiffened diaphragm	AISI 301 Cryo Form	7-3-69		In test
N_2O_4*	Arde	2	Ring-stiffened diaphragm (conospheriod)	AISI 301 Cryo Form	12-23-70		In test
N_2O_4*	Thiokol	3	Rolling diaphragm	Shell-200 maraging Diaphragm-1100-0	1-5-71		In test
ClF_5	Arde	2	Ring-stiffened diaphragm	AISI 301 Cryo Form	7-3-69		In test

* MSC-PPC-2A Specification N_2O_4

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

AUTHOR'S BIOBRAPHY

H. M. WHITE, 2nd Lt, USAF

Lt White was graduated cum laude from Lehigh University in 1969 with a Bachelor of Science degree in Chemical Engineering.

He has been a Project Engineer in the Propulsion Subsystems Branch of the Liquid Rocket Rocket Division of the Air Force Rocket Propulsion Laboratory since October 1969. At the laboratory, Lt White is responsible for the areas of storability, pressurization and expulsion of liquid rocket propellants.

APPENDIX

LABORATORY TEST REPORT
PROJECT 305805FRJ

LABORATORY TEST REPORT	Report Nr. -258	Date 2 Dec 70
Requesting Organization (Symbol and/or Name) RPRPC	Name of Requestor Lt. H. White	Phone Number 32282

Sample, Test or Project

305805FRJ

Work Required

ClF_5 Tank Failure Analysis

1. MATERIALS: 2219-T852 Al alloy tank bulkheads } 2319 Al alloy weld filler
2219-T31 Al alloy tank cylinder }
1100-0 Al alloy inlet & outlet burst discs
Ni relief valve rupture disc
6061-T6 Al alloy bobbin seal
300 series stainless steel tubing & plumbing fixtures.

2. BACKGROUND: Storage of ClF_5 in a 15-gal. Al alloy tank for 3 1/2 years at 85°F, 85% relative humidity was terminated due to severe corrosion of the relief valve rupture disc and scattered surface corrosion of other plumbing components.

3. CONCLUSIONS: ClF_5 entered the plumbing via tiny holes corroded through the periphery of the inlet burst disc and the bobbin seal foil. (Figs 1-5), The holes in the inlet burst disc (Fig. 7) were probably the result of a thin cross-section, about 0.002 in. in thickness, which contained voids (Fig. 6), and slight corrosion by the ClF_5.

4. TESTS & DISCUSSION: The ClF_5 leaked from the tank into the plumbing and subsequently corroded through the relief valve rupture disc. The exterior of the tank and its plumbing had a pock mark pattern indicative of ClF_5 spraying from the relief valve. The interior of the entire system generally exhibited no corrosion. Two exceptions were: a spring-loaded pin in the regulator had a thin, tenacious, yellow film on its tip; and the surface of the cavity directly behind the relief

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 G. Whiting, A1C	Name	Name H. REDE, Capt.
Name	Name	Title Chief Metallurgical Unit
		Chemical & Materials Branch

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valve rupture disc was corroded. With a stereo-microscope at 70X, three tiny corrosion passageways were detected at the periphery of the inlet burst disc,(Figs 1-4) and none on the outlet burst disc. Metallographic examination (up to 400X) of a cross-section of the inlet burst disc revealed voids in the metal (Fig. 6). The voids were apparently large enough in the rupture region (∿ .002" thick) of the disc so as to effect pitting and reduce the cross-section for holes to penetrate. A deposit on the outward side of the bobbin seal foil (Fig. 5) conclusively indicated that the ClF_5 leaked from the tank outward into the plumbing.

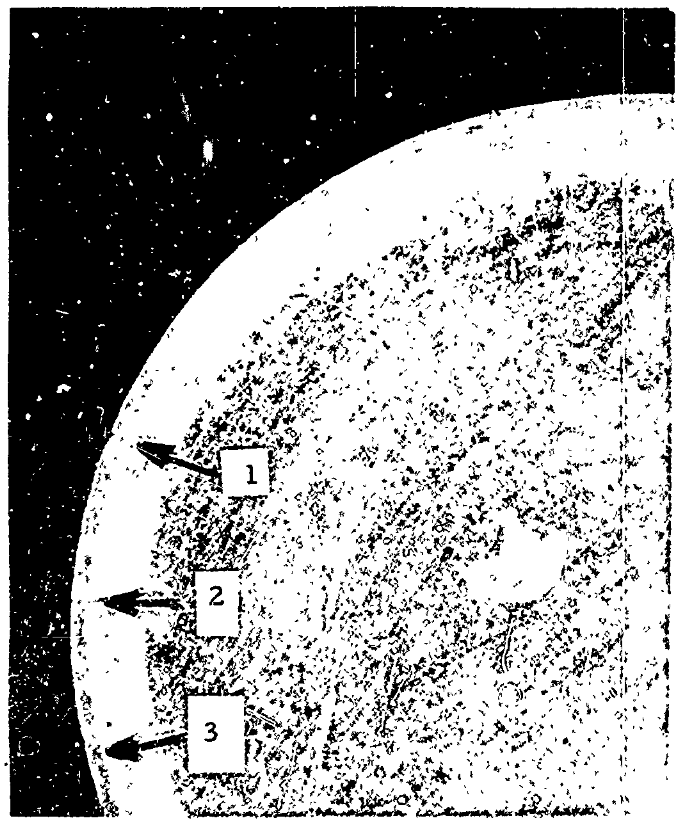

Figure 1. Leaks at Rim of Inlet Rupture Disc (5X)

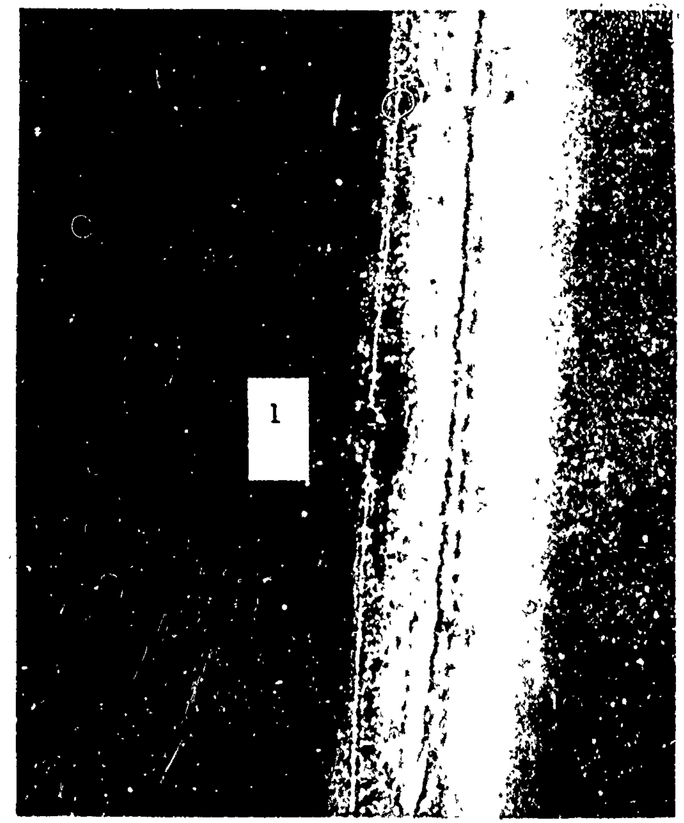

Figure 2. Leak at Rim of Inlet Rupture Disc (70X)

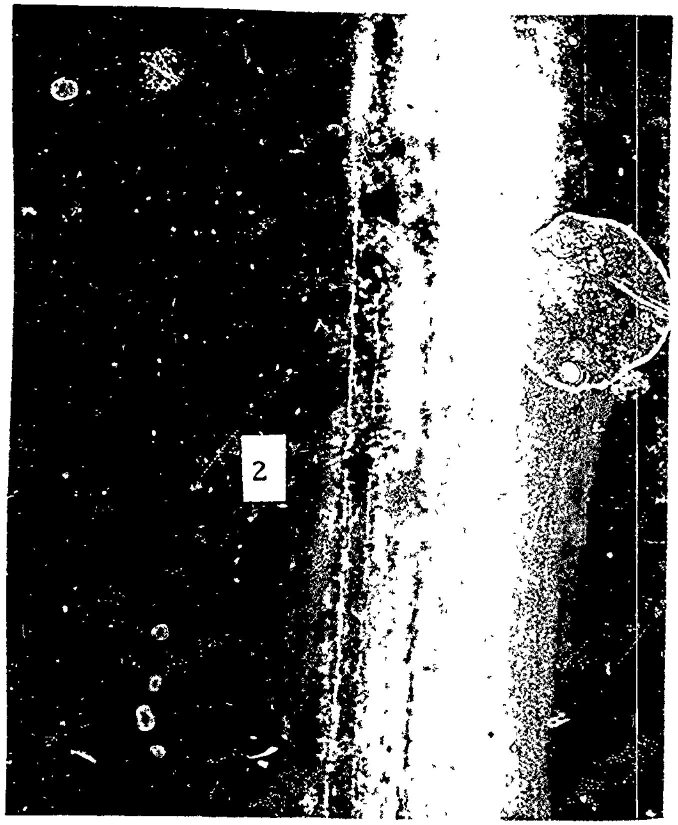

Figure 3. Leak at Rim of Inlet Rupture Disc (70X)

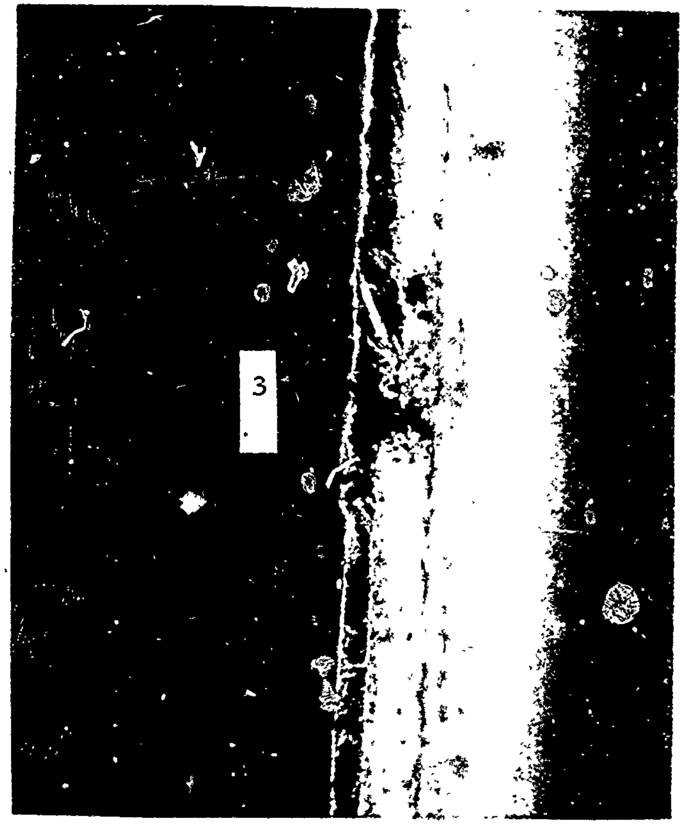

Figure 4. Leak at Rim of Inlet Rupture Disc (70X)

Figure 5. Deposit at Leak at Outward Side of Bobbin Seal (35X)

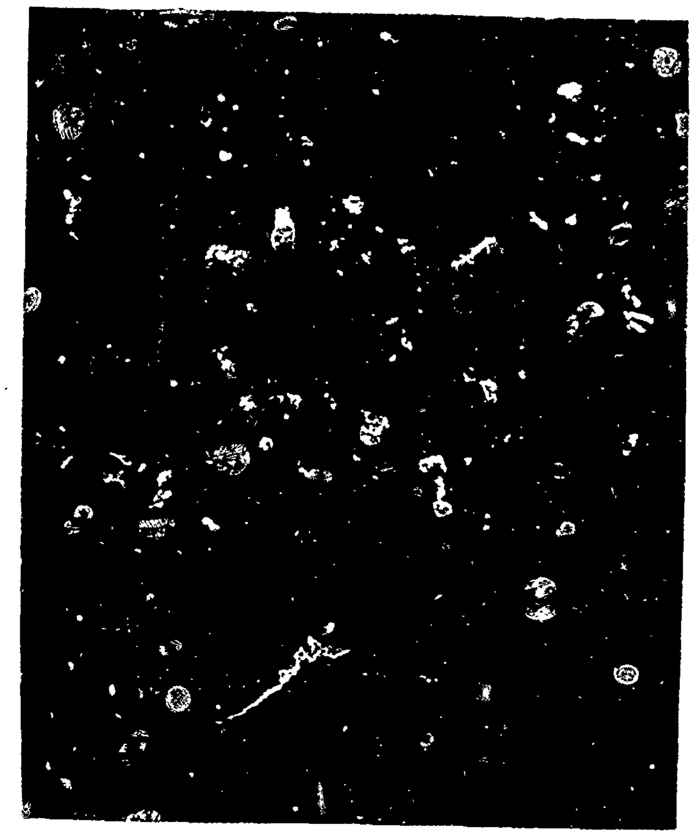

Figure 6. Cross Section of Inlet Rupture Disc Showing Voids (Light Areas) Near Periphery

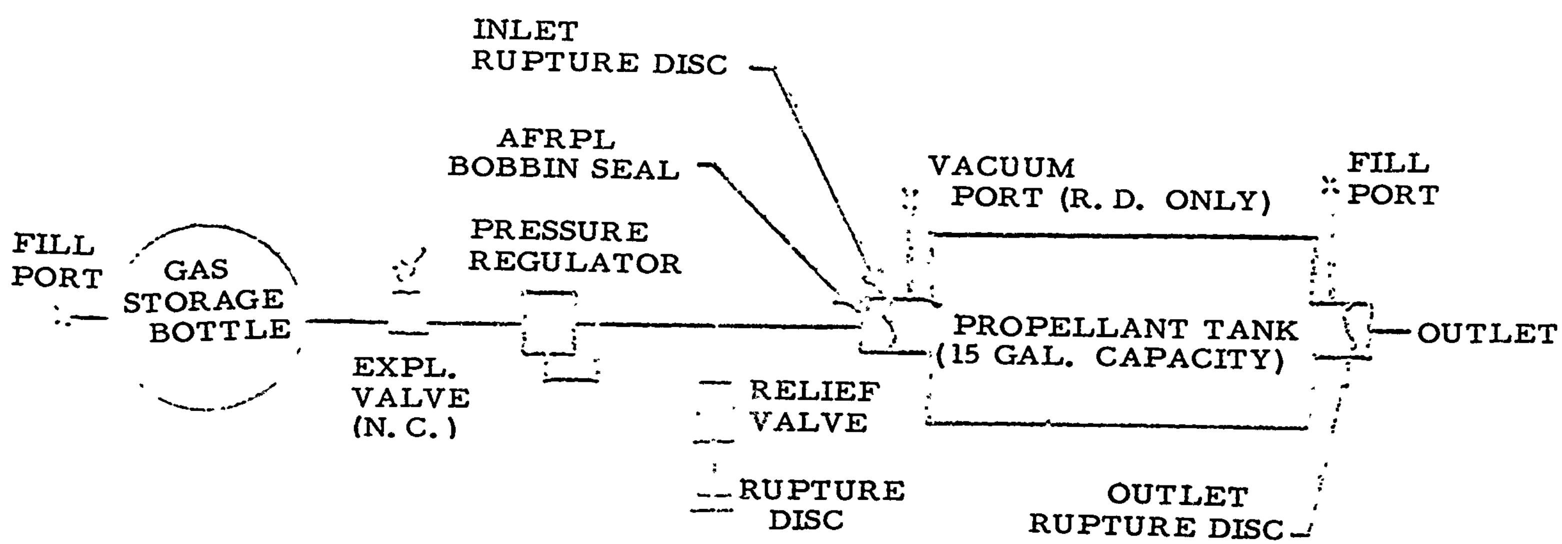

Figure 7. Stored Gas Device

LABORATORY TEST REPORT

Report No.	Date
156	16 Dec 70
Name of Requestor	Phone Ext.
Lt. White	32282

Requesting Organization (Symbol and/or No.)

RPF

Sample, Test or Project

305805 FRJ

Work Required

Failure Analysis on four 2014-T6 Al Alloy Tanks.

I. MATERIAL: 2014-T6 Al Alloy Tanks with 4043 aluminum alloy weld filler metal.

II. BACKGROUND: Tanks numbered 9, 73, 75 and 77 stored ClF_5 for 655 days before tank #75 developed a leak at the top boss weld area (Fig. 1). The other tanks were removed from test due to existing cracks (Fig. 2) at both the top and bottom boss weld areas.

III: CONCLUSIONS: Tank #75 failed as a result of intergranular corrosion at the top boss weld area. Intergranular corrosion existed on the other three tanks although the cracks had not yet progressed through the thickness of the weld bead.

IV: TESTS:

1. MACROEXAMINATION: All of the tanks were lightly etched over their entire external surfaces. Cracks were readily evident at the top and bottom boss welds of all of the tanks (Fig. 2). Tank #75 had a build-up of corrosion products at the top boss weld area. (Fig. 1) The internal surfaces of the tanks were not etched. A through crack (Figs. 4 & 5) was observed in Tank #75 opposite the corrosion products on the external wall. None of the other tanks had through cracks.

2. LEAK CHECK - The tanks were pressurized to 25-30 psi with GN_2 and leak tested with a soap solution. The only tank that leaked was #75 despite the fact that all of the tanks had developed cracks as gross as the one shown in Figs 2 & 3.

3. METALLOGRAPHIC EXAMINATION - Figs 6 & 7 show intergranular corrosion in the girth weld bead of Tank # 75. This type of corrosion was evident in the weld beads of all of the tanks, although corrosion attack was more severe in the top and bottom boss weld areas than in the girth welds.

Figs 8 & 9 show intergranular corrosion in the heat-affected-zone (HAZ) of a girth weld bead of tank #9. It is significant to note that this particular tank, which had not developed any leaks, was suffering corrosion attack from the inside

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 Capt. Rede	Name	Name HECTOR REDE, Capt.
Name	Name	Title Metallurgical Unit
		Chief Chemical & Materials Branch

RPL FORM MAR 68 31

(Fig 8) as well as from the outside (Fig. 9).

4. CORROSION PRODUCT ANALYSIS:

a. X-Ray Analysis - the white corrosion products from Tank #75 were heated to 920°C, then analyzed by x-ray diffraction. The products were identified as α-Al_2O_3, γ-Al_2O_3, and AlF_3.

b. Fluoride Analysis - The external wall of tank #73, which had not developed a leak, was rinsed with water and the washings analyzed for fluorides. This test was undertaken to determine whether HF attack occurred due to adjacent leaking tanks. Approximately 0.4 milligrams of water soluble fluorides were present from one-half of the surface of tank #73. This confirmed that HF attack from some external source had taken place.

V. DISCUSSION: Considerable literature research was undertaken during the analysis of this problem. (1, 2, 3, 4, 5).

Reference 3, reports no. 69/34R, 69/39R and 69/41R are failure analysis reports on 6061 aluminum alloy tanks that stored ClF_5. All three reports state that the cause of failure was external pitting and intergranular corrosion. The external corrosion, the reports state, was caused by ClF_5 from some adjacent leaking vessel which resulted in acid formation on the surface of the particular tank being analyzed.

The cracks (Fig 2) on the four tanks submitted to the Met Lab appear identical to the cracks formed on the 6061 aluminum alloy tanks referenced above. In addition, para. IV (3), (4) of this report describe the same failure mechanism, i.e, intergranular corrosion.

However, reference 1, pgs 296-297, indicates that in some commercial casting alloys, copper imparts moderately high strength and improved machinability, with reduced ductility and lower resistance to corrosion. In addition, the same reference, pg 231, describes the mechanism of intergranular corrosion in aluminum-copper alloys as being due to potential differences between the grain boundary region and the abutting grain bodies. This potential difference is due to (a) regions of solid solution in the grain bodies containing a relatively high amount of copper in solid solution(cathodes), and (b) a narrow band on each side of the grain boundaries that is relatively depleted of copper (anodes). The depletion of copper is due to the "tying-up" of the copper in the form of $CuAl_2$ precipitates at the grain boundary.

It was reported to the Met Lab by the project engineer, Lt. White, that the filler weld material used on the 2014-T6 aluminum alloy tanks was 4043 aluminum alloy. References (1) and (2) both indicate that 4043 aluminum alloy is indeed the best choice for welding 2014. However, Table 1 shows the copper content of 4043 standard (std) and what atomic absorption analysis showed the copper content to be for the different weld beads listed. Note that all of them contain an excess amount of copper relative to the standard. This, plus the fact that intergranular corrosion was taking place, led the author of this report to believe that there might be a deleterious amount of $CuAl_2$ precipitate at the grain boundaries of the weld material. "Deleterious amount" is nebulous terminology in that as far as this author could determine the literature does not provide information as to how much $CuAl_2$ at the grain boundaries would be "too much." Reference (1) pgs 59, 140, characterize aluminum-copper alloys as forming $CuAl_2$

and how the cooling rates and subsequent heat treatments affect the amount of this precipitate at the grain boundaries. As mentioned previously, this precipitate accounts for the mechanism of intergranular corrosion. Although the 4043 aluminum alloy weld is <u>not</u> considered an aluminum-copper alloy, it does have a prescribed amount of copper (0.3%) in it. This amount seems to have been exceeded (see Table 1) in all cases.

In view of the above, Sloan Research Industries, Santa Barbara, California, has been requested to conduct some microprobe analysis work to determine qualitatively and quantatively the precipitates present at the grain boundaries of some 4043 welds cut from the 2014-T6 aluminum alloy tanks submitted. The author feels that this work will confirm whether the failures are due solely to acid attack from previous leaking tanks or if the failure is due to a combination of the latter and excess $CuAl_2$(?) precipitates at the grain boundaries.

<u>NOTE</u>: The microprobe analysis results will be submitted as soon as the report is received from Sloan Research Industries.

TABLE I

SAMPLE	% Cu	% Ca**	% As**	% W
* 4043 STD	0.3	0	0	0
4043 Girth Weld (Tank #75)	1.3	0	0	0
4043 Boss Weld (Tank #75)	0.8	0	0	0
4043 Boss Weld (Tank #9)	1.3	0	0	0
4043 Boss Weld (Tank #73)	0.7	0	0	0
4043 Boss Weld (Tank #79)	1.4	0	0	0

* 4043 Standard has other alloying elements not shown in this table.

** Impurities (Ref. 2)

REFERENCES

1. K. R. Van Horn (ed), Aluminum, Vol. I, ASM, 1967

2. R. M. Evans and D. J. Maykuth, "Weldability of High-Strength Aluminum Alloys," DMIC Memorandum #216, August 22, 1966.

3. R. B. Mears, "Long-Term Storability of Propellant Tankage and Components," Interim Report #1, AFRPL - TR - 70 - 43, May 1970.

4. T. Lyman (ed.), Metals Handbook, Vol. 1, 8th Ed., ASM, 1969.

5. R. H. Greaves and H. Wrighton, "Practical Microscopical Metallography," Science Paperbacks, Chapman and Hall Ltd., 1967.

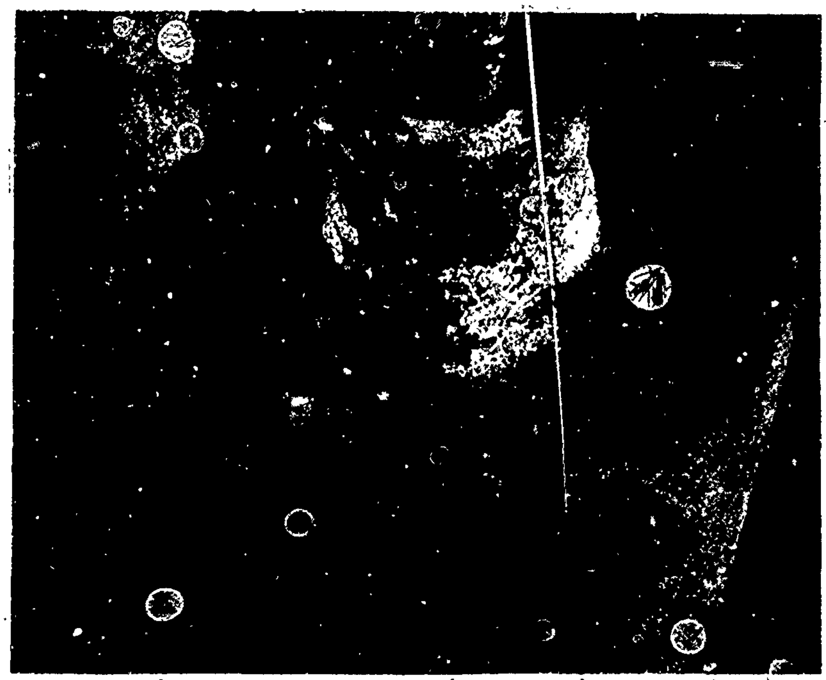

Figure 1. Tank No. 75 (1.5X)

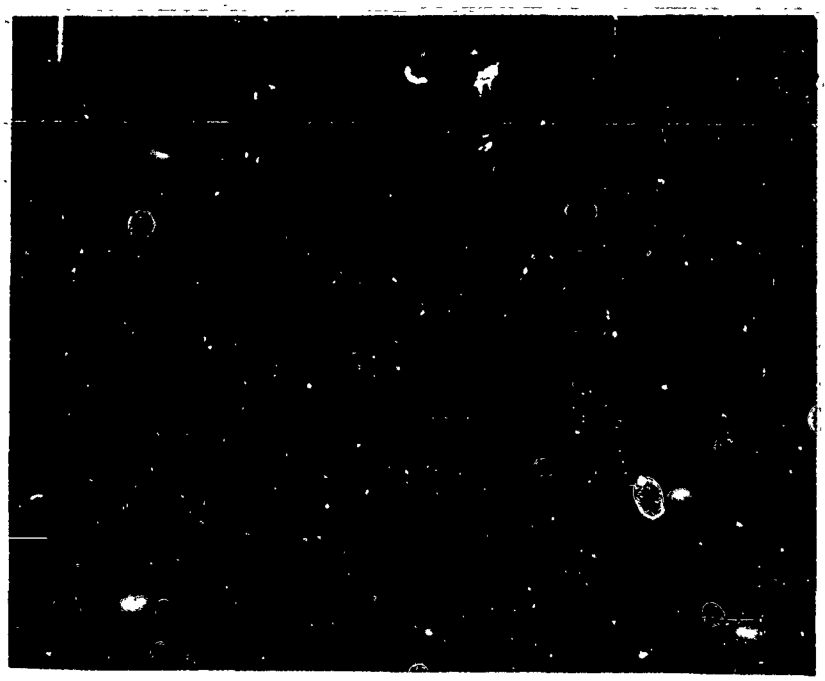

Figure 2. Typical Crack (1.5X)

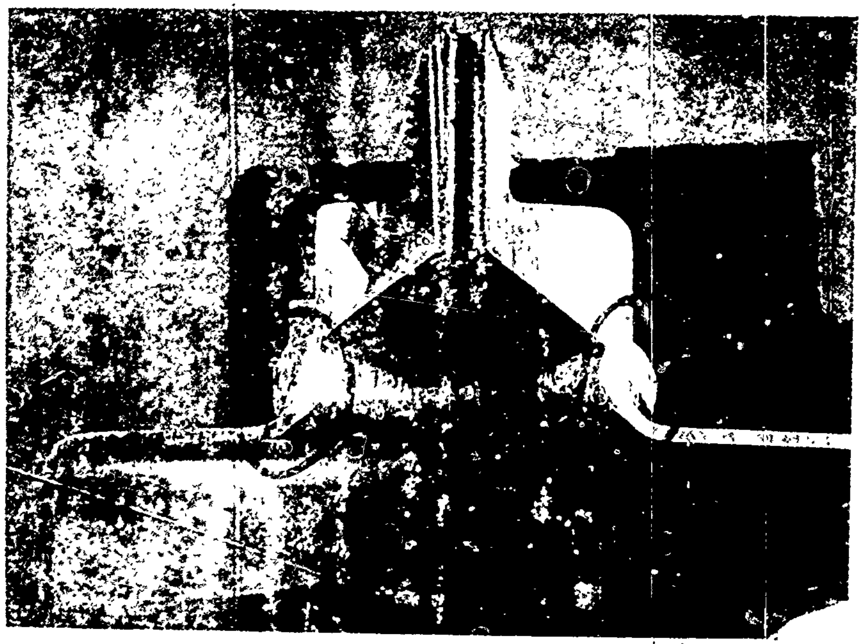

Figure 3. Typical Crack (1.5X)

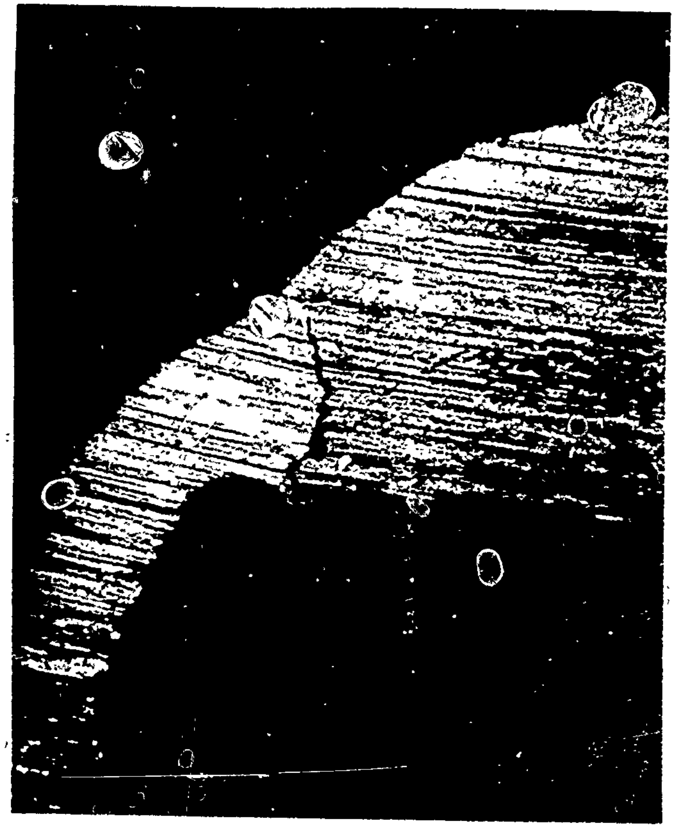

Figure 4. Internal View of Through Crack of Tank No. 75 (10X)

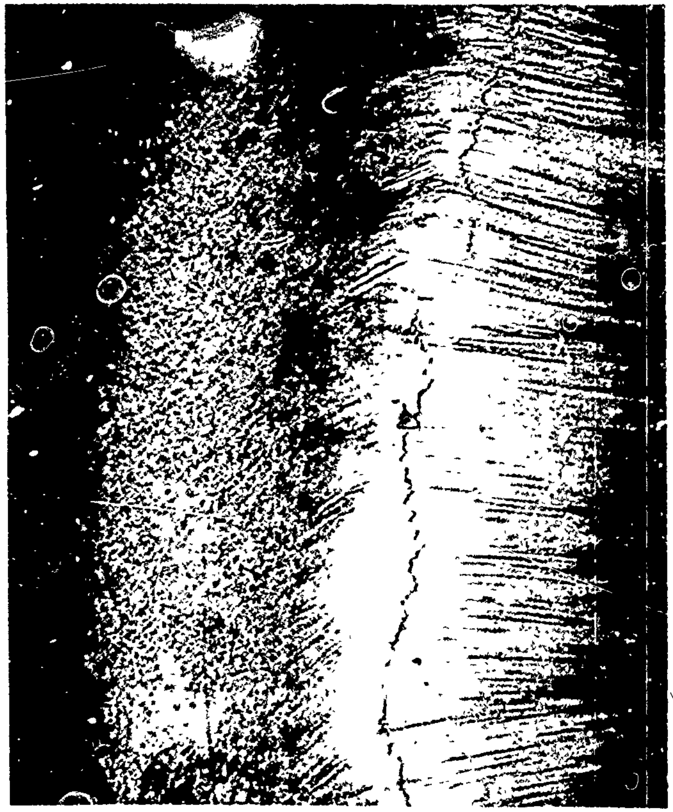

Figure 5. Internal View of Through Crack of Tank No. 75 (10X)

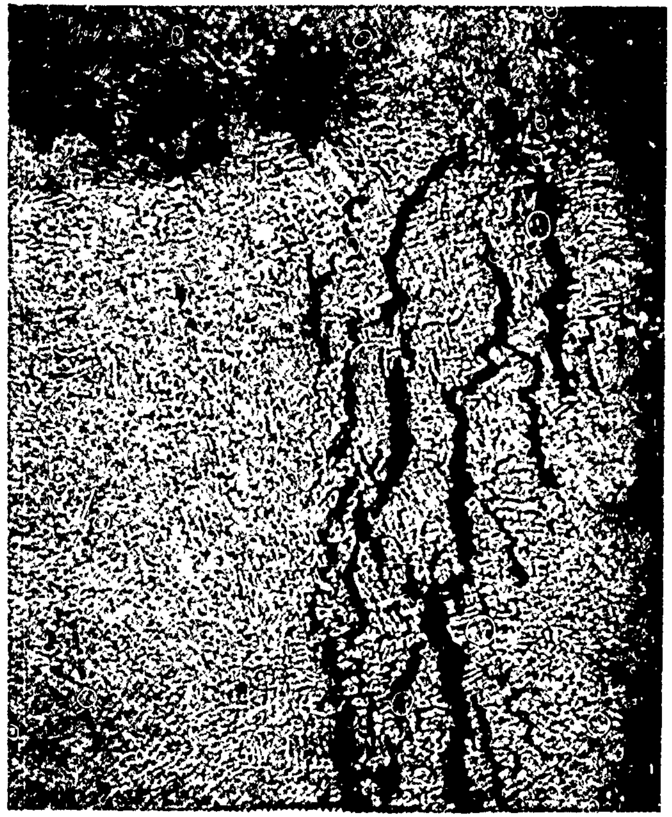

Figure 6. Intergranular Corrosion at Girth Weld (25X)

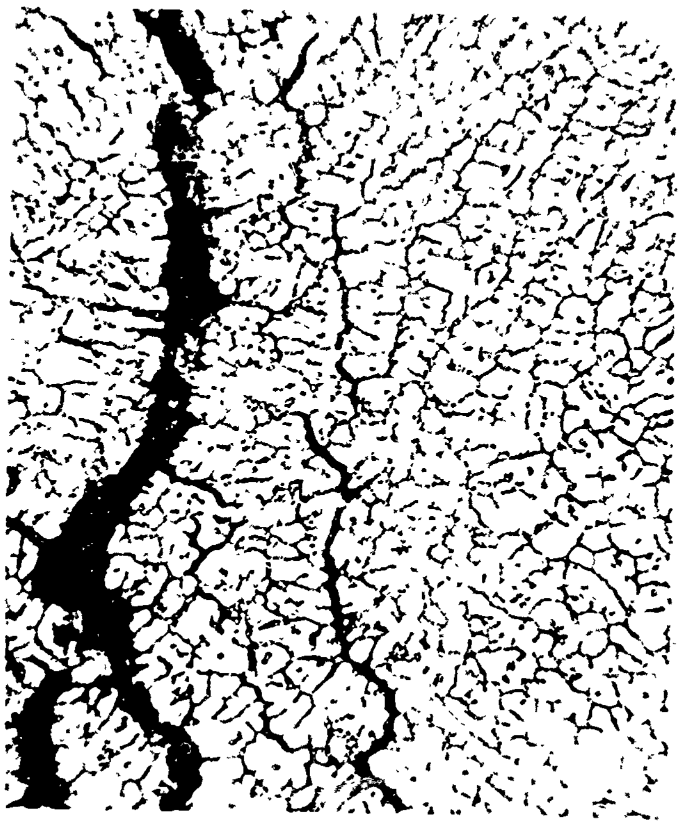

Figure 7. Intergranular Corrosion at Girth Weld (200X)

Figure 8. Internal Wall of Tank No. 9, Unetched Hazard Area of Girth Weld (200X)

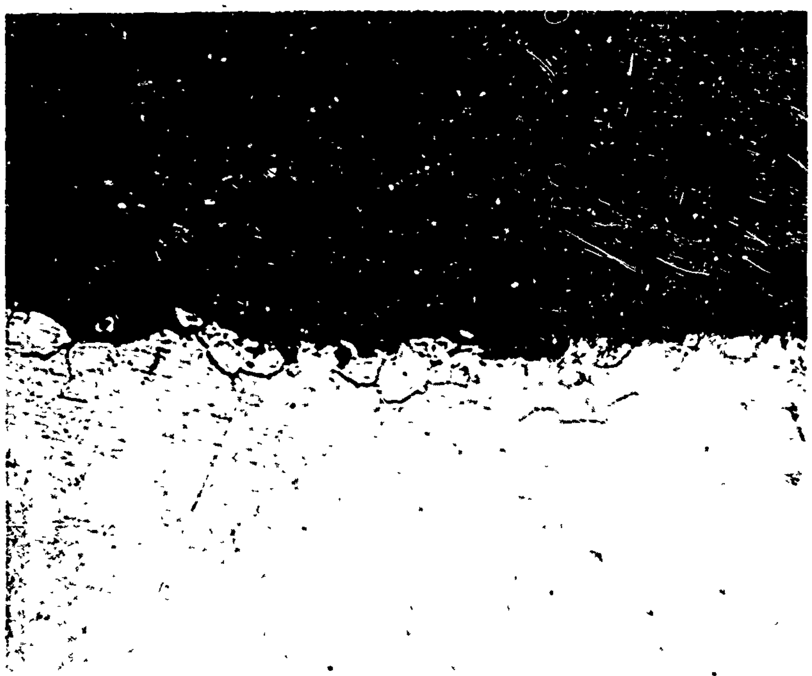

Figure 9. External Wall of Tank No. 9,
Unetched Hazard Area of
Girth Weld (200X)

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13. ABSTRACT

This report is the third in a series of progress reports for the Packaged Systems Storability Test Program, conducted at the Air Force Rocket Propulsion Laboratory. Tentative conclusions regarding storability as affected by environment, propellant chemistry, weld procedures, and stress levels are presented.

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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						