

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Memorandum 33-779

*Propellant / Material Compatibility
Program and Results*

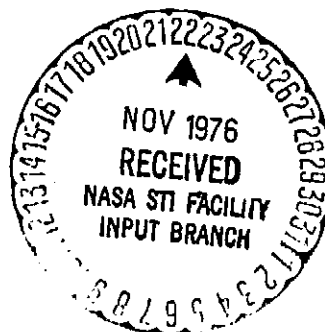
(NASA-CR-149149) PROPELLANT MATERIAL
COMPATIBILITY PROGRAM AND RESULTS (Jet
Propulsion Lab.) 89 p HC A05/MF A01

N77-11197

CSCL 21I

G3/28

Unclas
54497



JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

August 15, 1976

TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. 33-779		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle PROPELLANT/MATERIAL COMPATIBILITY PROGRAM AND RESULTS				5. Report Date August 15, 1976	
				6. Performing Organization Code	
7. Author(s) L. R. Toth, W. A. Cannon, C. D. Coulbert, H. R. Long				8. Performing Organization Report No.	
9. Performing Organization Name and Address JET PROPULSION LABORATORY California Institute of Technology 4800 Oak Grove Drive Pasadena, California 91103				10. Work Unit No.	
				11. Contract or Grant No. NAS 7-100	
				13. Type of Report and Period Covered Technical Memorandum	
12. Sponsoring Agency Name and Address NATIONAL AERONAUTICS AND SPACE ADMINISTRATION Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract This report gives the analyses and results of a program to establish the effects of long-term (up to 10 years) contact of inert materials with earth-storable propellants for the purpose of designing chemical propulsion system components that can be used for current as well as future planetary spacecraft. Phase I, which was concluded in 1967, was a pilot-type effort to evaluate a limited number of materials. Phase II is the primary experimental work, and results to date are reported herein. Investigations include the following propellants: hydrazine, hydrazine-hydrazine nitrate blends, monomethylhydrazine, and nitrogen tetroxide. Materials include: aluminum alloys, corrosion-resistant steels, and titanium alloys. More than 700 test specimen capsules were placed in long-term storage testing at 43°C (110°F) in the special material compatibility facility located at JPL Edwards Test Station, Calif. Material ratings relative to the 10-year requirement have been assigned.					
17. Key Words (Selected by Author(s)) Metallic Materials Propellants and Fuels			18. Distribution Statement Unclassified -- Unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 80	22. Price

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Memorandum 33-779

*Propellant / Material Compatibility
Program and Results*

L. R. Toth

W. A. Cannon

C. D. Coulbert

H. R. Long

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

August 15, 1976

Preface

The work described in this report was sponsored by the NASA/OAST Space Propulsion and Power Division and the NASA/OSS Planetary Programs Office and was performed by the Propulsion Division of the Jet Propulsion Laboratory.

Acknowledgment

Many people have contributed to the success of the JPL Propellant/Material Compatibility Program over the past nine years. The authors would like to particularly acknowledge the assistance and contributions of M. E. Guenther, R. F. Haack, O. F. Keller, C. M. Moran, J. W. Short, L. Taylor, and S. P. Vango.

Contents

I. Introduction	1
A. Nature and Result of Incompatibility Reaction	2
B. Impact on Early Space Missions	2
C. Impact on Future Space Missions	3
D. Objectives of the JPL Test Program	4
E. Scope of Program	5
II. Compatibility Test Program	5
A. Discussion	5
B. Early Work, Phase I	6
C. Current Test Methodology	8
III. Posttest Chemical Analysis Procedure	17
A. Discussion	17
B. Decomposition Gases	17
C. Residual Hydrazine	21
IV. Posttest Analysis Procedure for Specimens	21
A. Discussion	21
B. Specimen/Capsule Inspection	22
C. Metallic Specimen Examination	22
D. Nonmetallic Specimen Examination	24
V. Posttest Analyses and Results	25
A. Discussion	25
B. Summary of Posttest Analyses and Results	25
C. Hydrazine Material Compatibility and Surface Film Formation	25
D. Effect of Carbon Dioxide Contamination	26
VI. Material Ratings	27
A. Discussion	27
B. Rating System Factors and Criteria	27
C. Description of Classifications Used for Rating Materials	28
D. Correlation and Application	29
E. General Rating of Materials	29
F. Hydrazine/Materials, Ten-Year Compatibility Ratings	29

G. Hydrazine—Hydrazine Nitrate/Materials Ten-Year Compatibility Ratings	31
H. Monomethylhydrazine/Materials Ten-Year Compatibility Ratings	32
I. Nitrogen Tetroxide/Materials Ten-Year Compatibility Ratings	32
VII. Conclusions	33
A. Hydrazine Propellant	33
B. Hydrazine—Hydrazine Nitrate Blends	34
C. Monomethylhydrazine	34
D. Nitrogen Tetroxide	34
E. Cleaning Solvents	34
F. Ten-Year Design Data	34
G. Procedures and Standards	34
H. Multiyear Design Data	34
References	35
Appendix A. Specimens Posttest Analyses and Results	39
Appendix B. Test Units in Storage	61
Appendix C. Propellant Specifications and Assays	67
Appendix D. Method for Determining Carbon Dioxide Content in Hydrazine	71
I. Determination of Carbon Dioxide Absorbed by Hydrazine	72
II. Calculation for Carbon Dioxide Content	73
III. Conclusion	73
Appendix E. Data Summary Sample Format	75

Tables

1. Material wetted by hydrazine in Mariner Venus/Mercury 1973 propulsion system	4
2. Material wetted by monomethylhydrazine and nitrogen tetroxide in Viking Orbiter propulsion system	4
3. Material wetted by hydrazine in Mariner Jupiter/Saturn 1977 propulsion system	5

4. Compatibility of CRES and hydrazine doped with CO ₂	25
5. Summary of compatibility ratings for materials in contact with hydrazine for ten years at 43°C (110°F)	32
6. Summary of compatibility ratings for materials in contact with hydrazine—hydrazine nitrate for ten years at 43°C (110°F)	32
7. Summary of compatibility ratings for materials in contact with monomethylhydrazine for ten years at 43°C (110°F)	33
8. Summary of compatibility ratings for materials in contact with nitrogen tetroxide for ten years at 43°C (110°F)	33
A-1. Summary of posttest analyses and results—hydrazine	40
A-2. Summary of posttest analyses and results—hydrazine— hydrazine nitrate	51
A-3. Summary of posttest analyses and results—monomethylhydrazine	53
A-4. Summary of posttest analyses and results—nitrogen tetroxide	54
A-5. Summary of detailed posttest analyses and results—hydrazine	55
A-6. Summary of detailed posttest analyses and results— hydrazine—hydrazine nitrate	58
A-7. Summary of detailed posttest analyses and results— monomethylhydrazine	59
A-8. Summary of detailed posttest analyses and results— nitrogen tetroxide	59
B-1. Test specimens in hydrazine storage (Spec. MIL P-26536B)	62
B-2. Specimens in hydrazine—Viking Lander '75 grade material (STM NO20, July 14, 1972, Rev. 2)	63
B-3. Specimens in test, hydrazine—hydrazine nitrate (75% N ₂ H ₄ ; 24% N ₂ H ₅ NO ₃ ; 1% H ₂ O)	64
B-4. Specimens in monomethylhydrazine (MIL-P-27404A)	64
B-5. Specimens in nitrogen tetroxide (Spec. MSC-PPD-2B)	64
B-6. Chemical composition of specification-type ferrous and nonferrous alloys	65
C-1. Assays of hydrazine—hydrazine nitrate	68
C-2. Assay of monomethylhydrazine	69
C-3. Assay of nitrogen tetroxide	69

Figures

1. Material Compatibility Program—implementation and documentation	6
2. Phase I metal sample	7
3. Phase I elastomeric sample	7
4. Compatibility test capsule container and metal sample	8
5. Compatibility test capsule with pressure gauge	8
6. Phase II standard metallic specimen	9
7. Metallic specimen types	10
8. Metallic specimen test combinations	10
9. Metallic specimen preparation flow chart	11
10. Stressed specimen loading fixture and strain measurement	12
11. Test coupon stress versus retaining fixture interference	13
12. Phase II test specimen/capsule	13
13. Material compatibility test facility schematic	14
14. Material compatibility test facility	15
15. Test rack for storing specimen/capsule test units	15
16. Facility special access door used for installing and removing test units	16
17. Procedure for complete posttest chemical analysis (with distillation)	18
18. Procedure for limited posttest chemical analysis (without distillation)	19
19. Specimen/capsule test opening fixture	20
20. Metallic specimen analysis procedure	22
21. Nonmetallic specimen analysis procedure	22
22. Flaking of oxide film from surface of titanium specimen	26
23. Aluminum oxide film at the liquid-vapor interface on aluminum specimen	26
24. Factors leading to propellant/material long-term (10-year) rating determination	27
25. Typical criteria for determining propellant/material long-term (10-year) rating	28
26. Correlation between typical criteria, test results, and assigned ratings	29
D-1. Apparatus for analysis of CO ₂ in hydrazine	72
E-1. Sample of liquid-vapor interface (a) at 135×, (b) at 360×, and (c) at 1450×	80

Abstract

This report gives the analyses and results of a program to establish the effects of long-term (up to 10 years) contact of inert materials with earth-storable propellants for the purpose of designing chemical propulsion system components that can be used for current as well as future planetary spacecraft. Phase I, which was concluded in 1967, was a pilot-type effort to evaluate a limited number of materials. Phase II is the primary experimental work, and results to date are reported herein. Investigations include the following propellants: hydrazine, hydrazine-hydrazine nitrate blends, monomethylhydrazine, and nitrogen tetroxide. Materials include: aluminum alloys, corrosion-resistant steels, and titanium alloys. More than 700 test specimen capsules were placed in long-term storage testing at 43°C (110°F) in the special material compatibility facility located at JPL Edwards Test Station, Calif. Material ratings relative to the 10-year requirement have been assigned.

Definition of Terms

AF-E-102 (-332, -411)	ethylene propylene terpolymer composite (Hystyl)
CRES	corrosion-resistant steel
ELI	extra-low interstitial grade
EPT	ethylene propylene terpolymer
ETS	JPL Edwards Test Station
FEP	fluorinated ethylene propylene
Hz	hydrazine
H-HN	hydrazine-hydrazine nitrate
LOX	liquid oxygen
MMH	monomethylhydrazine
NTO	nitrogen tetroxide
SEM	scanning electron microscope
TFE	tetrafluoroethylene
UDMH	unsymmetrical dimethylhydrazine
VAR	vacuum arc remelt

Propellant/Material Compatibility Program and Results

I. Introduction

Chemical propulsion system materials selection requires a base of experimental long-term (up to ten years) propellant/material compatibility data, since the performance and interactions between the liquid propellants and materials cannot with the current state of knowledge be satisfactorily predicted.

The best rocket propellants are usually the most difficult to contain for the length of time before they are needed. Typical liquid propellants are both toxic and reactive with other materials. The advance to higher energy propellants that has occurred over the last twenty-five years has been possible due to considerable materials research as well as the more visible rocket engine research.

Under NASA Contract NAS7-100 with the Jet Propulsion Laboratory, a program has been established to determine acceptably inert materials in contact with earth-storable propellants for use in the design of chemical propulsion system components that can be utilized on current as well as future planetary spacecraft. The emphasis has been on propellants appropriate to small

rocket systems (as opposed to large launch vehicle systems). These propellants include the following:

- (1) Hydrazine or Hz (N_2H_4),
- (2) Hydrazine-hydrazine nitrate or II-HN (75% N_2H_4 + 24% $N_2H_5NO_3$ + 1% H_2O by weight),
- (3) Monomethylhydrazine or MMH (CH_3NHNH_2),
- (4) Nitrogen tetroxide or NTO (N_2O_4).

The overall program was divided into two subprograms: Phase I was a pilot-type effort to evaluate a limited number of materials, and this precursor work was concluded in CY 1967. The Phase II program is the primary effort, and the results to date of this ongoing experimental work are presented herein. The investigations included the above propellants and materials such as aluminum alloys, corrosion-resistant steels, and titanium alloys.

The emphasis is on hydrazine because of its great value as a monopropellant and its accompanying recognized chemical instability. Hydrazine-hydrazine nitrate has also been studied because of its higher performance and lower

freezing point. It also shares hydrazine's instability and less is known about it, as it has not been flown yet. Monomethylhydrazine and nitrogen tetroxide receive minimum emphasis because their short-term stability and compatibility have been verified, leaving just the long-term compatibility in possible doubt.

Most reported research on propellant compatibility with container materials was designed to detect major incompatibility reactions that might degrade short missions. The comparatively longer planetary missions flown by JPL for NASA necessitated propellant-material compatibility research that goes beyond short-term studies to focus on more subtle reactions that might degrade missions lasting as long as ten years. The data reported here summarizes individual tests lasting more than four years. Since the test program is continuing with approximately 578 specimen capsules still in active test, and most approaching the 6.5-year exposure period, future reports will summarize results for the longer test durations.

The ideal propellant would be unreactive with the metals and polymers commonly used in commercial tanks, tubing, valves and other components of storage systems. However, few such materials exist for any given propellant because of the innate reactivity of this class of compounds. The same reactivity usually exists in the more esoteric and expensive materials. Therefore, propellant/material compatibility testing is required to determine the degree and significance of the chemical reaction. Such programs can be quite large because there are many materials to test, and because the possibility exists that there are unreactive materials for a specific propellant that can only be identified properly through testing. With such test data, materials can be rated for their suitability for use with a specific propellant, such as is done in this report for the subject propellants.

It is recognized that data is also required for the fracture growth properties of materials used in propulsion system components where operational stresses are near the yield stress regime. Typical components, such as tankage, plumbing, and thin membranes or diaphragms, must be intolerant of flaw growth during operational service.

However, this report deals with only those nonfracture behavior aspects of long-term compatibility, including material corrosion, property changes, and propellant decomposition. A high degree of procedural control has been exercised throughout the program to obtain the best experimental results. Emphasis was placed upon stan-

dardization during all aspects in order to provide reliable engineering data for design purposes.

A. Nature and Result of Incompatibility Reaction

Any reaction between a propellant and the material it wets can alter either the propellant, the material, or both. For instance, the propellant alone can change through a reaction catalyzed by the material, a problem that exists especially with monopropellants like hydrazine and hydrazine-hydrazine nitrate. The material alone can be degraded through stress corrosion. However, in most cases some of both the propellant and the material are consumed in the reaction, resulting in a new compound in the system. This general case can be tolerated if the new compound is tightly adherent to the container material, thus protecting it from further attack because it serves as a form of passivation. If the compound is not tightly bound to the container, it can be troublesome, even intolerable.

The simple case of one propellant and one material involving few chemical elements is not a realistic condition. Other variables enter into the analysis of a practical system, such as various impurities in the propellant arising from the manufacturing process or later storage. Then, besides the range of ingredients allowed in modern alloys, there are the residual effects on the material of processing, preparation, and cleaning operations. Thus, the interaction between just one propellant and one material can be quite complex, and the material's utility cannot be properly rated until it is established whether or not reaction arises from its innate properties or the effects of subtle processes due to contaminants.

Propellant/material incompatibility can lead to a wide variety of problems. The reaction can result in propellant decomposition that can adversely affect the performance of the liquid propulsion system, and insoluble gases that can adversely affect the fluid dynamics involving small constrictions, metering orifices, and capillary tubes. The reaction can also result in corrosion and the formation of insoluble salts or other corrosion products that can plug filters and orifices, allow seal leakage, affect valve operation, weaken structural members, and affect overall propulsion feed system performance.

B. Impact on Early Space Missions

How many of the entries in the preceding category have actually occurred in spaceflight is difficult to say. If evidence of a problem does not appear in spacecraft telemetry, then it will never be found for lack of a post-

mortem examination. Probably few catastrophic failures can be laid to propellant/material incompatibility because the short-term tests run by most rocket organizations eliminated the combinations resulting in gross reactions, and subtler reactions are tolerated by a somewhat conservative system design. However, some cases of incompatibility have been seen in spacecraft telemetry.

Noncatastrophic propellant/material incompatibility was indicated in the telemetry from early Mariner spacecraft flights. A continuous increase in the hydrazine tank pressure was found after normalization for tank temperature. Additional ground storage tests proved that the reactive material was one of the constituents of the butyl rubber bladder, probably the lamp black used as a filter. The butyl rubber had to be used over a number of flights in spite of this problem, because considerable time was required to develop and qualify a superior replacement material. The reactivity varied dramatically from flight to flight and ground test to ground test (Ref. 1), as might be expected in a case where there are so many variables.

Although understanding of incompatibility mechanisms and the test methods for them have improved with time, new tests sometimes find previously unknown cases of incompatibility.

Such a case is reported in Ref. 2 where hydrazine-related fuels were found to cause stress corrosion in some materials already successfully used in flight applications. Such materials will probably not be withdrawn from flight use altogether, but rather used where their incompatibility is of no consequence. Thus, the book is never closed on any material.

C. Impact on Future Space Missions

Even given the pool of existing data and repetitive successful use of certain propellants which are slowly becoming "standards," considerably more compatibility testing is necessary for future missions. This conclusion follows from a number of observations. First, the existing data pool is inadequate for future missions, because it is not complete and its elements generally cannot be correlated with today's knowledge. Correlation is difficult because of differing test methods, test objectives (and thereby thoroughness), and level of detail reported in the literature. While this data has value, its value is considerably less than would have been the case if all researchers had used a single thorough test procedure.

Also, new types of data are needed. Future missions will last up to ten years, and existing data rarely exceeds one year. No acceptable techniques for accelerating test time or extrapolating short-term data to long-term applications have yet been demonstrated, although significant advances have been made in both these technology areas. Brown (Ref. 3) has developed an electrochemical method that appears promising for accelerated testing with hydrazine and metallic samples. He used the results presented in Appendix A of this report to verify that his method was producing valid data.

Green et al. (Refs. 4, 5) have developed a method whereby long-term material compatibility predictions can be made from short-term data. The prediction method utilizes a system of flow diagrams showing analysis paths, decision points, and required data inputs. The concept is based upon generating short-term compatibility data using sensitive testing and measurement techniques such as radioactive tracers, atomic absorption spectroscopy, palladium foil analyzer (for hydrogen gas), and the electrochemical method noted above. The test results generated are applied using the procedures of the prediction method. The final output is the long-term performance of the material/propellant combination being investigated. The sophistication of future missions demands some new materials, such as nonmagnetic metals, that will not interfere with science experiments or materials that are not damaged by nuclear radiation inherent in a radioisotope power source or planetary radiation belts. An illustration of the synergism of these factors and others for an advanced mission is reported in Ref. 6.

Therefore, considerably more compatibility testing remains to be completed. Only those materials actually wetted by the propellant are of interest in a compatibility study. Two recent JPL propulsion systems are typical of those using the propellants covered in this report: Table 1 (Refs. 7 and 8) lists the materials from the Mariner Venus/Mercury 1973 monopropellant hydrazine system and Table 2 those of the Viking Orbiter 1975 bipropellant MMH/NTO system. Table 3 listing the materials from the Mariner Jupiter/Saturn 1977 monopropellant hydrazine system is included for comparison with Table 1 to illustrate the material changes encountered in going from one system to the next using the same propellant.

Essentially the same limited list of materials appears in each table. Thus, at first sight the test program looks small; however, by the time each propellant is tested with each material, and processing differences between different applications of the same material are tested, and

Table 1. Material wetted by hydrazine in Mariner Venus/Mercury 1973 propulsion system

Component	Part	Material
Tank	Shell	6Al-4V Titanium
	Diaphragm	EPT-10
	Transition tube	6Al-4V Titanium/ 304 L VAR ^a
Lines	—	304 L VAR ^a
Pressure transducer	Inlet tube and header	304 L
	Isolator and diaphragm	17-4
Service valve	Outlet tube and body	347
	Ball	Aluminum oxide (Al ₂ O ₃)
	Lubricant	Krytox 143 AB
Filter	Inlet and outlet tubes and body	304 L
	Screen element	304 L
Solenoid valve	Armature and body	446
	Armature tip	Stellite 6 (Co-Cr puddle weld)
	Seat and insert	AM 355
	Seat seal	TFE Teflon
	Spring	Inconel-X (Inconel X-750)
	Other	304
		304 L
		316
		321
		347
	17-4	
	17-7	
	Chrome alloy plating (on 446)	
	Ni-Cr weld (for 446)	
	FEP Teflon lubricant	
	Krytox 143 AB lubricant	

^aVacuum arc remelt

combinations of materials that are mechanically attached or welded are tested for synergistic effects, the test program is rather large. The program can be trimmed back somewhat by emphasizing the materials that present the largest area to the propellant, but the lesser materials

Table 2. Material wetted by monomethylhydrazine and nitrogen tetroxide in Viking Orbiter 1975 propulsion system

Component	Part	Materials	
Tank	Shell and propellant management device	6Al-4V Titanium	
	Gasket seal	6061-T4 Aluminum	
	Lines	—	
Service valve	Inlet tube and body	347	
	Ball	Aluminum oxide (Al ₂ O ₃)	
	Lubricant	Krytox 143 AB	
Pyrotechnic valve	Tubing	347	
	Ram	17-4	
Filter	All parts	304 L	
Latch valve	Inlet and outlet tubes, body casting, filter, and poppet lifter	304 L	
	Seat	Teflon	
	Bellows housing, solenoid shaft	17-4	
	Bellows housing end fitting free, and fixed end, bellows housing	304 L, 321 or 347 355	
	Main bellows,	350	
	Isolation bellows	321	
	Poppet guide	301 or 302	
	Pressure transducer	Inlet tube and header	304 L
		Isolator and diaphragm	17-4
	Flex hose	Tube and sheath	304 L
Bellows		321	
Engine valve	Body and flapper assembly	17-7	
	Filter assembly	304 L	
	Body seal	Teflon coated 17-7	
	Seat seal	Teflon (TFE)	

cannot be deleted altogether because they are often used in sensitive parts such as springs and bellows where second-order incompatibility reactions can be important.

D. Objectives of the JPL Test Program

The basic objective of the JPL propellant/material compatibility test program is to obtain detailed com-

Table 3. Material wetted by hydrazine in Mariner Jupiter/Saturn 1977 propulsion system

Component	Part	Materials
Tank	Shell	6Al-4V Titanium
	Diaphragm	AF-E-332
	Transition tubes	6Al-4V Titanium/ 304 L VAR ^a
Lines	—	304 L VAR ^a
Pressure transducer	Inlet tube and header	304 L
	Isolator and diaphragm	17-4
Service valve	Outlet tube and body	304 L
	Poppet	17-4
Filter	Inlet and outlet tubes	304 L
	Case assembly	304 L and 321
	Filter element	304 L, 321, and 347
Solenoid valve	Inlet and outlet tubes	347
	Filter retainer and filter element, magnetic insulator, end cap, mandrel, and sleeve	304 L
	Body, shunt, and core	430
	Spacers, armature, and pole piece	430 F
	S-Springs	17-7
	Seat seal	AF-E-411
	Latching valve	Inlet and outlet tubes and body
	Poppet assembly	347
	Seat seal	AF-E-102
	Armature	446
	Spring	302
	Flexure assembly	347
	Spacers	347

^aVacuum arc remelt

patibility data for periods up to ten years. Concomitant objectives are the development of: (1) a standard test methodology, (2) basic procedures for compatibility testing and analysis, and (3) a rating of the materials for compatibility relative to long-term application.

E. Scope of Program

The scope of the test program established by JPL serves the needs of planetary spacecraft like those described in Tables 1, 2, and 3.

The major parts of the total program from the basic plan to the final documentation are depicted schematically in Fig. 1.

Specialized processing, handling, and analytical procedures have been developed for each propellant. The test program for propellants and materials is comprehensive. Single materials are tested unstressed and stressed in the propellant. Groups of materials are tested in separated, mechanically joined, welded, brazed, plated, and coated configurations. Control units are used to monitor the behavior of the test apparatus itself. A summary of the specimens currently in storage test, along with material compositions (Refs. 7, 8) is presented in Appendix R.

The origin and current methodology of the JPL program are discussed in the next section.

II. Compatibility Test Program

A. Discussion

The "real-time exposure testing" approach was selected as the best and most positive method for determining and establishing acceptable inert materials of construction for chemical propulsion systems. It follows logically then that in order to provide reliable engineering data, all aspects of the total program must be considered. Uniformity of methods and retrievability of data are clearly two of the primary requirements that must be applied to each aspect. For example, pretest details should be well defined and recorded. The test component should be considered as a total system and consist of material, propellant, container, test environment, and instrumentation. A high degree of control should be maintained throughout the program; and posttest analyses and results should be well documented.

The major considerations or categories deemed essential to the total program include:

- (1) Standardization of all methods, procedures, and processing
- (2) Material selection
- (3) Propellant selection

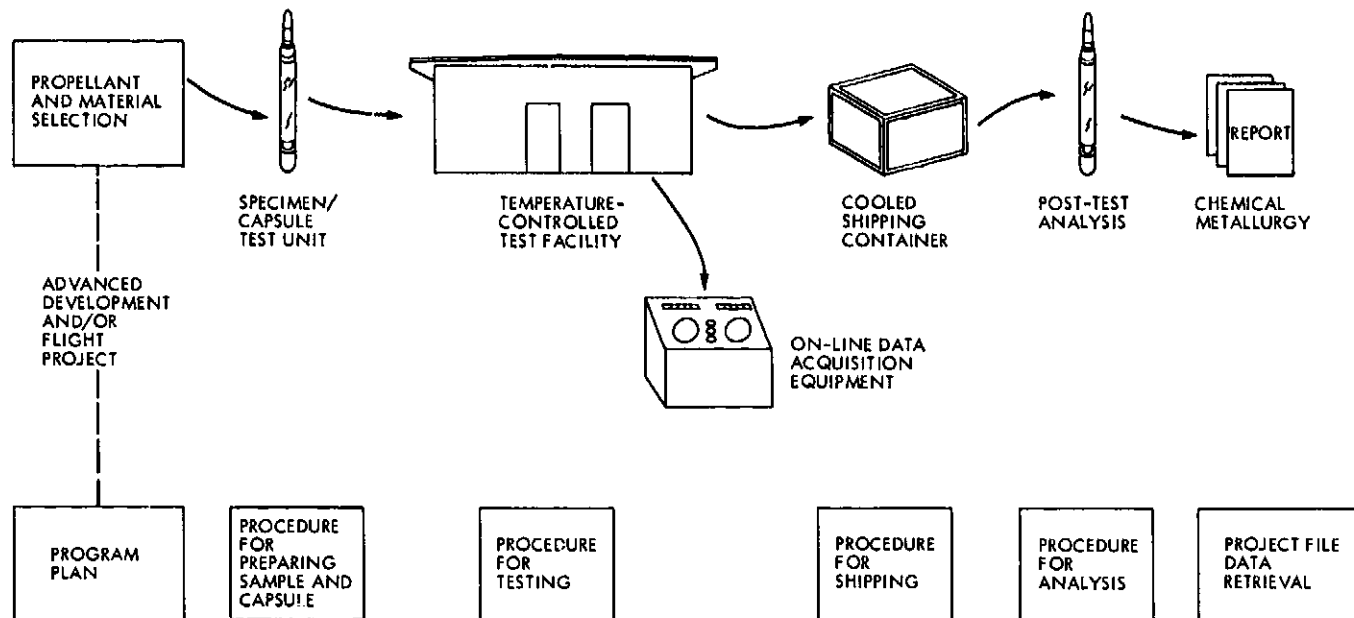


Fig. 1. Material Compatibility Program—implementation and documentation.

- (4) Test specimen configuration(s)
- (5) Test fixture and test container configuration(s)
- (6) Test environment
- (7) Instrumentation
- (8) Facility for storing test items
- (9) Pretest and posttest analysis
- (10) Data retrieval (permanent archive)
- (11) Rating of materials and propellants taking into account gross and subtle effects
- (12) Final documentation

In order to meet programmatic goals, the scope of the work was divided into two separate subprograms. These were identified as the pilot (or screening) and standard (or basic) phases. The rationale for this approach was that real-time testing and pathfinder experience would be accumulated concurrent with the evolution of the very important second phase or basic program.

B. Early Work, Phase I

This was mainly a pilot (or screening) type effort. The work was initiated in early 1962 and concluded in late 1967. Program details, progress, and data resulting from this phase are reported in Refs. 9 through 25.

The program was organized to test several earth-storable propellants with a limited variety of materials of construction which would have a high probability of being used in future spacecraft chemical propulsion systems.

The specification grade propellants consisted of amine-fuels and one oxidizer. Specific ones selected were:

- (1) Hydrazine
- (2) Hydrazine-hydrazine nitrate mixture
- (3) 50-50 hydrazine-unsymmetrical dimethylhydrazine (UDMH), also known as Aerozine 50
- (4) Nitrogen tetroxide

The materials of construction were initially screened by checking their short-term compatibility from known experience and as reported in the literature. The materials included: ferrous and nonferrous alloys, coatings, and elastomeric compounds. Wherever possible these were procured and certified to meet Military Specifications or equivalent specifications commonly used in aerospace applications. The metallic types were mainly aluminum alloy, corrosion-resistant steel (CRES), and titanium alloy. Nonmetallic types included: fluorocarbon base coating or grease, both ethylene propylene terpolymer and butyl rubber compound elastomers, and alumina-sintered ceramic. These materials are identified in Tables 1, 2, and 3.

1. Test Specimen Description

a. Metallic. These samples were standardized as cylindrical slugs (Fig. 2). This configuration was established based upon factors of material availability and low cost of manufacturing or producibility. The 0.637-cm-diam (0.250 in.) rod material was readily procured under proper certifications (Military Standards or equivalent). The small diameter rod form lent itself to precision centerless grinding with very little removal of surface material to the final dimension of 0.582-cm diam (0.230 in.).

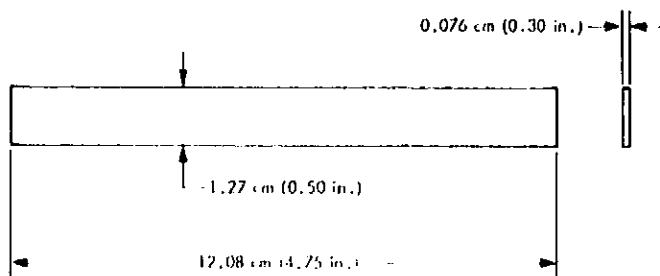
b. Nonmetallic. These samples were standardized as thin rectangular sheets (Fig. 3). The test items were generally elastomeric materials made from different compounds that were representative of propellant expulsion bladders or diaphragms.

c. Passivation and cleaning. Passivation of metallic samples was accomplished with procedures that were



NOTE: ALL FINISHES 0.4 μm (16 $\mu\text{in.}$) MAX

Fig. 2. Phase I metal sample



NOTE: ALL FINISHES 0.8 μm (32 $\mu\text{in.}$) MAX

Fig. 3. Phase I elastomeric sample

updated from those presented in Ref. 26. Typical procedures used have been presented in Appendix A of Refs. 19 and 20.

Each metallic or nonmetallic specimen was cleaned (at JPL) in accordance with paragraph 3.4.5 a or b of specification 30009 Ref. 27.

After processing and cleaning, each specimen was inspected to verify that the surfaces were free of contamination, and then sealed in a polyethylene bag. During this test unit processing and cleaning, care was taken to maintain uniform standards and a high degree of control over all operations.

2. Immersion Testing. During the early planning stages of the program, two test conditions were established. The test environment or ambient temperature of 43°C (110°F) was selected and used throughout the program; this value was based upon the spacecraft Flight-Type Approval requirement of 49°C (120°F) for propulsion systems and components. Also, a test termination cutoff value of 27.6 N/cm² (40 psia) internal pressure was established for those ampules incorporating visual pressure gauges (Figs. 4 and 5). This was based solely upon safety conditions of the glass test container.

3. Test Results. The posttest analyses included results from both chemical and metallurgical determinations. The detailed information including results and conclusions from this preliminary test program are summarized in Refs. 14 and 15 for evaluation as may be required. Definitive information was generated under the Phase I effort regarding compatibility of propellants and materials. Based upon these results, it was concluded and recommended that the more commonly used materials such as aluminum 6061-T6, corrosion-resistant steel types 303, 304, and 317, and titanium 6Al-4V, be investigated in more depth under the standard or Phase II program.

4. Test Container Design. One of the Phase I program initial goals was to establish and standardize the test container design prior to initiation of any exposure testing. Three important considerations were: low cost, since it was an expendable item; it should allow visual observation of test samples; and it should be a closed system. A test container made of borosilicate glass produced by Corning Glass per code number 77-10, annealed condition (trade name, "Pyrex") was selected for this purpose. The basic configuration shown in Figs. 4 and 10, and defined under Ref. 28 was used throughout the overall program. The glass ampule mean value internal volume was 52.0



Fig. 4. Compatibility test capsule container and metal sample

cm³ (5.0 in.³). Maximum envelope dimensions were 2.80-cm diameter (1.102 in.) and 20.30-cm length (8.00 in.). Glass ampules used in the early tests or Phase I are shown in Figs. 4 and 5. The closed-type test unit (Fig. 4) was sealed with the propellant in the frozen state; this style was used during the early part of Phase I and primarily with low-risk material propellant combinations. The style shown in Fig. 5 was used in Phase I, starting in October 1962 in order to measure internal pressure rise as a function of real-time exposures. Corrosion-resistant steel Bourdon-type gauges (LOX cleaned and adjusted to read absolute pressure) were attached to the glass capsules by means of Kovar tubing-to-glass seals. After the introduction of sample and propellant, the capsules were sealed off under a vacuum of 6.7 N/m² (0.050 mm of mercury) or less. During the exposure tests of up to 3 years, internal pressure measurements were recorded periodically.

Posttest analyses revealed the possibility of gauge material interaction with the test specimen propellant combination. It was found that the Kovar metal used to connect the glass capsules to the pressure gauges was



Fig. 5. Compatibility test capsule with pressure gauge

not completely inert. The amount of corrosion products of the Kovar metal ranged from unobservable to readily apparent quantities in capsules containing nitrogen tetroxide (N₂O₄) propellant. The Bourdon tubes were not visibly attacked. Complete details regarding this problem are discussed in Refs. 19 and 20.

To summarize, the use of pressure gauges with Bourdon tubes exposed to the propellant is not recommended for this application because of the inherent problem described above.

C. Current Test Methodology

The effort for the standard program, or Phase II, was initiated after the pilot subprogram, Phase I, was well-established and storage testing underway. The program details and progress are discussed in Refs. 21-23. The total program was planned on the basis of a multiyear (approximately ten years) level of effort. Each major part of the total program indicated in Fig. 1 was reviewed in

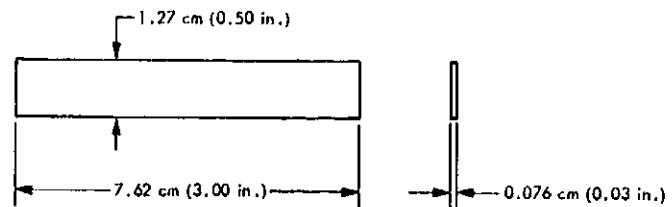
adequate detail for implementation. As part of this review, the different alternative routes or options were examined and assessed for conducting the program phases in order that (1) reliable engineering information would be generated, and (2) cost effectiveness would be achieved, but not to the point of compromising the results. Test variables assessed included the number of materials and combinations to be studied based upon foreseeable needs of future spacecraft; propellants; types of specimens, tests, and manufacturing processes; posttest analysis, and documentation. The facility design and operational requirements related to handling and transportation were also assessed.

Based upon this information, an overall plan was finalized, and schedules established. Implementation of long lead-time items was given particular attention; for example, the design and construction of the special test facility for conducting the exposure testing. Each category of the program was carefully designed and documented so that major objectives would be met during the course of the work. Improvements based upon Phase I results or observations and updated literature (Refs. 24 and 25) were also incorporated to assure that the subsequent work included the latest technology.

1. **Test Specimen Description and Preparation.** A rectangular shaped test specimen was established as the standard for Phase II. Actual dimensions are 7.62 cm (3.00 in.) long, 1.27 cm (0.50 in.) wide, and 0.076 cm (0.030 in.) thick (Fig. 6 and Ref. 29). This configuration was selected over other forms, because it results in the most meaningful geometrical shape.

To summarize, the rectangular shape provides the following advantages:

- (1) It has a large surface-to-volume ratio.
- (2) It can be readily converted to different types of test forms (i.e., on a "make-from" basis).
- (3) The stressed specimen requirement can be met with a simple bent-beam specimen.
- (4) The flat rectangular shape can be fabricated economically with semiproduction manufacturing equipment generally used in the aerospace industry.
- (5) The pretest and posttest examinations for inspection or metallurgical purposes can be accomplished with relative ease and with equipment commonly available.



NOTE: ALL FINISHES 0.4 μm (16 $\mu\text{in.}$) MAX

Fig. 6. Phase II standard metallic specimen

The apparent disadvantage is associated with determining tensile mechanical properties. The rectangular specimen cannot be conveniently subjected to tensile testing, because of the proclivity to break where the material is gripped in the jaws of the tensile machine.

Using the rectangular shape as the basic form, other generic types of specimens were added that would also result in essential material compatibility information. The classification of these specimens according to configuration is as follows: slug or coupon, bimetal-contact, bimetal-separated, stressed, welded, brazed, coated, plated, and screens. These are illustrated in Figs. 7 and 8. Bimetal-contact specimens are similar to the slug-type, with the exception that one of the two specimens has an offset bend to facilitate contact at the specimen ends. A glass C-type clip is used to maintain contact between the ends of the bimetal-contact specimens. The bimetal-separated specimens are also similar to the slug-type specimen, or coupon. In this case, a glass separator prevents any contact between the two specimens. A specially designed stressing fixture maintains slug-type specimens at 67% of yield stress while undergoing immersion testing. Welded specimens are similar to the slug-type configuration with the weld bead running in a longitudinal direction. Similarly, the brazed specimens are of the slug-type configuration with the brazed joint oriented in a longitudinal direction. Coated and plated specimens are obtained by coating or plating slug-type specimens. Screens for use in surface-tension studies are cut in the shape of the slug-type specimen.

One of the program goals was to maintain a high degree of control over all phases of specimen preparation including dimension and configuration control. As previously noted in Section II-A, a major consideration involved standardizing processes to produce uniform test samples throughout the program. Very rigid fabrication procedures were instituted, and carefully followed to produce the quality that would meet the specified dimensions and tolerances indicated on the specification

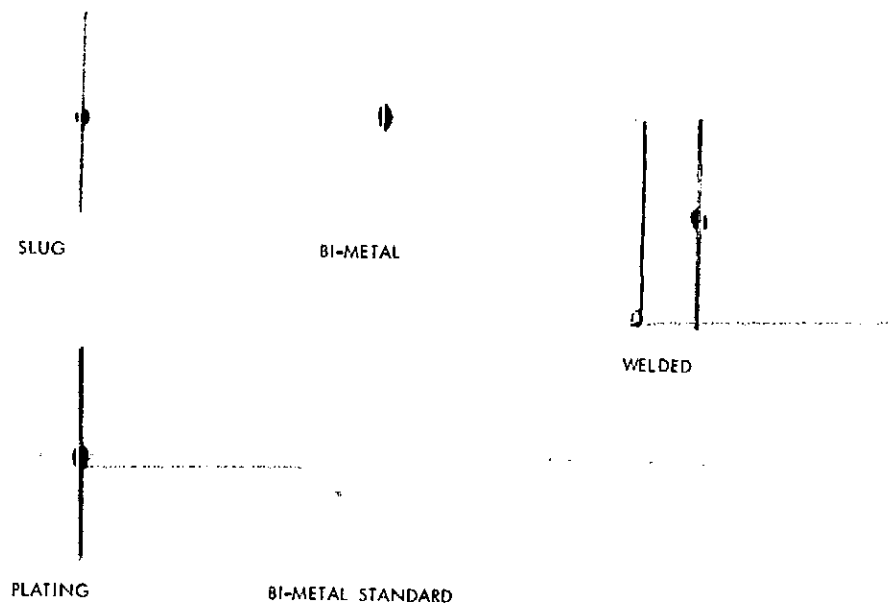


Fig. 7. Metallic specimen types

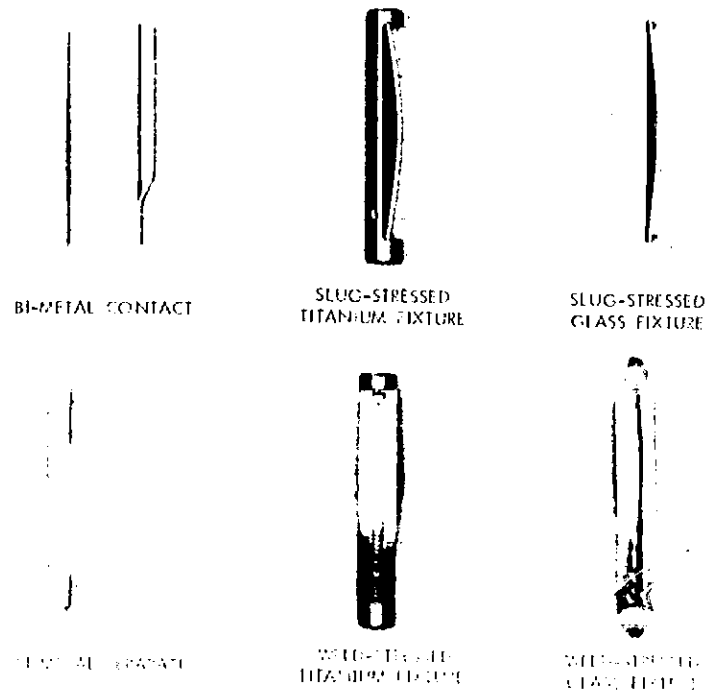


Fig. 8. Metallic specimen test combinations

drawings (Refs. 28 through 31). Particular attention was given to obtaining details on raw materials in order to meet the prerequisite of ensuring complete traceability. Prior to fabrication each metallic sample was required to have documentation giving material certification, alloy designation, specification number, producer, chemical composition, heat number, metallurgical state, and processing history. Nonmetallic specimens had similar information, as available. These data are maintained as part of the permanent project file for each specimen along with a portion of material from the original raw stock for subsequent use.

The production steps and flow sequence for preparing the metallic specimens are shown in Fig. 9. Specimen production was carried out with carefully controlled procedures and single-purpose equipment so as to eliminate contaminating the surfaces with foreign substances. Each group of machine cutting tools, grinding wheels, and fixtures were only used on specific materials. The machines were completely cleaned, and new coolant used prior to processing the different materials. The cost implications of this approach were recognized at the start, but these procedural methods were necessary in order that the final product would meet the requirements of the program.

The final surface finish was predetermined to be a key factor at the outset of Phase II. Variations in the actual surface area due to imperfections and asperities had to be minimized to ensure repeatability and provide meaning to the compatibility information being generated. The typical surface finish, including edges, of 0.2 to 0.4 μm (8 to 16 μ in.) was judged to have the desired characteristics for achieving uniformity, and for being representative of functional spacecraft propulsion elements.

Finish machining of metallic specimens was accomplished in the following steps: (1) edges were milled (Note: shearing was not permitted at any time to avoid introducing residual stresses); (2) flat surfaces were double disk ground to within 0.00762 cm (0.003 in.) of the final part dimension; and (3) all surfaces and edges were lapped to the final part dimensions.

Following fabrication of specimens to other test types and precleaning, all physical dimensions, weight, and surface finish were obtained and recorded. These data are maintained as part of the permanent project file.

For a more detailed description of specimen preparation under contract, see Refs. 30 to 32.

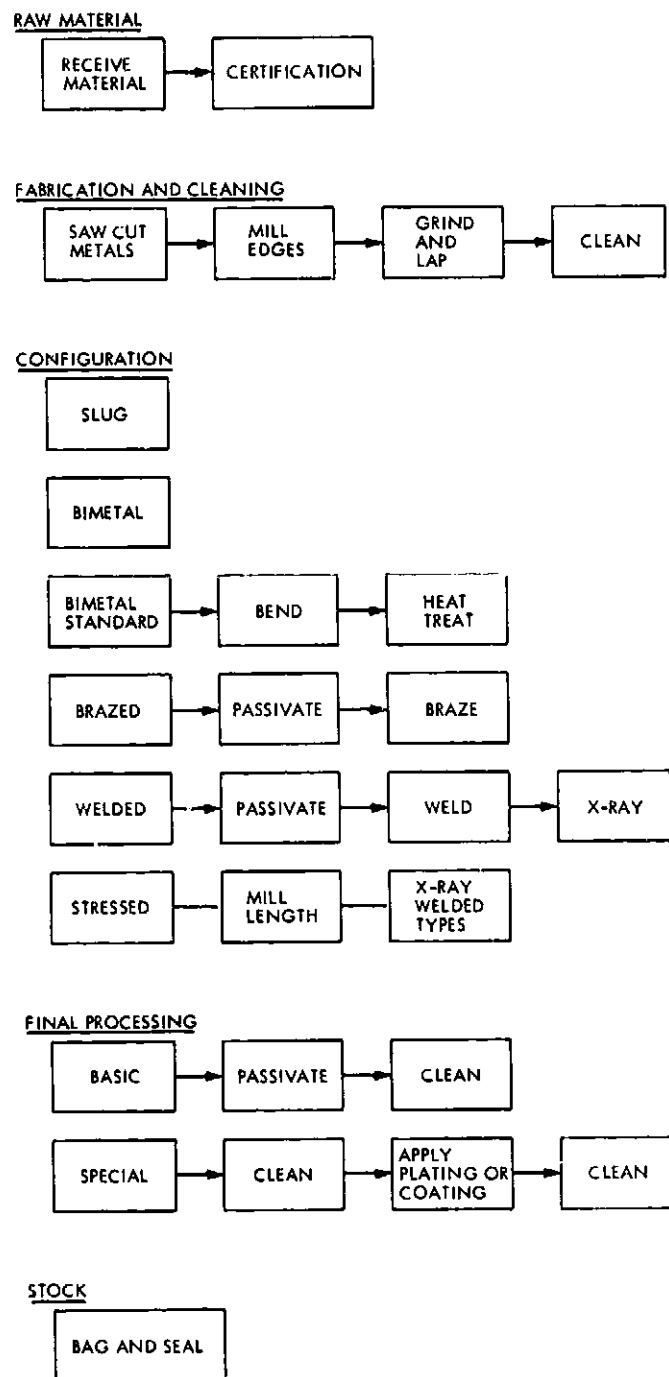


Fig. 9. Metallic specimen preparation flow chart

2. Fixtures. The variety of test combinations are illustrated in Figs. 7 and 8. Of these, only the stressed type presented a problem. The requirement for stressed samples was met by using a simple deflected beam which was stressed to 67% of the yield stress for the particular material being tested.

Based upon economic considerations, the fixture gap length was established as the constant dimension, and the specimen free length was varied with an appropriate dimensional length to obtain the desired stress level or 67% yield point when installed. These lengths (different for each material) were determined analytically (Refs. 30 and 33) and verified experimentally as discussed later in this section.

The stressing apparatus was designed to allow positioning the completed assembly of fixture and specimen through the 1.90-cm (0.748 in.) diameter opening of the test container. For the most part the material is identical to the test sample. The disadvantage of utilizing a metallic fixture is the effect the additional material in test has in increasing the surface-to-volume ratio. These effects were accounted for in posttest analyses, and details are discussed in those sections. The alternative is to use an inert material such as glass. The design developed and utilized is illustrated in Fig. 8. The glass fixture approach is a practical and viable solution with fragility being the major disadvantage.

A nontrivial problem existed when it was necessary to load stressed specimens into the metal holding fixture without overstressing the test specimen. Likewise, removal after tests was aggravated as a result of exposure to the environmental conditions; for example, any corrosion buildup, however slight, would make it more difficult to dislodge the specimen. The solution was provided by a simple manually operated mechanical device which was designed solely for this operation (Fig. 10 and Ref. 34).

The stressed-type specimens and fixture combination were investigated experimentally to measure the stress levels reached during installation and applied under the final loaded condition to determine effect of thermal stability; and to demonstrate physical stability. The components used for these tests were selected from a regular test lot. The three 6Al-4V titanium (fully heat-treated) specimens were instrumented with a conventional strain gauge attached to the convex or tension surface of the specimen when loaded. Both 6Al-4V titanium (fully heat-treated) and Pyrex glass (Corning Glass, Code Number 7740) fixtures were used. The fixtures had been sized to provide 0.221-cm (0.087 in.) compression or desired interference fit to each specimen in order to produce the 67% yield stress level.

Care was taken during installation and removal to stress the specimen only to the point necessary for a slide

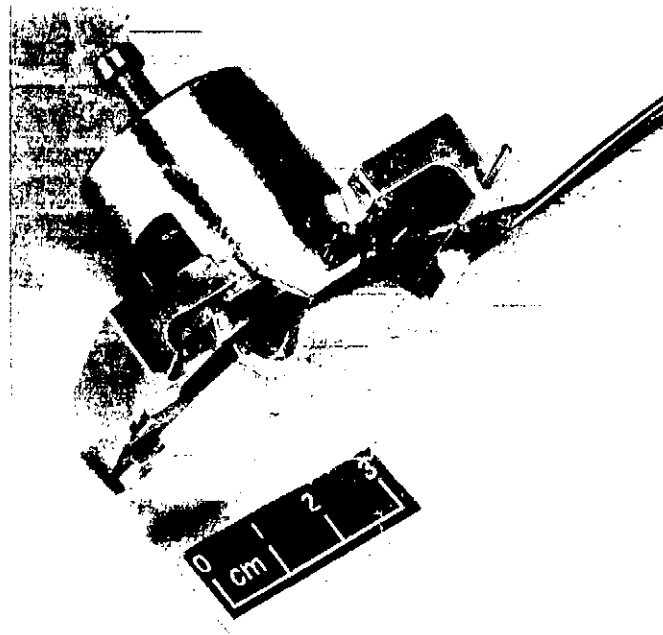


Fig. 10. Stressed specimen loading fixture and strain measurement

fit into the recess of the fixture. Cocking of the loaded specimen was avoided to assure uniform bearing stresses on each edge.

The specimen stresses were measured resulting from installation, final test position in the holder, and removal. Other measurements were taken with special fixtures of varying interference lengths to obtain different stress levels. These results are presented in Fig. 11. The lower curve representing the final test condition indicates compliance with the stressed specimen requirements of 67% of allowable yield stress for 6Al-4V titanium fully heat-treated. The upper curve shows that installation stresses do not exceed the allowable yield stress.

Thermal stability tests were conducted at 21°C (70°F) temperature and 46°C (115°F) temperature to simulate the long-term storage condition. The results indicated that the stress level decreased approximately 3.5 MN/m² (0.5 ksi) in the titanium fixture and increased approximately 2.0 MN/m² (0.3 ksi) in the glass fixtures.

The physical stability of the three specimens was demonstrated by installing and removing the first specimen from its titanium stress fixture twice, each time checking the strain gauge zero point with the specimen in the relaxed state. Each of the two remaining specimens were

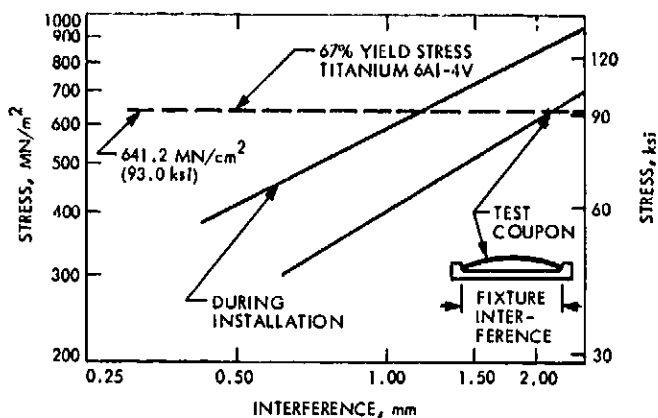


Fig. 11. Test coupon stress versus retaining fixture interference

cycled once. No shift exceeded 6.9 MN/m^2 (1.0 ksi). Also, all specimens left in the titanium stress fixture for seven (7) days at 74% yield, and in the glass fixture for 39 days at 62% yield returned to within 6.9 MN/m^2 (1.0 ksi) of the original zero point when removed from the respective stress fixtures.

The above data validate the accuracy of the analytical method for determining the stressed specimen conditions and attendant handling techniques.

3. Capsule Final Design. The glass ampule or test container configuration (Fig. 4) was established under the Phase I subprogram. Final improvements were incorporated in Phase II to provide the optimum test container for storage testing. Two significant improvements are discussed which cover method of test and means of sensing internal pressure.

In order to obtain the best possible experimental results, it is clear that two conditions must be met. First, the test reactions between the test item and fluid must be completely isolated within the test container. Second, external influences, other than the ambient temperature of 43°C (110°F), must be eliminated or prevented from affecting the chemical or electrochemical reactions taking place. A typical interaction problem is covered in Section II-B-1.

It is axiomatic that hermetic sealing of the test item and fluid satisfies both requirements. Encapsulation was accomplished by hermetically sealing the upper portion of each capsule. A typical test specimen/fluid/capsule combination is shown in Fig. 12. The capsule is made from Pyrex glass and carefully annealed to avoid internal stresses (Ref. 28). A transition section, also of Pyrex glass, was fused to the capsule opening and finally, at the top,

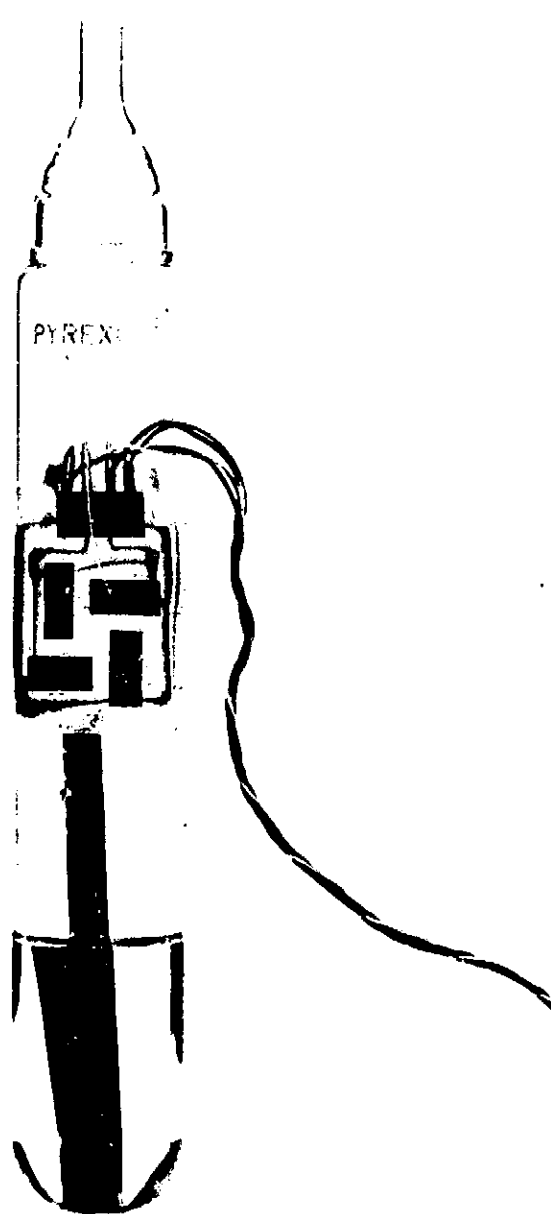


Fig. 12. Phase II test specimen/capsule

a hermetic seal was made by glass fusion to contain any pressure generated within the capsule during test. During the final fusing operation, the propellant was in a frozen state, and the capsule in an evacuated condition. Since glass is noncrystalline in nature, the working stress within

COMPATIBILITY OF THE
AL, PAGE IS POOR

the glass was kept low, on the order of 6.0 MN/m² (0.88 ksi), to avoid any tendency for glass creep to occur at the ambient test temperature of 43°C (110°F) and the normal test termination pressure of 34.4 N/cm² (50 psia) that was established for this program. Another pertinent change involved the method of sensing and measuring the internal capsule pressure. The new method consisted of using an externally mounted transducer located on the cylindrical portion of the capsule (Fig. 12). Specifically the transducer, consisting of four strain gauges, connected as a Wheatstone bridge, was carefully bonded to each glass capsule for the purpose of both sensing capsule internal pressures and converting these pressures to electrical signals that could be monitored remotely. The transducer generates an electrical signal of 2 μ V for each 0.025 μ m (1 μ in.) expansion or contraction of the capsule. A transducer output of 4 μ V is equivalent to 0.69 N/cm² (1.0 psi) differential pressure across the capsule wall. Because of the sensitive nature of the transducer, the proper processing of the glassware and curing of the bonding material is important. Each specimen/capsule was calibrated as a unit from 0-44.8 N/cm² (0 to 65 psia) at 43°C (110°F), prior to the propellant filling operation, to correct for variations in glass thickness, bonding techniques, and electrical characteristics. The problems associated with this usage were recognized and appropriate technology developed prior to use in Phase II (Refs. 30 to 31).

After completing the final seal, the specimen/capsule combination, at all times, was maintained with the propellant in frozen condition to allow handling and shipping, and to prevent, or severely inhibit, any premature chemical reaction from taking place until placed in test.

In summary, the foregoing final test configuration represents the preferred standard for this application. The advantages include ability to visually observe ongoing testing, and measure internal pressure changes. The use of fragile glassware did add certain complications; however, these were resolved and controlled successfully with the use of special handling procedures. The final product was produced on a semiproduction basis at reasonable unit costs. The specimen capsules were prepared in a clean room with a Federal Standard 209A, Class 100 certification.

For a more detailed description of capsule preparation under contract, see Refs. 30 to 32.

4. Test Description

a. Test Facility. A special test facility was designed and constructed (Figs. 13 and 14; Refs. 35 and 36) for this material compatibility program to provide the necessary environment for specimens undergoing multiyear compatibility storage. The facility is located at the JPL Edwards Test Station, Edwards, Calif.

The structure consists of four test rooms separated by 30.48-cm (12 in.) thick steel-reinforced concrete walls. Each room is provided with mechanical equipment to permit independent operation with a controlled environment. This includes separate controls, heaters, blowers, exhaust fans, drain lines, and instrumentation. Each wall is insulated and covered with aluminum sheeting for RF shielding. Separate heating loops can heat each bay from ambient to 65.5°C (150°F) temperature.

The test bays identified as test rack rooms (Fig. 13) are used exclusively for conducting this multiyear storage program. Ambient temperature is maintained at 43°C (110°F) and special baffling provides a uniform temperature gradient within the test bay from wall to wall and floor to ceiling.

Each test bay is equipped with a circular rotatable storage rack or lazy-susan type of arrangement with a capability to hold over 900 test capsules (Fig. 15). The

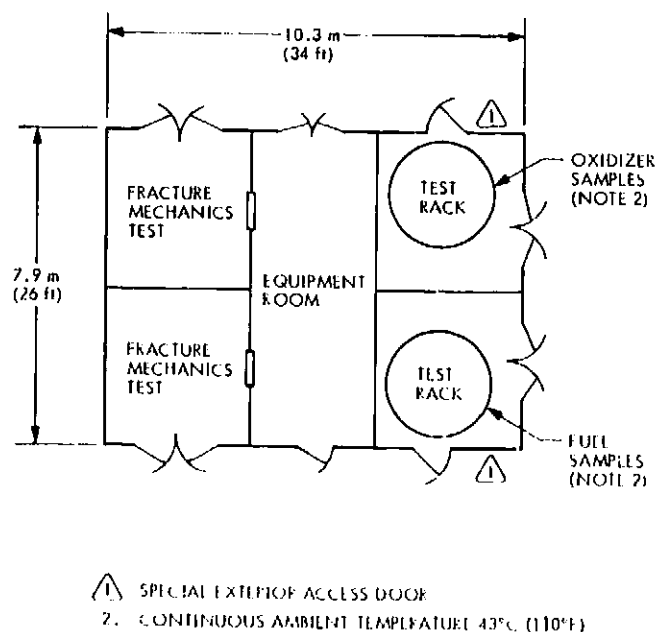


Fig. 13. Material compatibility test facility schematic



Fig. 14. Material compatibility test facility

rack (made from aluminum alloy) is approximately 2.13-m-diam (84 in.) with a 2.08-m (82 in.) height. The individual test capsule compartment is illustrated in Fig. 16 and includes: means for retention in a vertical position, electrical terminals for connection to the strain gauge, compartment walls acting as protective shields, and horizontal channels for draining purposes in the event of capsule failure and subsequent propellant spillage. Special access openings allow single installation (Ref. 37), single removal (Ref. 38), and visual observation of test capsules from outside of the building through the 2.54-cm (1 in.) thick transparent panels that are explosion resistant. The test rack is rotatable manually (by means of crank and gear drive) around its vertical axis to a position such that each test capsule position is safely accessible by opening one of the single doors provided for each tier or row of test units. Figure 16 also shows an operator wearing the prescribed safety equipment, and removing a hazardous test capsule from the circular test rack.

Under Section II-B-2 the two critical test conditions were discussed. It is appropriate to qualify those statements with the following information.

Under the general program plan, a few test capsules are removed semiannually for posttest analysis. During this operation, capsules are subjected to a very slow rotational movement as the rack is being positioned. In addition, the test units are exposed to photochemical reaction during the period that the exterior access door is open (Fig. 16). These induced and natural environmental conditions are considered to have a negligible effect on the overall test results because of the infrequency of occurrence.

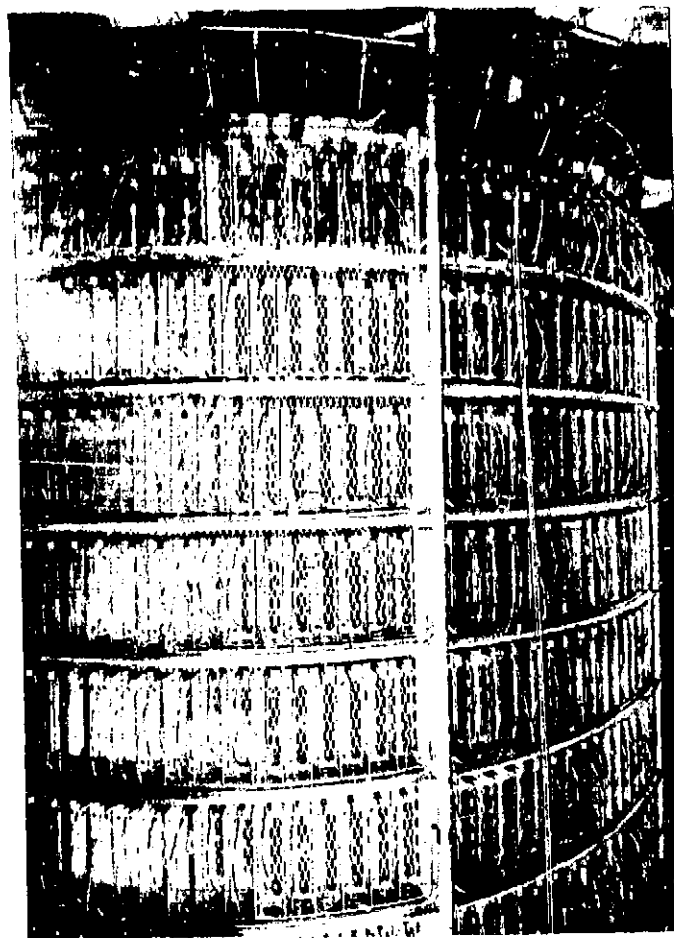


Fig. 15. Test rack for storing specimen/capsule test units

b. Procedures. Program objectives and details discussed in Section I-D indicate that a carefully planned and systematically executed program is a prerequisite for obtaining the technical information that can be applied with a high degree of confidence. The scope of procedures and specifications included all aspects of the total program. The purpose has been to maintain a high degree of control over all phases during implementation, and provide the necessary information to meet the program requirements. A list of typical items includes raw materials, propellants, preparation and processing of test samples cleaning aspects, encapsulation of test materials and propellants, pre- and posttest handling and transportation, test operations, posttest analysis, facilities, and safety considerations for personnel.

Because of the many variables, there is a continuing effort to focus on standardization of methods in order to provide uniform test standards and minimize costs.



Fig. 16. Facility special access door used for installing and removing test units

c. Test Termination. The implications of terminating a test because of questionable materials or for examination were carefully considered because of the potential hazards involved in handling the sealed test capsule. The most critical operation occurs during the removal from the test cell and transfer to the next storage facility.

The safety measures prescribed for personnel during this transfer operation are illustrated in Fig. 16. The special features of "capsule size" single-access door, handling tool, along with safety equipment provide the maximum protection to personnel.

The criterion decided upon for terminating a test and removing the test unit was based upon the glass ampule allowable stress. Each capsule was proof pressure tested to 114.0 N/cm^2 (165 psig) before use. Since a factor safety of 3.0 was considered adequate, a nominal termination pressure of 34.4 N/cm^2 (50 psia) was established for automatic removal from active storage testing. The capsule internal pressure is determined from the strain gauge measurements.

Capsules removed from test are placed in a mechanically refrigerated chamber where the temperature is continuously maintained at -45.5°C (-50°F). At this low temperature, the test unit is considered relatively safe because of the reduced vapor pressure and because any further chemical reactions are severely inhibited. Test units remain under refrigeration at the JPL Edwards Test Station until transfer to Pasadena for posttest analysis.

5. Posttest Analysis. The scope of this program incorporates a large variety of specimens (base materials, bimetal, weldments, and stressed specimens) and the ongoing, real-time exposure testing provides results on a continuing basis.

A rationale has been developed for applying this data bank to fit the needs of Advanced Development Work and Flight Projects. The basic rationale applied to posttest evaluations consists of the following:

- (1) Establishing proper criteria for selecting materials to be removed for posttest analysis as opposed to a fixed or predetermined pullout schedule, regardless of interactions or degradation.
- (2) Pulling out of test only those units displaying obvious incompatibility (pressure rise, propellant discoloration, etc.) for characterization.
- (3) Providing units of basic or critical importance to specific project needs.
- (4) Minimal evaluations that depend on the latest advances in this field.
- (5) Flexibility to offer the option of more detailed characterization where necessary.

This last item is important since it is not always possible to anticipate the extent of interactions that might occur during the exposure test. The number and types of additional tests above the minimum or nominal level are dependent upon the particular case and are identified at the time of analysis.

A considerable number of test capsules from the Phase II program have been subjected to posttest analysis. To date, material evaluations and propellant characterizations have been accomplished using over 90 test units, and the results of these analyses are included in this report and Appendices A and C. The work was primarily directed toward investigation of fuel-type specimens.

Propellant characterization analyses are performed to determine particulate content and nonvolatile residue, decomposition products, and gas products.

Material evaluations of specimens include weighing, examination, and the determination of physical and metallurgical changes. Typically, this covers such items as dimensional changes, and type of damage (i.e., general corrosion, stress-corrosion cracking, intergranular corrosion, pitting, embrittlement, staining, and coating or scaling).

One important finding deals with the use of cleaning solvents. Four test specimens of 6Al-4V titanium in as-received hydrazine, removed from the fuel test-bay at JPL Edwards Test Station, were evaluated extensively by JPL (Ref. 23) and the Stanford Research Institute (Ref. 39) to determine the reason for the occurrence of hydrogen embrittlement. The conclusion reached was that decomposition of the hydrazine and corrosion of the titanium resulted from a reaction between the hydrazine and Freon-TF used as a cleaning agent. Thus, isopropyl alcohol is the recommended cleaning and rinsing agent for all 6Al-4V titanium that will be in contact with hydrazine; the use of Freon, or Freon-type materials, should be prohibited as cleaning or rinsing agents for all 6Al-4V titanium that will be in contact with liquid or gaseous hydrazine. Isopropyl alcohol is better than Freon for removing organic material and does not interact with the hydrazine or the titanium. This information has been included in NASA Pre-Alert No. E4-70-03A (Ref. 40). As a result, the cleaning procedure for this program was changed on October 1970 to use only isopropyl alcohol.

Complete details of posttest evaluations are presented in subsequent sections along with methods and descriptions of laboratory equipment used for this purpose.

III. Posttest Chemical Analysis Procedure

A. Discussion

Two basic posttest analysis procedures, shown schematically in Figs. 17 and 18 were developed and used in this program. The procedure with the distillation process (Fig. 17) provides for a complete analysis of all components. The procedure without the distillation process (Fig. 18) provides for a limited analysis. A preselected item is subjected to analysis; for example, CO₂.

The choice of the posttest analysis procedure to be applied is dependent upon the test unit history, and the level of information required to permit satisfactory assessment of results. Details of these operating procedures are discussed next.

1. Procedure—Complete Analysis. This procedure, shown in Fig. 17, involves distillation of chemical and gaseous components. The propellant is frozen by immersion in liquid nitrogen (LN₂), and the capsule is placed in the opening fixture (Fig. 19). The capsule tip is broken and the volume of noncondensable gases (mostly N₂ and H₂) measured in a calibrated vacuum system. The hydrazine is thawed and refrozen at -30°C (-22°F) and the gas at that temperature, mainly NH₃, is measured. The purity of the residual hydrazine is determined by gas chromatography which measures NH₃, H₂O, MMH, and UDMH. Aniline is determined colorimetrically. Metal content is analyzed by atomic absorption techniques. A turbidimetric method is used for low concentrations of chloride; higher concentrations are titrated. Fluoride is determined colorimetrically.

2. Procedure—Limited Analysis. This procedure, shown in Fig. 18, does not include the distillation process. Specifically, this is an abbreviated version of the above analysis, Section III-A-1, and involves the measurement of only the noncondensable gases, hydrogen and nitrogen. The residual hydrazine is removed from the capsule using a syringe and is analyzed by gas chromatography for NH₃ and H₂O. If the NH₃ content is high, there may be an error due to NH₃ evolution before analysis. Chloride and fluoride ion contents are determined as above.

B. Decomposition Gases

1. Composition. The contents of the posttest capsule are frozen in liquid nitrogen and then prepared for sampling as follows: The strain gauge is very carefully scraped off with a sharp razor blade, a small scratch is made on the neck of the capsule, and the capsule is then enclosed in the CRES opening fixture (Fig. 19). The system is pumped down for several hours to remove moisture from the outside of the capsule. The fixture is then filled with dry helium to 0.5 atmospheres, to aid in heat transfer, and immersed into liquid nitrogen to a depth equal to one-half of the capsule. After about an hour, the helium is pumped out. When a satisfactory vacuum has been attained (1.3×10^{-3} N/m²), the gas sampling system is isolated from the vacuum pump, and the neck of the capsule is broken by turning the handle on the fixture. By means of a vacuum (Toeppler) pump, the

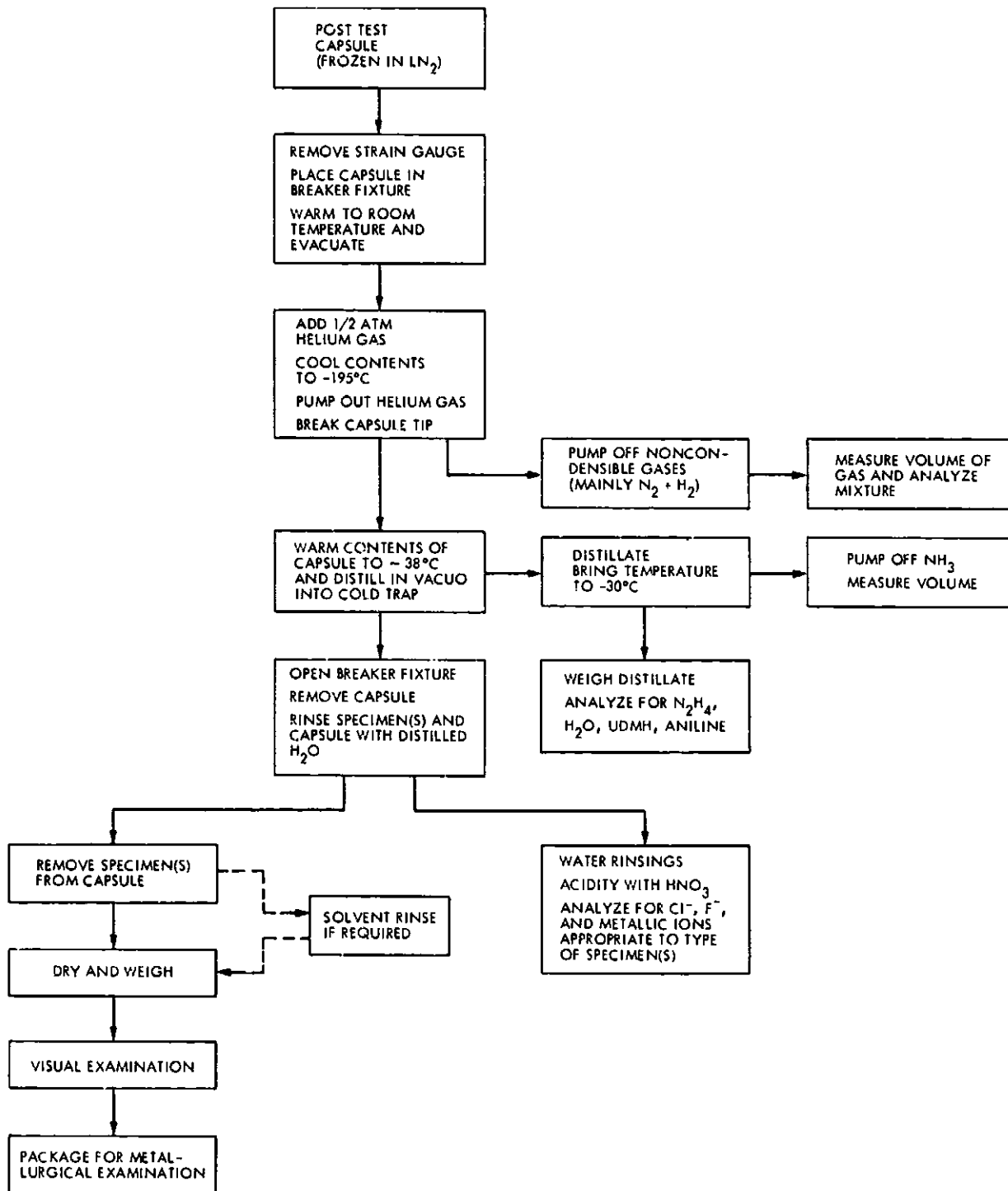


Fig. 17. Procedure for complete posttest chemical analysis (with distillation)

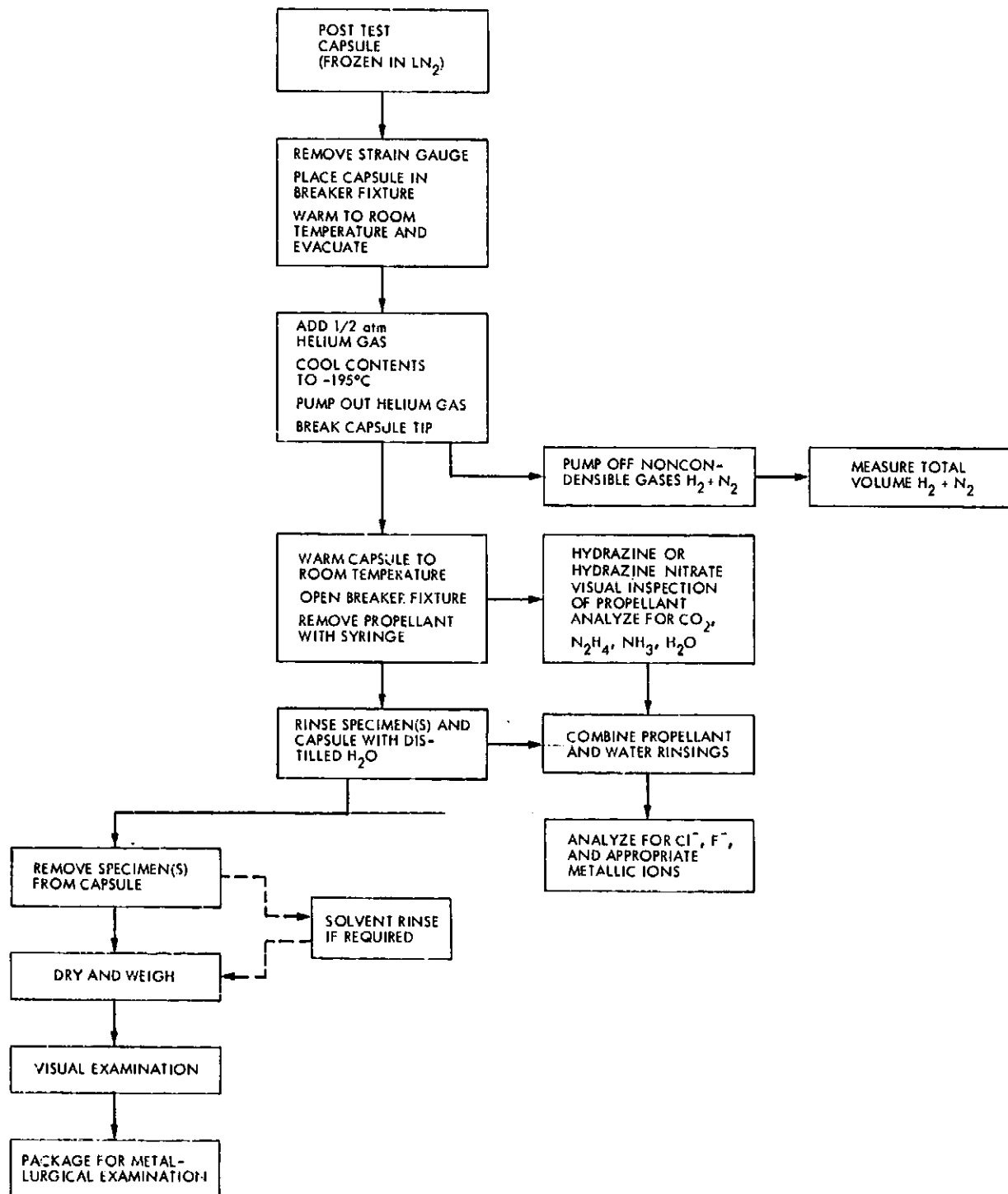


Fig. 18. Procedure for limited posttest chemical analysis (without distillation)

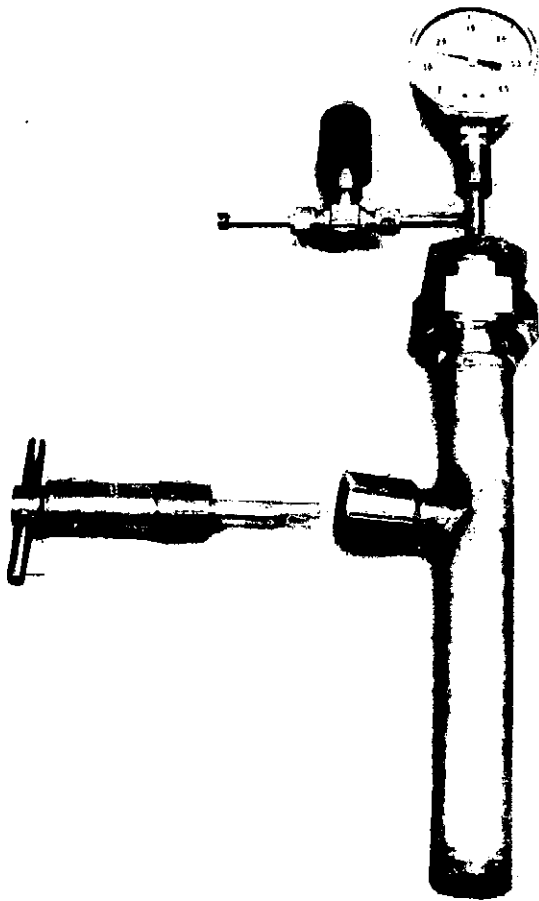


Fig. 19. Specimen/capsule test opening fixture

released noncondensable gases are pumped off through a liquid nitrogen trap. The volume of the collected gases is measured manometrically and a sample is taken for analysis by a mass spectrometer.

The propellant is thawed and distilled, *in vacuo*, into traps cooled by liquid nitrogen. The liquid nitrogen traps are replaced by traps at -30°C (-22°F). After repeated thawing and refreezing of the hydrazine, the remaining condensable gases (mainly NH_3) are pumped off, measured and sampled.

2. **Calculated Final Capsule Pressure.** The mean volume of the test capsules is $82 \pm 1 \text{ cm}^3$. With 20 g of hydrazine and a standard metal coupon, the ullage is about 60 cm^3 at 43°C (110°F). If a stress fixture is present, or if there are nonmetals in the capsule, the ullage is recomputed accordingly. The pressure calculations de-

pend upon the volume of nitrogen plus hydrogen (assuming negligible solubility in the hydrazine) and the volume of ammonia in the vapor phase.

The contributions of nitrogen and hydrogen are calculated from the perfect gas law:

$$P_1 = \frac{NRT}{V} \quad (1)$$

P_1 = partial pressure of gas in atmospheres

N = moles of gas = $\text{cm}^3 \text{ gas (STP)}/22,400$

R = universal gas constant = $82.06 \text{ cm}^3\text{-atm/deg-mole}$

T = 316.6 K (110°F)

V = ullage volume of capsule, cm^3

The calculation of pressure due to the ammonia is not so simple and straightforward. Ammonia is highly soluble in hydrazine and may not necessarily be considered an ideal gas at the temperature and pressures considered.

Fortunately, solubility data for ammonia in hydrazine are available (Ref. 41). Although the data do not cover the temperature of interest, viz., 43°C (110°F), it is possible to extrapolate the data of the above referenced report. It can be shown that for ammonia dissolved in hydrazine, the following relationship can be used to determine the ammonia pressure as a close approximation:

$$P \cong \frac{N/m}{K} \quad (2)$$

where

P = partial pressure of ammonia, atm

N = moles of ammonia in system

m = moles of hydrazine in system

K = equilibrium constant (0.0455 at 43°C , 110°F).

A similar expression can be derived for the pressure of ammonia over monomethylhydrazine. The value of K in this case is 0.064 at 43°C (110°F).

3. **Pressure Rise Rate.** It would be of interest, both practically and theoretically, to have curves expressing pressure as a function of time for each test capsule. Unfortunately, due to aging of the bonding material, some of the strain gauge data have proven to be unreliable.

For this reason, no data for the internal pressure rise as a function of time are being presented in this report.

4. Percentage of Hydrazine Decomposed. The percentage of hydrazine decomposed is calculated from the total weight of the gaseous products of decomposition—viz., nitrogen, hydrogen, and ammonia. Some hydrogen may arise from the attack of metals by acidic constituents, but the error, if any, is insignificant particularly because of the low molecular weight of hydrogen.

C. Residual Hydrazine

The residual hydrazine is removed from the capsule by distillation, *in vacuo*, into a liquid nitrogen cooled trap after the decomposition gases are removed and analyzed as described above.

1. Impurities

a. NH₃ and H₂O. The NH₃ and H₂O contents of the hydrazine are analyzed by gas chromatography using a 0.0065-m-diam × 2-m-long (1/4 in. × 6 ft) column filled with powdered Teflon coated with 15% of triethanolamine. The inlet and column temperatures are held at 90°C (194°F) and the helium flow set at 100 cm³/min. This column separates NH₃, H₂O, and N₂H₄, in that order.

b. Aniline. Aniline is determined spectrophotometrically by diluting 0.5 ml N₂H₄ with water to 50 ml and determining the absorbance in a 1.0-cm cell at 280 nm.

2. Contaminants

a. Metals. The capsule is cut open and the metal sample rinsed, while adhering material is rubbed loose with a rubber policeman. Any residue in the capsule is also rinsed out. All washings and residue are acidified with 5% HNO₃, diluted to a known volume with water and analyzed for the appropriate metals by atomic absorption.

b. Halogens. An aliquot of the acidified washings is checked for chloride by turbidimetry. If the chloride content is high, titration can be used. The fluoride ion content is determined by a spectrophotometric method based on the bleaching of a zirconium alizarin color complex by fluoride ion. The absorbance is measured at 525 nm.

c. Carbon dioxide. Hydrazine reacts with carbon dioxide to form the salt, hydrazinium carbazate. The equation for this reaction is



The method of analysis involves the addition of a sample of hydrazine to an excess of sulfamic acid. The sulfamic acid causes the liberation of CO₂ from the hydrazinium carbazate. Sulfamic acid was selected for use in the analysis because hydrazinium sulfamate is soluble in water and sulfamic acid is nonvolatile.

The liberated CO₂ is swept out of solution with helium gas, through a trap containing concentrated sulfuric acid to remove the water, and then through a special trap containing small glass beads where the CO₂ present is frozen out at liquid nitrogen temperature.

The trap containing the frozen CO₂ is provided with a special 4-way stopcock which permits the CO₂ to be isolated in its loop. This trap is attached to a special sample introduction system on a custom built chromatograph which permits the collected CO₂ to be quantitatively transferred through a chromatographic column for separation and assay. Refer to Appendix D for details of this method.

IV. Posttest Analysis Procedure for Specimens

A. Discussion

Each specimen is examined and tested to determine if physical or metallurgical changes have taken place. Surface conditions are examined at low magnifications with a microscope. Selected surface areas and/or sample cross sections are examined at higher magnifications with a scanning electron microscope. Mechanical properties tests are conducted in certain cases to establish ultimate and yield tensile properties and percent elongation.

The important categories are listed below:

- (1) Weight.
- (2) Appearance and location of the liquid/vapor interface boundary.
- (3) Presence and distribution of formations, colored stain, or film.
- (4) Streaks, mottling, and spotting of surface.
- (5) Presence of crystalline deposits.
- (6) Flaking and cracking of scale (bare spots).

- (7) Physical change: degree of etching over entire surface or a local area such as the liquid end, edges, or bimetal contact area, etc.
- (8) Extent of pitting: identification, size, and distribution.
- (9) Extent of cracking: identification, size, and distribution.
- (10) Mechanical properties test.
- (11) Environment sensitivity.

The details of this operating procedure are discussed next and are also shown schematically in Figs. 20 and 21.

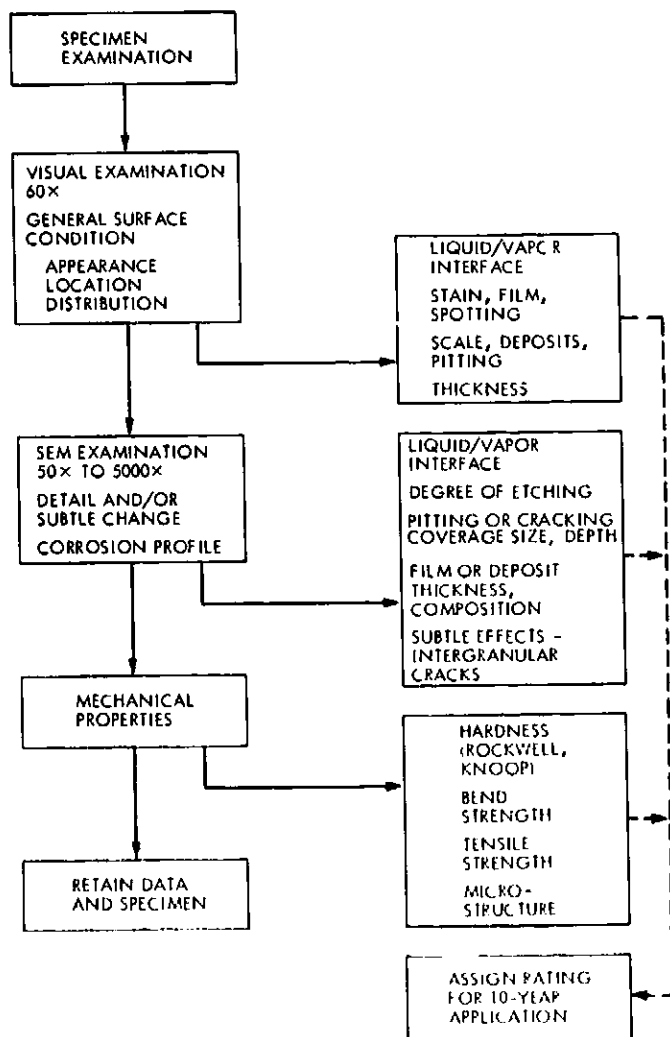


Fig. 20. Metallic specimen analysis procedure

B. Specimen/Capsule Inspection

The first visual inspection is the appearance of the specimens as viewed within the capsule. At normal compatibility the liquid is clear (water white) and the specimen is unchanged. At higher hydrazine contamination levels, the liquid usually turns pink or red and the vapor-exposed end of the specimen appears darkened, either uniformly or in a blotchy manner.

C. Metallic Specimen Examination

After removal of the liquid, the specimen was placed in a beaker where it was washed with water and also organic solvent, if required, to remove any organic coat-

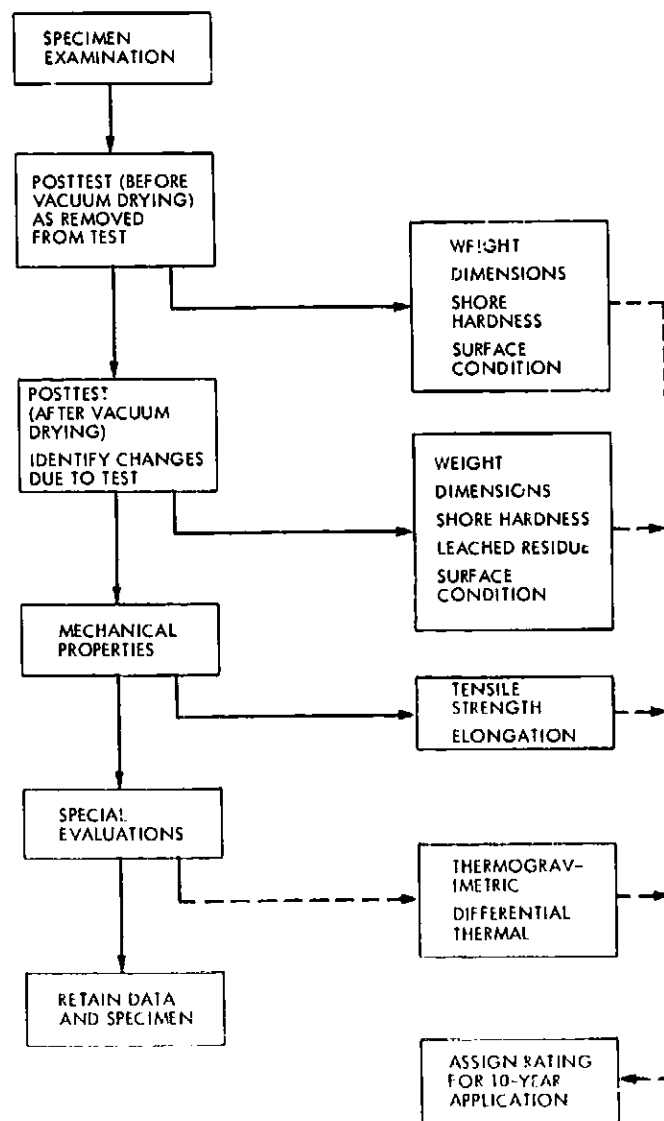


Fig. 21. Nonmetallic specimen analysis procedure

ings. In the early posttest studies, the loose scale and film was removed and collected using a rubber policeman. All the loose scale and film were analyzed as part of the metallic residue in the propellant, and thus the residue included both dissolved metal ions and the metal in the loose oxide scale. Later specimens were not rubbed but only washed, and the specimen retained more of the loose oxide scale and rust crystals on the surface which was then examined microscopically. The washed specimen was oven dried at 75°C (167°F) and examined visually at a magnification factor of 60.

1. Mass Change. The metal specimen mass was measured to within ± 0.1 mg after distilled water rinsing and air oven drying at 75°C (167°F). This mass was compared with the pretest specimen mass measured after cleaning and passivation. This posttest mass included both the effects of mass loss due to metal dissolved and mass gains due to oxide film buildup. Usually, the vapor exposed surface exhibited more oxide film buildup than the wetted surface. The mass of the metal residue in the posttest hydrazine was taken as the mass loss of the wetted surface. Only when the total corrosion was relatively large did the measured specimen weight change agree with the mass of metal residue. For small amounts of corrosion, the measured mass changes were as often positive as negative.

2. Liquid-Vapor Interface. The liquid immersed area (apparent wetted surface as opposed to actual wetted surface that includes effects of pits and scratches) was usually indicated by the visible location of the liquid-vapor interface (L-V) boundary marked by a distinct change in appearance, concentration of surface film, or corrosion. For slug specimens immersed in 20 cm³ (1.2 in.³) of hydrazine this depth of immersion typically was 4.45 cm (1.75 in.), giving an immersed surface apparent area for a typical slug specimen of 11.97 cm² (1.86 in.²). In 20 cm³ of hydrazine the typical specimen wetted area to propellant volume ratio (s/V) was 0.6 cm⁻¹. The immersed area for other specimen geometries was measured similarly.

3. Surface Condition. Specimen surface stains of a definite color (e.g., blue, green, or red) on the specimen surface was an indication of thin film approximately 0.2 to 0.4 μm thick. The color was due to spectral interference in the reflected light passing through the film. When the film was thicker than 0.5 μm , the surface usually appeared darkened. These film thicknesses were confirmed by scanning electron microscope (SEM) examination in which film thickness could often be measured to 0.1 μm .

Visual characteristics may be observed under the microscope by lightly scratching the surface with a sharp hardened steel scribe. The ductility and hardness of the surfaces could be compared in this way. Aluminum, corrosion-resistant steels, and titanium appeared soft and ductile as they were being scratched. Chrome plate and tungsten carbide were not affected by the steel scribe. An Exacto blade was used to scrape areas of the film from the surface. Some films less than 2 μm thick were not visible at 60 \times , but a waxlike residue could be scraped from the surface in sufficient quantity to be visible at 60 \times . This material from selected specimens was transferred to a graphite mount for subsequent SEM analysis by X-ray dispersion. Some colored stains were swabbed with an organic solvent (acetone) to determine if the film was a soluble organic residue or an oxide film resulting from corrosive attack. Surface films 2 μm (0.0001 in.) could be scraped off the specimen so that thickness with and without the film could be recorded. Thinner films could not be successfully removed over a large enough area to measure the thickness of the specimen without the film. However, such films were hard enough and usually cracked such that the film thickness down to 0.1 μm could be estimated from the SEM photographs at 2000 \times to 5000 \times magnifications.

4. Physical Change. The only metal dimensional change of significance was the specimen thickness change. This was measured with or without surface films, using a 0-2.54 cm (0-1 in.) micrometer at locations every 0.65 cm (0.25 in.) to 1.3 cm (0.5 in.) along the specimen length. Readings of thickness, nominally 0.076 cm (0.0300 in.), were read to 0.00025 cm (0.0001 in.) and in general, the readings were accurate and repeatable to ± 0.00025 cm (± 0.0001 in.). In addition to the visual observations described above, the surfaces were examined using the SEM and on selected specimens the surface finish was measured using a Bendix Proficorder.

The Cambridge SEM used was capable of holding three or more complete flat metallic slug specimens (a total specimen viewing size of 3.8 cm \times 7.6 cm) mounted at a 45-deg viewing angle. The specimens were held in the SEM in an aluminum foil backing by folding the foil over the specimen edges. This mounting procedure permitted mounting the specimens without the use of conducting cement and with minimum contamination of both the posttest specimens and the pretest reference specimens. Because of the large specimen size, the mount was constrained to a fixed viewing angle and limited traverse across the specimen faces. For more flexibility in examining the ends of the specimens and viewing at different

angles and viewing stereoscopically, it was necessary to cut the slug specimen to a smaller size.

Using these sizes, such as a 2.5-cm (1 in.) portion of the specimen which included the contact area of a bimetal couple, it was also possible to use the energy dispersive X-ray analysis capability of the SEM to identify the metallic composition of the specimen surface films and artifacts. For instance, it was found that aluminum oxide lapping compound particles were smeared into the specimen surface during the slurry lapping process. Also, in bimetal couples of an aluminum alloy and stainless steel, it was found that aluminum oxide was deposited on the stainless steel surfaces.

The areas to be examined and photographed in the SEM were identified and marked, using the 60 \times light microscope. The areas were usually marked by a small ink dot and/or a steel scribed rectangle ($\sim 1 \text{ mm}^2$) on the specimen surface. A sequence of photo magnifications (e.g., 50 \times , 500 \times , 5000 \times) was used to locate and isolate particular significant areas. Readily identified surface features included surface finish, pitting depth and diameter to 0.1 μm , film and scale, organic, and nonconducting surface contamination. Where general surface etching occurred as revealed by the SEM, thickness change measurements were usually consistent with metal residue measurements. Pitting was described in terms of size range of major pit diameters, e.g., 0.2–0.8 μm (10–40 $\mu\text{in.}$) and apparent pit depth, and percentage of surface covered by the pits.

The dimensional changes and surface topography changes were noted down to 0.1 μm and compared with similar pretest reference specimens prepared under the same specified methods.

5. Mechanical Property Tests. Mechanical property changes were determined, based upon measurements or evaluations of hardness profiles, bend strength, tensile strength, and microstructure.

Superficial hardness (Rockwell) and microhardness (Knoop) measurements were taken on the specimen surfaces. Microhardness profile measurements were taken across the specimen cross section after metallographic polishing to detect any change. Specimens were tested in three-point loading at a controlled deflection rate of 0.05 cm/min (0.02 in./min). Load/deflection curves were recorded and compared at 0.1% offset yield strength and at their ultimate flexure strength.

Tensile tests were conducted on specimens in the existing condition or rectangular shape.

D. Nonmetallic Specimen Examination

On elastomeric materials examination procedures were employed to evaluate the chemical interaction between the elastomer and propellant and the change in the elastomer properties. Procedures included the following steps:

- (1) Specimen weight (blotted, but prior to vacuum drying).
- (2) Specimen dimensions (prior to vacuum drying).
- (3) Calculated density and volume change (prior to vacuum drying, based on weight and dimensions).
- (4) Shore hardness, and visual appearance.
- (5) Final weight after 167 hr vacuum drying at 60°C (140°F).
- (6) Final Shore hardness (after drying).
- (7) Leached residue (Si, S, Zn from EPT-10).
- (8) Tensile strength and elongation, using miniature dog-bone coupons cut from the 2.54 cm \times 1.27 cm (1.0 \times 0.5 in.) specimens after 167 hr of vacuum drying.
- (9) Thermogravimetric analysis (TGA).
- (10) Differential thermal analysis (DTA).

The TGA analysis provided a graphical plot of specimen weight loss as a function of temperature in an N_2 atmosphere. A 2- to 3-mg sample of the elastomer was heated at a uniform temperature rise rate between room temperature and 500°C (930°F). The weight loss, indicative of volatilization and decomposition of the material components, was evaluated by comparison to the results from an unexposed specimen.

The DTA analysis provided a graphical temperature plot of endothermic or exothermic reactions taking place within the elastomer specimen as it was heated at a uniform rate between room temperature and 500°C (930°F). The results were interpreted by comparing the results from an untested control sample. In the thermal evaluation of EPT-10, it was found that a product was formed during hydrazine immersion and the new product decomposed exothermically around 200°C (390°F).

V. Posttest Analyses and Results

A. Discussion

So far in this program over ninety (90) test units have been removed from storage testing and subjected to post-test examinations. The results from these immersion tests are presented in this section.

Posttest analyses were conducted using the procedures described in Sections III and IV. The detailed results were documented with written reports, and also recorded on "data summary forms" of the type shown in Appendix E. Complete information is retained in a permanent archive file for retrieval at any time upon request of users. In addition, pertinent details of two important facets of these analyses are presented.

B. Summary of Posttest Analyses and Results

A large amount of detailed information has been generated and documented based upon:

- (1) The different analyses performed on each test unit.
- (2) The total number of test units subjected to analyses.

However, for purposes of this report, only a summary of this data is considered appropriate. Accordingly a summary of the specimens and propellants analyzed and major results are tabulated in Appendix A.

C. Hydrazine Material Compatibility and Surface Film Formation

For hydrazine propellant the primary criterion for compatibility has been the decomposition rate of the hydrazine. In general, it has been found that metal corrosion itself has been a secondary consideration except for the generation and accumulation of corrosion residue which can potentially cause valve sealing problems, filter clogging, small tube clogging, or catalyst bed poisoning.

The buildup of soluble metal product was measured directly in the hydrazine analysis. It was found that the metal product was in accord with the composition of the immersed alloy, and was approximately proportional to the acid-forming contaminant (see total halide contamination level in Table A-1). In the case of the bimetallic couples, cathodic protection was afforded the more noble of the metals in the couple; i.e., aluminum was usually more severely corroded when coupled with corrosion-resistant steel or titanium.

The SEM examination of specimen surfaces revealed subtle effects giving new insights into the mechanism of material reactions with hydrazine and its contaminants. One facet of the corrosion process revealed by the SEM was the formation of thin oxide films on aluminum, CRES, and titanium materials which, when dried, tended to shrink and flake off the specimen surface when the

Table 4. Compatibility of CRES and hydrazine doped with CO₂

CRES	CO ₂ , ppm	15 Days		30 Days		45 Days		91 Days	
		Percentage of N ₂ H ₄ decomposition	Fe, μg	Percentage of N ₂ H ₄ decomposition	Fe, μg	Percentage of N ₂ H ₄ decomposition	Fe, μg	Percentage of N ₂ H ₄ decomposition	Fe, μg
303	27	0.018	4	—	—	0.015	3	0.040	4
	52	0.015	4	0.033	4	0.048	8	0.101	10
	90	0.025	4	0.045	7.5	0.069	10	0.132	13
	230	0.050	23	0.099	27.5	0.170	38	0.534	80
304 L	27	0.038	6	0.022	5	0.112	15	0.046	3
	52	0.017	2	0.024	2	0.028	3	0.044	3
	90	0.022	2	0.033	2	0.026	5	0.042	3
	230	0.022	3	0.022	4	0.059	10	0.229	25
347	27	0.016	2	0.027	2	0.025	3	0.018	3
	52	0.025	4	0.043	2	0.169	8	0.093	4
	90	0.035	3	0.050	5	0.088	5	0.203	3
	230	0.069	3	0.285	10	0.579	15	1.259	25

Pretest assay of hydrazine at all four CO₂ levels indicated an initial Fe content of less than 1.0 ppm (μg Fe/2 ppm Fe).

film thickness exceeded 1 or 2 μm (Fig. 22). It is postulated from the analyses and observations that the surface films were formed as hydrous oxides as a result of the reaction of water with the metal salts formed by acidic contaminant (halide, carbon dioxide, air, etc.) attack of the metal specimens. The shrinking and flaking most likely occurred when the specimen was dried.

For conditions of very low levels of contamination, the oxide film which formed on aluminum and titanium during 3-4 year exposure periods resulted (upon drying) in oxide flakes 1- or 2- μm thick and 10- to 20- μm across (Fig. 23).

On aluminum, this film was mostly over the vapor-exposed surface and thickest at the liquid-vapor boundary. On titanium, the film extended over the whole specimen with an uneven distribution of thickness from 0-2 μm . This potential problem area could affect the performance of such components as valving and metering devices.

D. Effect of Carbon Dioxide Contamination

A study was made to determine the effects of contaminants such as carbon dioxide or air on hydrazine propellant and corrosion-resistant steel type materials. The hydrazine and materials used in these experiments were taken from Phase II stock items.

The hydrazine was doped to CO_2 content levels of 27, 52, 90, and 230 ppm. Test samples (CRES, 303, 304L, 347)

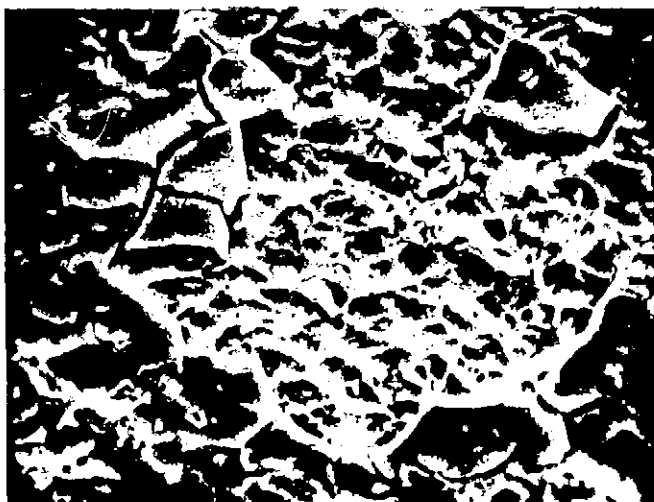


Fig. 22. Flaking of oxide film from surface of titanium specimen

measured $0.6 \times 1.2 \times 0.076$ cm, and each sealed glass capsule contained 2.0 cm^3 of hydrazine (s/V ratio 0.7 cm^{-1}). Exposure testing was conducted at 43°C (110°F) ambient temperature. A summary of the data is shown in Table 4.

There was a general trend toward more hydrazine decomposition and more dissolved iron as the CO_2 content was increased and as the test time was lengthened. It appears that a CO_2 content of 50 ppm in the hydrazine would be acceptable for long-term contact with all three metals (decomposition generally less than 0.5% per year). At a CO_2 content of 90 ppm, the decomposition rate was moderate in the presence of CRES 303 and 304L, but significantly higher with CRES 347. A CO_2 content of 200 ppm would be unacceptable because of severe corrosion of all three metals and the subsequent high degree of hydrazine decomposition. A qualitative evaluation of the observable extent of corrosion was made using the scanning electron microscope. It revealed that the severity of pitting and etching of the metal surfaces was directly related to the quantity of iron dissolved in the hydrazine.



Fig. 23. Aluminum oxide film at the liquid-vapor interface on aluminum specimen

VI. Material Ratings

A. Discussion

This section is concerned with the conversion of the test specimen/propellant performance and results, reported herein, into a rating for the different materials relative to the long-term (10-year) compatibility requirements delineated in Section I-D.

The posttest examinations and analytical results are based upon real time, conjoint test properties, and indicate in terms of descriptions and measurable values, the effects of the propellant on the material, and conversely the effects of the material on the propellant.

In order to derive the overall information required for this type of a program, a considerable amount of data is generated for each test unit, because of the completeness of the analyses. Pertinent results are summarized in the tables in Appendixes A and C.

The next logical step is to translate or reduce the accumulated information from this complex detailed form, and replace it with a system of standard descriptive terms or values to provide a simpler expression of the compatibility results. The product of this compression, subsequently identified as a rating, is more amenable to dissemination of generic type compatibility information on a direct basis, and also facilitates usage in such practical areas as determination of overall performance, design application, comparison, or cost-effective measures.

B. Rating System Factors and Criteria

The conversion of experimental results into a comprehensive and meaningful output by means of assessments and interpretations presents a difficult problem, because of the different conditions, factors, variables, and complex interactions involved with each material/propellant combination and test.

The general scheme for determining the final rating is depicted in Fig. 24, and identifies the key subdivisions involved in the regression process.

The primary multivariant factors influencing the compatibility phenomena (conditions) provide qualitative and quantitative information. These data are systematically evaluated (effect and degree), and performance characterized using the general criteria indicated in Fig. 25.

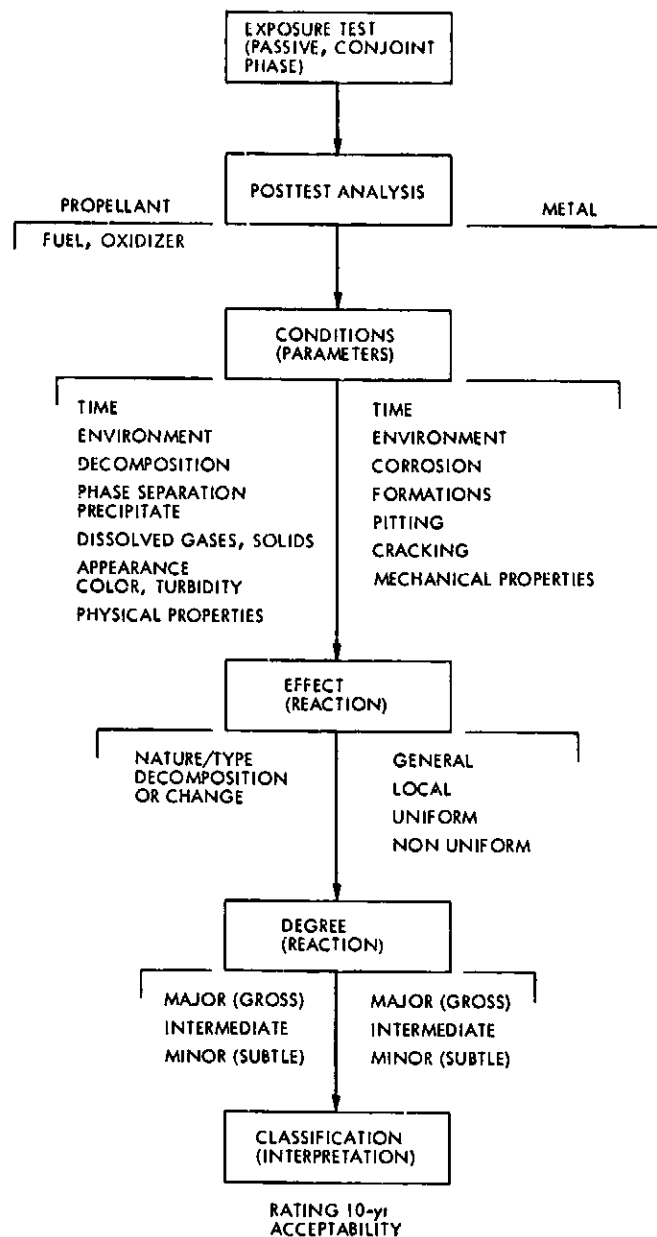


Fig. 24. Factors leading to propellant/material long-term (10-year) rating determination

By way of clarification, these standards have been evolved to serve the needs for design purposes of the JPL advanced development and flight projects for long-term planetary spacecraft applications, and are considered both current and representative for practical application. The availability of more real-time data on the propellant/metal interactions will permit refinements of these standards. It is axiomatic that spacecraft popul-

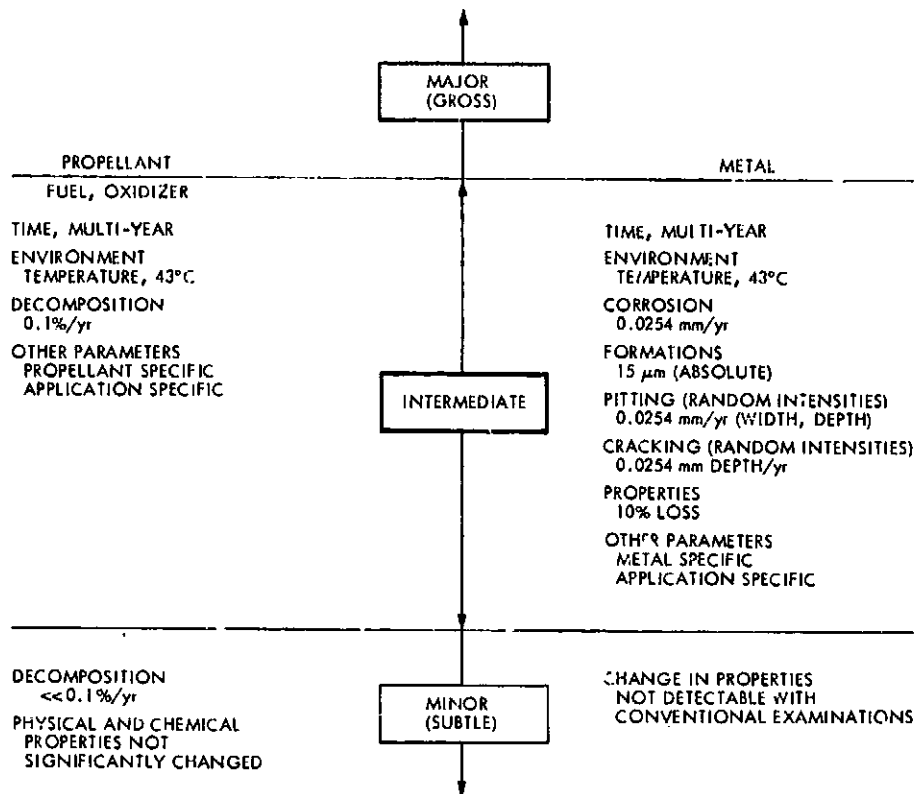


Fig. 25. Typical criteria for determining propellant/material long-term (10-year) rating

sion components utilize weight-sensitive highly stressed structural materials. A better understanding of the performance over the long duration, especially as it affects minor or subtle changes, will lead to more reliable and improved designs.

C. Description of Classifications Used for Rating Materials

A classification system has been established for rating the materials relative to compatibility behavior.¹ This is shown in Fig. 24 as the last step, and expresses the material compatibility performance in its simplest form.

The classifications and symbols used are:

- A = acceptable
- N = not acceptable
- I = incomplete
- R = restricted

Specific materials for a given application are determined to be either acceptable (A) or not acceptable (N), in terms of compatibility with environmental fluids over the time and dynamics of the mission. However, since an A rating is, in fact, a prediction based on available data, a qualifying code is required to define the basis and validity of the prediction. The approach used is to add a rating qualifier or modifier to each where required. The symbols used are I for incomplete, and R for restricted; thus materials are rated as follows: A, A-I, or A-R or N. The I and R in each case would be explained with background information. The definitions of I and R are as follows:

I = Incomplete compatibility data (a data void) with respect to conditions or time.

R = Restricted compatibility indicated by corrosive degradation or propellant contamination at conditions that could influence the mission, component, or operating specifications (requires analysis of the specific application).

¹Other typical systems are presented in Refs. 42-44.

D. Correlation and Application

To complete the discussion of ratings, brief comments are made regarding details of the classification category (final subdivision shown in Fig. 24).

1. **Correlation.** This aspect is very important, because of the consequences or implications that are associated with the final output or rating. The approach taken was to derive the ratings based upon practical treatment of the many variables and interpretation of results.

To help visualize the steps involved in this transitional process, the correlation between the criteria for determining compatibility and classifications is illustrated in Fig. 26. The level of acceptability for test data is established based upon the comparison of the subject results with the standard criteria (intermediate category, Fig. 25). The rating is then assigned based on results of such comparison(s).

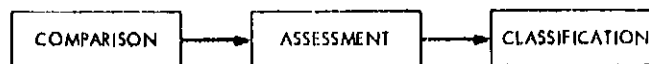
2. **End-Point Application.** To summarize, a materials rating system has been established to derive engineering information and design guidelines from the JPL current test program. In consonance with the program goals, the system provides for:

- (a) A basis for selecting structural or component material candidates based on the application and operating environment.
- (b) A basis for rating the candidate acceptable materials in terms of the best data currently available.

E. General Rating of Materials

The material compatibility ratings and qualifiers have been assigned for the different materials and propellants evaluated to date under this program. Influencing factors leading to the specific ratings are presented in the next Sections VI F through I. These material ratings will be updated as new knowledge becomes available from the JPL test program.

In conclusion, it should be noted that no material is rated completely acceptable, without qualification, for the ten-year requirement at this time. A large number of specimen/capsules have been in test for over six years and, based upon visual observations, will apparently last longer. However, there are no generally accepted extrapolation rules that can be applied at this time to bridge the gap between six and ten years.



INPUT	CRITERIA	POTENTIAL USAGE	RATING
POSTTEST ANALYSES RESULTS	MAJOR (GROSS)	QUESTIONABLE	NOT ACCEPTABLE
	INTER-MEDIATE (STANDARD)	ACCEPTABILITY (DEGREE)	ACCEPTABLE INCOMPLETE RESTRICTED
	MINOR (SUBTLE)	PROPERTIES UNCHANGED OR EFFECT(S) INSIGNIFICANT	ACCEPTABLE INCOMPLETE ACCEPTABLE

Fig. 26. Correlation between typical criteria, test results, and assigned ratings

F. Hydrazine/Materials, Ten-Year Compatibility Ratings

1. **Hydrazine.** The primary effect has been established as the decomposition of the propellant resulting from impurities in solution and metal contact.

Rating: Specification grade: Acceptable-Restricted (A-R)

A = Potentially acceptable

R = The catalytic activity of impurities produce reactions which result in a very slow, but measurable increase in the rate of decomposition.

Rating: Refined Grade or Uncontaminated Form:

Acceptable-Incomplete (A-I)

A = Potentially acceptable. This propellant grade is considered a low risk.

I = Data lacking for 10-year period

2. **Aluminum Alloy, Types 2219-T86, 6061-T6.** The primary effects have been established as formations and pitting. The oxide film buildup is very thin (on the order of 1.0 μ m thick), and does not contribute to decomposition. The shallow pitting is well below the criteria limit.

Rating: Acceptable-Incomplete (A-I)

- A Potentially acceptable. The tendency is toward minor compatibility effects.
- I Data lacking for 10-year period.

3. Corrosion-Resistant Steel, Types 302, 303, 304, 304L, 316, 321, and 347. The primary effects have been established as: (1) varying from random corrosion to discrete pitting, and (2) formations. The corrosive attack is non-uniform with a proclivity for the numerous pits, as they become larger than $1.0 \mu\text{m}$, to join other pits, and develop an etched area. The net effect falls between non-uniform corrosion and pitting. The oxide film formed is very thin (approximately $1.0 \mu\text{m}$) and porous. The quantity of metal, mainly iron, transferred to solution and as residue increases the rate of hydrazine decomposition.

Rating: Acceptable-Restricted (A-R)

- A The materials are considered potentially acceptable, as noted.
- R The performance tends to remain in the intermediate range with movement toward a major effect, if contamination levels and environments are uncontrolled.

4. Corrosion-Resistant Steel, Types 350, 355, 416, 446, 17-4, and 17-7. The general effects have been established as formations and pitting. The demarcations are considered minor, and require further subdivision from the primary criteria for more accurate descriptions of effects. The film formed consists of localized surface discolorations and tarnishes. The minute pitting is strictly within the criteria limit. Hydrazine decomposition is also within the criteria limit.

Rating: Acceptable-Incomplete (A-I)

- A Potentially acceptable. The performance tends to remain in the intermediate range.
- I Data lacking for 10-year period.

5. Nickel Base Alloys

a. *Hastelloy and Inconel*. The general effects have been established as corrosion, formations, and pitting. Nonuniform and limited effects were indicated in the form of a dull metallic finish, faint tarnish, and scattered minute pitting. The alloying promotes hydrazine decomposition.

Rating: Acceptable-Restricted (A-R)

- A The materials are considered provisionally acceptable, and as noted.
- R The performance tends to remain in the intermediate range with movement toward a major effect, if contamination levels and environments are uncontrolled. Because of this sensitivity to promote decomposition, these materials are considered less compatible with hydrazine than the CRES type alloys, items F3 and F4. In view of the degrading influences of these restrictions, specific application factors must also be considered.

b. *Nickel*. The general effects are similar to those described for Hastelloy and Inconel, Item F5a. The nickel promotes hydrazine decomposition.

Rating: Acceptable-Restricted (A-R)

- A The material is considered marginally acceptable, and as noted.
- R All restrictions stated in Subsection VI-F-5-a are applicable with the added liability that the metal is less compatible with hydrazine than Hastelloy and Inconel.

6. Titanium Alloy

a. *Type 6Al-4V*. The general effects have been established as formations and pitting. The oxide film buildup is very thin (on the order of $1.0 \mu\text{m}$ thick). These effects fall well below the criteria limit. It is noted that chloro-carbon cleaning solvents can interact with this combination, thus leading to serious loss of mechanical properties (embrittlements). Therefore, these characterizations and ratings are based upon the specific use of isopropyl alcohol for all processing.

Rating: Acceptable-Incomplete (A-I)

- A Probably acceptable. This material is rated the best, because of the excellent performance. Accordingly, a higher rating is assigned. The qualifier is maintained for consistency of reporting.
- I Data lacking for 10-year period.

7. Others

a. *Gold and chrome plating*. The primary effects have been established as pitting and formations. Imperfections (pitting or porosity) in the plating allow the propellant to

interact with the substrate metal. This interaction beneath the plating produces nonuniform blistering which also affects the local bonding integrity of the plating to the metal. Effects are considered within the criteria limit.

Rating: Acceptable-Incomplete (A-I)

A = Potentially acceptable

I = Data lacking for 10-year period

b. *Tungsten carbide*. The primary effect has been established as propellant decomposition. The cobalt binder is known to be incompatible with hydrazine. Criteria limits are exceeded resulting in major effects.

Rating: Acceptable-Restricted (A-R)

A = Marginally acceptable

R = Additional compatibility information is required to demonstrate performance over much longer periods of time. The condition for acceptance is based upon minimizing the metal and binder area in contact with hydrazine, hence, application specific.

c. *Molybdenum*. The primary effect has been established as propellant decomposition.

Rating: Not acceptable (N)

N = The material is incompatible with hydrazine, and results in excessive decomposition.

8. Polymeric

a. *Ethylene propylene terpolymer (EPT-10)*. The primary effects have been established as material property changes, loss of elemental constituents through leaching, and propellant decomposition. These effects are typical for polymeric materials. Mechanical property changes were less than 10% of original values. Zinc (0.09 mg) was extracted, but the zinc ion apparently did not catalyze hydrazine decomposition. The presence of 6Al-4V titanium metal did not produce any significant adverse synergistic effect on either the polymer or metal.

Rating: Acceptable-Restricted (A-R)

A = The EPT-10 material is considered provisionally acceptable and as noted.

R = The characteristics of EPT-10 indicate a tendency toward remaining in the intermediate range. The main problem is the lack of multi-

year data which necessitates a "provisional" assignment to the rating.

b. *Perfluoroelastomer (LRV-448)*. This polymeric material is in the experimental stage of development. Accordingly, no rating is assigned.

9. Lubricant

a. *Krytox 240AC*. The effect of Krytox 240AC, a wet lubricant, is not clearly definable. It is stable and compatible, but it does not seem to inhibit corrosion nor hydrazine decomposition and does seem to allow free diffusion of both the metal and halide ions.

Rating: Acceptable-Incomplete (A-I)

A = Potentially acceptable

I = Data lacking for 10-year period

These ratings are summarized in Table 5.

G. Hydrazine-Hydrazine Nitrate/Materials Ten-Year Compatibility Ratings

1. *Hydrazine-Hydrazine Nitrate: (75% N₂H₄, 24% N₂H₄NO, 1% H₂O)*. The primary effect has been established as the decomposition of the propellant resulting from impurities in solution and metal contact.

Rating: Acceptable-Restricted (A-R)

A = Marginally acceptable

R = The catalytic activity of impurities produce reactions which result in an increased rate of decomposition.

2. *Aluminum Alloy, Type 6061-T6*. The primary effect has been established as corrosion. The heavy corrosion exceeded the criteria limit approaching a major effect.

Rating: Acceptable-Restricted (A-R)

A = Marginally acceptable

R = High corrosion rate presents a serious problem.

3. *Corrosion-Resistant Steel, Types 303, 304L, and 347*. The primary effect has been established as corrosion which produces a major effect.

Rating: Not acceptable (N)

N = CRES materials are incompatible with H-HN because of excessive corrosion.

Table 5. Summary of compatibility ratings for materials in contact with hydrazine for ten years at 43°C (110°F)

Material	Rating	Qualifier
Aluminum alloy 2219-T86, 6061-T6	A	I
Corrosion-resistant steel 302, 303, 304, 304L, 316, 321, 347 350, 355 416, 446 17-4, 17-7	A	R
Nickel base alloys Hastelloy Inconel Nickel	A	R
Titanium Alloy 6Al-4V	A	I
Others Chrome plate Gold plate Tungsten carbide Molybdenum	A	I
Polymeric Ethylene propylene terpolymer EPT-10 (JPL)	A	R
Lubricant Krytox 240AC (Dupont)	A	I

A = Acceptable; N = Not acceptable; I = Incomplete; R = Restricted

4. Titanium, Type 6Al-4V. The primary criteria has been established as corrosion and formation. Corrosion is considered nonuniform. The film formed (titanium oxide) is brittle, 2 μ m thick, and covered with fine cracks. The results are within the criteria limit.

Rating: Acceptable-Incomplete (A-I)

A = Provisionally acceptable

I = Data lacking for 10-year period.

These ratings are summarized in Table 6.

H. Monomethylhydrazine/Materials Ten-Year Compatibility Ratings

1. Propellant, monomethylhydrazine; materials, CRES (Types 303, 304L, and titanium 6Al-4V). The number of posttest analyses performed to date is very limited. However, it was concluded that these combinations exhibited

Table 6. Summary of compatibility ratings for materials in contact with hydrazine-hydrazine nitrate for ten years at 43°C (110°F)

Material	Rating	Qualifier
Aluminum alloy 6061-T6	A	R
Corrosion-resistant steel 303, 304, 347	N	-
Titanium Alloy 6Al-4V	A	I

more compatibility than the same materials with hydrazine.

Rating: Acceptable-Incomplete (A-I)

A = Potentially acceptable

I = Additional data required. Data lacking for 10-year period.

2. Polymeric: Teflon, FEP. The primary effect has been established as material changes. Tensile strength and elongation properties were lowered; for example, the reduction in tensile strength was 19.31 to 15.17 MN/m² (2800 to 2200 psi). These results are considered acceptable because of the influence of the "miniature configuration" of the dog-bone tensile specimens used.

Rating: Acceptable-Restricted (A-R)

A = Potentially acceptable

R = Relatively stable material; however, additional multiyear data is required.

These ratings are summarized in Table 7.

I. Nitrogen Tetroxide/Materials Ten-Year Compatibility Ratings

1. Nitrogen Tetroxide. The propellant (MSC-PPD-2B) is a stable oxidizer; therefore, no primary or specific effects are defined.

Rating: Acceptable-Incomplete (A-I)

A = Potentially acceptable

I = Data lacking for 10-year period

Table 7. Summary of compatibility ratings for materials in contact with monomethylhydrazine for ten years at 43°C (110°F)

Material	Rating	Qualifier
Corrosion-resistant steel 303, 304	A	I
Titanium alloy 6Al-4V	A	I
Polymeric Teflon (FEP)	A	R

2. Aluminum Alloy, Type 6061-T6. The primary effects have been established as corrosion and formations. Corrosion was uniform with a depth of 1.0 μm . The uniform formation of rough porous oxide film was less than 0.2 μm thick.

Rating: Acceptable-Incomplete (A-I)

A = Potentially acceptable

I = Data lacking for 10-year period

3. Corrosion-Resistant Steel, Type 347. The primary effects have been established as corrosion and formations. The corrosion was very minor. Oxide particles were less than 1.0 μm in size.

Rating: Acceptable-Incomplete (A-I)

A = Potentially acceptable

I = Data lacking for 10-year period

4. Titanium Alloy, Type 6Al-4V. The primary effects have been established as corrosion and formations. The corrosion was very minor. Formations were nonuniform and spotty gray. The 2.0- μm -thick oxide film exhibited numerous cracks with most of the film adhering to the titanium specimen. This is opposite to the effect on CRES alloys where the product dissolves into the propellant.

Rating: Acceptable-Incomplete (A-I)

A = Potentially acceptable

I = Data lacking for 10-year period

These ratings are summarized in Table 8.

Table 8. Summary of compatibility ratings for materials in contact with nitrogen tetroxide for ten years at 43°C (110°F)

Material	Rating	Qualifier
Aluminum alloy 6061-T6	A	I
Corrosion-resistant steel 347	A	I
Titanium alloy 6Al-4V	A	I

VII. Conclusions

A. Hydrazine Propellant

(1) Under controlled environmental conditions and in the absence of known degrading contaminants such as carbon dioxide, the primary criteria for determining materials compatibility has been the decomposition rate of the hydrazine propellant. It has been found that metal corrosion itself has been a secondary consideration. The presence of metallic ions in solution and transitional metal ions from exposed surfaces, catalyze the reaction, and cause an increase in the rate of hydrazine decomposition.

(2) The metal ions or corrosion products of aluminum (6061-T6) and titanium (6Al-4V) alloys cause an insignificant amount of decomposition of the hydrazine. Hence, these alloys could be used for long-term (of up to ten years) mission applications with assurance of a suitable level of performance and reliability.

(3) The metal ions or corrosion products of corrosion-resistant steel (sometimes referred to as stainless steel), are active catalysts for decomposition, although the specific ions responsible have not been identified. The compatibility of this class of materials is marginal with hydrazine. Usage on long-term (of up to ten years) missions requires a careful assessment of the specific mission conditions and requirements.

(4) The carbon dioxide content in hydrazine should be kept at a low level to minimize the effect of corrosion. The maximum level of carbon dioxide should not exceed fifty parts per million (50 ppm), particularly if 347 CRES is being used in the system.

B. Hydrazine-Hydrazine Nitrate Blends

As a generalization, it is obvious that this blend is not compatible with CRES type of materials. Excessive pressure rise and etching of the test specimen surface was experienced after relatively short exposure periods varying from 5 to 78 days.

C. Monomethylhydrazine

All specimen/capsule units still in active test after six years exposure reveal no serious problems.

D. Nitrogen Tetroxide

All specimen/capsule units still in active test after six years exposure reveal no serious problems.

E. Cleaning Solvents

It has been found that the carbon-chlorine type solvents used for contamination control can interact with hydrazine and titanium 6Al-4V resulting in embrittlement of the titanium material. The use of carbon-chlorine type solvents should be eliminated to avoid the possibility of contaminating and affecting liquid propulsion elements, particularly where fuel-type propellants are involved. Specifically, the use of halogenated solvents such as Freon or Freon-type materials, should be prohibited.

Isopropyl alcohol is more suitable than Freon for removing organic material, and does not interact with the hydrazine or titanium material. Isopropyl alcohol should be used for cleaning, processing, or other pertinent operations for fuel-side propulsion elements.

F. Ten-Year Design Data

The rate expression for the compatibility phenomena as a function of long-term storage needs to be defined for a ten-year period. Experimental results are required to establish whether the "total compatibility changes" continue linearly or level off as a function of multiyear storage duration.

G. Procedures and Standards

The essence of this compatibility program is uniformity of implementation and methodical control of the numerous and complex factors involved for each phase of work. This has been accomplished by the standardization of all methods, procedures, and processes. The adequacy of these procedures and standards has been demonstrated in the accomplishment of each major phase. These include: preparation of approximately 900 specimen/capsule combinations using semiproduction techniques; conducting test operations and storage testing as planned; and performing posttest analyses on over 90 test units involving metallurgical examinations and propellant characterizations. It is felt that the procedures and standards evolved and used in this work provide a reliable means for carrying out long-term compatibility investigations, and identifying potential propellant/material interactions whether gross or subtle in effect.

H. Multiyear Design Data

The results being generated after multiyear real-time exposure periods are considered to be representative criteria. The data derived from this long-term experimental program can be used for propulsion design purposes in any system.

References

1. Rowley, R. W., "Mariner Spacecraft Experience With Monopropellant Hydrazine Propulsion Systems," paper presented at the 12th CPIA Liquid Propulsion Meeting, Las Vegas, Nev., Nov. 17-19, 1970.
2. Gilbreath, W. P., and Adamson, M. J., *The Stress Corrosion Susceptibility of Several Alloys in Hydrazine Fuels*, TN D-7604, National Aeronautics and Space Administration, Washington, D. C., February 1974.
3. Brown, C. T., *Determination of Long-Term Capability of Hydrazine With Selected Materials of Construction*, United Technologies Research Center, Hartford, Conn., USAFREL Contract F04611-74-C-0041 (current program).
4. Green, R. L., et al., *Advanced Techniques for Determining Long-Term Compatibility of Materials With Propellants*, Reports D 180-14839-1 and -2, under NASA Contract NAS7-789, Boeing Aerospace Co., Seattle, Wash., December 1973.
5. Pullen, K. E., *Radioactive Nondestructive Test Method*, Reports D 180-12741-1 and D-180-14227-1, NASA Contract NASA-779, Boeing Aerospace Co., Seattle, Washington, December 1971.
6. Long, H. R., and Bjorklund, R. A., *Trajectory Correction Propulsion for TOPS*, Technical Report 32-1571, Jet Propulsion Laboratory, Pasadena, Calif., Nov. 15, 1972.
7. *Military Standardization Handbook, Metallic Materials and Elements for Aerospace Vehicle Structures*, MIL-HDBK-5B, September 1971.
8. *Aerospace Structural Metals Handbook*, AFML-TR-68-115, Department of Defense, Army and Mechanics Research Center, Watertown, Mass., 1975.
9. Koch, E. F., et al., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-15, Vol. IV, pp. 153-155, June 30, 1962.
10. Weiner, R. S., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-17, Vol. IV, p. 198, Oct. 30, 1962.
11. Weiner, R. S., "Materials Compatibility Tests," in *Supporting Research and Advanced Development*, Space Programs Summary 37-20, Vol. IV, pp. 82-83, April 30, 1963.
12. Weiner, R. S., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-22, Vol. IV, pp. 133-134, August 31, 1963.
13. Porter, R. N., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-23, Vol. IV, p. 131, October 31, 1963.
14. Porter, R. N., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-33, Vol. IV, pp. 169-170, June 30, 1965.

15. Porter, R. N., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-34, Vol. IV, pp. 177-179, August 31, 1965.
16. Stanford, H. B., "Hydrazine Sterilization Tests," in *Supporting Research and Advanced Development*, Space Programs Summary 37-35, Vol. IV, pp. 155-157, October 31, 1965.
17. Toth, L. R., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-44, Vol. IV, pp. 175-179, April 30, 1967.
18. Rush, F. A., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-46, Vol. IV, pp. 163-167, August 31, 1967.
19. Muraca, R. F., et al., *The Results of Long-Term Tests for Compatibility of Nitrogen Tetroxide With Various Spacecraft Materials*, Report 951581-2, Stanford Research Institute, Menlo Park, Calif., May 15, 1967.
20. Muraca, R. F., et al., *The Results of Long-Term Storage Tests for Compatibility of Spacecraft Materials With Hydrazine and Hydrazine Mixtures*, Report 951581-6, Stanford Research Institute, Menlo Park, Calif., Oct. 1, 1967.
21. Toth, L. R., and Keller, O. F., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-60, Vol. III, p. 211, Dec. 31, 1969.
22. Keller, O. F., and Toth, L. R., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-61, Vol. III, p. 250, Feb. 28, 1970.
23. Keller, O. F., and Toth, L. R., "Materials Compatibility," in *Supporting Research and Advanced Development*, Space Programs Summary 37-65, Vol. III, p. 180, Oct. 31, 1970.
24. Salvinski, R. J., et al., *Advanced Spacecraft Valve Technology Compilation*, NASA Contract NAS7-717, Report 12411-6012-R000, TRW Systems Group, Redondo Beach, Calif., July 1970.
25. Salvinski, R. J., et al., *Investigation of the Formation and Behavior of Clogging Material in Earth and Space Storable Propellants*, Report 08113-6007-R000, 08113-6016-R000, and 18113-6025-R000, TRW Systems Group, Redondo Beach, Calif., NASA Contract NAS7-549, October 1967.
26. "Process Specification, Liquid Propulsion System Cleaning and Packaging of System Components," JPL Specification 30009, Revision N/C (JPL internal document).
27. "Process Specification, Liquid Propulsion System Cleaning and Packaging of System Components," JPL Specification GMM-30009-PRS-A, Revision N/C (JPL internal document).
28. "Test Capsule, Materials Compatibility, Liquid Propellant Type II A," JPL Drawing 1003009 (JPL internal document).
29. "Metallic Specimen Slug Type," JPL Drawing 10040103 (JPL internal document).

30. "General Specification Long-Term Compatibility Testing," JPL Specification GMZ-50521-GEN-A (JPL internal document).
31. "General Specification Pressure Measurement System for Liquid Propellant Compatibility Testing," JPL Specification GMZ-50522-GEN-A (JPL internal document).
32. *Specimen/Capsule Preparation Used on the JPL Material Compatibility Program, Final Report*, PSI Report No. 525902-1, Pressure Systems, Inc., Los Angeles, Calif., April 1970.
33. Marks, L. S., *Mechanical Engineers Handbook*, Fifth Edition, p. 465, January 1951, McGraw Hill Pub. Co., New York.
34. "Material Compatibility Test, Stressing Fixture," JPL Drawing 10062134 (JPL internal document).
35. "Propellant Compatibility, Building E-75, Floor Plan, Finish Schedule and Details," JPL Drawing E75/3-0 (JPL internal document).
36. "Hydrazine Test Fixture and Cell Assembly," JPL Drawing 9117157 (JPL internal document).
37. "Installation of Glass Test Capsules," JPL Procedure 384E-75-1231-JWS (JPL internal document).
38. "Removal of Glass Test Capsules," JPL Procedure 384E-75-1232-JWS (JPL internal document).
39. Tolberg, W. E., et al., "Chemical and Metallurgical Analysis of 6Al-4V Titanium Test Specimens Exposed to Hydrazine (N_2H_4) Liquid Propellant," Report 951586-11; Stanford Research Institute, Menlo Park, Calif., April 15, 1971.
40. *NASA Pre-Alert: Test Specimen, Metallic, 6Al-4V Titanium Immersed in Hydrazine, and Glass-Encapsulated, Alert E4-70-03A*, National Aeronautics and Space Administration, Washington, D.C., Aug. 16, 1971.
41. Chang, E. T., et al., *Solubilities of NH_3 , CO, CO_2 , and SF_6 in Liquid Propellants*, The Aerospace Corp., El Segundo, Calif., Air Force Report SAMSO-TR-71-17, November 1970.
42. Champion, F. A., *Corrosion Testing Procedures*, Second Edition, John Wiley and Sons, New York, 1965.
43. Uncy, P. E., and Fester, D. A., *Material Compatibility With Space Storable Propellants, Design Guidebook*, Martin Marietta Corp., MCR-72-26, March 1972.
44. *Aerospace Fluid Component Designer's Handbook*; Report AFRPL-TDR-64-25, Sect. 12.5, TRW Systems Group, Redondo Beach, Calif., February 1970.

Appendix A
Specimens Posttest Analyses and Results

THIS PAGE BLANK NOT TO BE

Table A-1. Summary of posttest analyses and results—hydrazine

Specimen number	Duration of test, days	Specimen				Propellant			
		Material	Configuration	Remarks	Weight change, mg	Capsule pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg
1073	1153	6061-T6 Al	Slug Krytox coated	Clean below liquid level, slight tarnish above. No pitting	-0.2	1.03	0.05	Very little decomposition Trace of white residue	0.4
3193	1198	2219-T86 Al	Slug	Very slight corrosion	-0.1	0.97	0.02	Very little decomposition Clear, water white	<0.2 ND
0509	967	6061-T6 Al	Bimetal Std	Very slight tarnish	+0.9	43.2	2.5	Moderate decomposition	6.1
		347 CRES	Bimetal	Very slight tarnish	+0.6				
0531	1231	6061-T6 Al	Bimetal Std	Slightly etched Numerous minute pits	+0.7	51.7	2.2	Moderate decomposition Small quantity residue	3.5
		302 CRES	Bimetal	Shiny below liquid, tarnished above Numerous minute pits	+1.0				
0535	967	6061-T6 Al	Bimetal Std	Slightly etched Minute pits below liquid	+0.9	39.3	2.9	Moderate decomposition	3.5
		303 CRES	Bimetal	Blue corrosion below liquid Brown film above Rust pitting above liquid	+0.6				
0537	1313	6061-T6 Al	Bimetal Std	Dark stain below liquid, light tarnish above Minute pits at contact	+2.0	46.9	3.2	Moderate decomposition Pink residue	4.3
		303 CRES	Bimetal	Slightly stained Filiform pitting at contact	-0.9				
0539	1231	6061-T6 Al	Bimetal Std	Slightly etched Very numerous, minute pits	+0.4	44.1	3.1	Moderate decomposition Pink residue	3.2
		304L CRES	Bimetal	Shiny below liquid, tarnished above No pitting	+1.6				
0541	967	6061-T6 Al	Bimetal Std	Slightly etched Very numerous, minute pits	-1.3	62.1	4.6	Severe decomposition	5.6
		304L CRES	Bimetal	Red film below liquid, tarnish above No pitting	+1.0				

Table A-1 (contd)

Specimen Number	Specimen				Propellant				
	Duration of test, days	Material	Configuration	Remarks	Weight change, mg	Capsule pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg
0543	405	6061-T6 Al 321 CRES	Bimetal Bimetal	Slightly etched Gray tarnish, darker below liquid	+1.1 +0.4	75.8	—	Faint pink color	—
0657	592	6061-T6 Al 347 CRES	Bimetal Bimetal separated	Slightly etched Light gray tarnish	+1.9 +2.3	102.0	—	Not examined	—
0679	1781	6061-T6 Al	Bimetal	Etched below liquid No pitting	+2.0	67.5	4.8	Severe decomposition Red residue	3.8
0683	967	302 CRES 6061-T6 Al	Bimetal Bimetal separated	Spotty corrosion Numerous minute pits below liquid	+0.5	50.3	3.8	Severe decomposition Pink residue	3.0
3053	506	6061-T6 Al 6Al-4V Ti	Bimetal Bimetal	Slightly tarnished Scattered, minute pits	+1.5 -0.1	0.34	<0.01	Very little decomposition Water white, no residue	<0.3 ND
1051	232	347 CRES	Slug Krytox coated	Etched below liquid Numerous, minute pits	-1.3	59.4	4.1	Severe decomposition White residue	2.0
1061	720	347 CRES	Slug Gold plated	Clean and shiny Few blisters in plating	+1.0	44.1	0.83	Slight decomposition	3.9
1243	59	302 CRES	Slug Krytox coated	Dark gray corrosion overall No pitting	-0.3	42.8	3.3	Moderate decomposition	4.7
1245	305	302 CRES	Slug Krytox coated	Dark gray corrosion overall Pits from pre-test etching	+0.5	46.2	3.6	Fairly severe decomposition	1.1
1259	59	303 CRES	Slug Krytox coated	Dark gray corrosion overall No pitting	+2.3	—	—	Not examined	10.4

Table A-1 (contd)

Specimen Number	Duration of test, days	Specimen			Propellant				
		Material	Configuration	Remarks	Weight change, mg	Capsule pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg
1277	141	304L CRES	Slug Krytox coated	Dark below liquid level Etched at interface. Spots above liquid Minute pits localized at interface	-2.8	76.7	5.8	Severe decomposition	5.9
1295	723	316 CRES	Slug Krytox coated	Clean and bright No pitting	+0.2	49.6	3.7	Fairly severe decomposition	<0.3 ND
1297	594	316 CRES	Slug Krytox coated	Clean and bright Slightly darkened below liquid. Few, minute pits below liquid	+0.6	60.5	4.6	Severe decomposition	<0.7 ND
1315	59	321 CRES	Slug Krytox coated	Clean and bright No pitting	+1.2	0.7	0.05	Very little decomposition	0.03
1317	422	321 CRES	Slug Krytox coated	Slightly stained Pits from pre-test etching	+1.1	29.6	2.4	Moderate decomposition	<0.3 ND
1323	407	416 CRES	Slug Krytox coated	Very dark below liquid Slightly dark above Scattered minute pits below liquid. Very numerous, minute pits above liquid	-4.7	11.2	0.84	Slight decomposition	1.5
1339	1171	17-4PH CRES	Slug Krytox coated	Faintly tarnished Numerous, minute pits	-0.5	25.5	1.8	Moderate decomposition	<0.2 ND
1347	1784	17-7PH CRES	Slug Krytox coated	Spotty blue tarnish Minute pits localized along edges	+1.5	42.1	3.2	Moderate decomposition	0.3
1551	1063	347 CRES	Slug	Clean and bright. Faint line at interface No pitting	+1.3	1.0	0.08	Very little decomposition No residue	<0.2 ND
3055	786	304L CRES	Slug	Clean and bright, faint line at interface No pitting	-0.2	0.8	0.07	Very little decomposition No residue	<0.2 ND

Table A-1 (contd)

Specimen Number	Duration of test, days	Specimen			Weight change, mg	Capsule pressure, N/cm ² at -43°C	Propellant		
		Material	Configuration	Remarks			Decomposition, %	Remarks	Halide content, mg
3039	721	304L CRES	Slug	Bright and shiny below liquid, faint tarnish above No pitting	-0.2	0.7	0.07	Very little decomposition	<0.2 ND
3045	721	17-7PH CRES	Slug	Clean and bright Faint line at interface No pitting	-0.4	0.7	0.07	Very little decomposition	<0.2 ND
3053	1321	446 CRES	Slug	Clean and bright Faint line at interface No pitting	-0.1	2.3	0.19	Very little decomposition	<0.2 ND
3077	706	446 CRES	Slug	Clean and bright No pitting	-0.1	0.7	0.08	Very little decomposition	<0.2 ND
3079	704	446 CRES	Slug Chrome plated	Slight tarnish above liquid Plating blistered	-0.6	1.3	0.11	Very little decomposition	<0.2 ND
3081	909	AM355	Slug	Clean and bright Faint line at interface No pitting	-0.1	1.6	0.12	Very little decomposition No residue, water white	<0.2 ND
3095	704	AM350	Slug	Slight tarnish above liquid Moderate number of minute pits	-0.3	54.5	3.8	Fairly severe decomposition	<0.2 ND
3097	690	AM355	Slug	Faint tarnish above liquid No pitting	-0.2	<0.7	0.04	Very little decomposition	<0.2 ND
0455	252	347 CRES	Bimetal Std	Clean and bright except faint tarnish above liquid Numerous, minute pits Severely corroded Porous, oxide film	+12.4	44.1	2.5	Moderate decomposition Yellow color, no residue	28.5
0459	1078	347 CRES	Bimetal Std	Clean and bright except faint tarnish above liquid Very numerous, minute pits Spotty corrosion	+10.8	51.0	4.0	Severe decomposition Pink residue	3.6
		6061-T6 Al	Bimetal	Very numerous, minute pits below liquid	+5.1				

Table A-1 (contd)

Specimen Number	Duration of test, days	Specimen				Capsule			Propellant	
		Material	Configuration	Remarks	Weight change, mg	pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg	
0461	252	347 CRES	Bimetal Std	Severely corroded Mainly oxide film	+9.1	60.0	3.9	Severe decomposition Dark red color, much residue	29.5	
0463	68	6061-T6 Al	Bimetal	Slightly etched below liquid Numerous, minute pits localized at contact	-2.1	-	-	Not examined	43.2	
0467	68	347 CRES	Bimetal Std	Etched below liquid Numerous, minute pits	+7.3	-	-	Severe decomposition	68.0	
0469	68	6Al4V Ti	Bimetal	Etched below liquid Pits from pre-test etching	-6.4	57.2	3.7	Severe decomposition	43.8	
0475	515	347 CRES	Bimetal Std	Etching in contact area Numerous, minute pits Dark and flaking below liquid	-0.7	53.1	4.7	Severe decomposition	19.0	
0477	68	6Al4V Ti	Bimetal	Clean except for a few black spots Numerous, minute pits Dark film below liquid	+0.1	87.9	6.9	Severe decomposition Brown residue	-	
0483	68	347 CRES	Bimetal	Severe corrosion	0	105.5	-	Brown color	26.0	
0487	68	2014-T6Al	Bimetal	Severe corrosion	-5.7	116.5	7.8	Very severe decomposition Brown color, much residue	-	
0493	68	347 CRES	Bimetal	Slightly etched below liquid Severe corrosion below liquid	+0.1	-	-	-	-	
0497	68	2014-T6Al	Bimetal	Severe corrosion below liquid	-4.1	-	-	-	-	
0503	68	347 CRES	Bimetal	Etched below liquid, spotty tarnish above No pitting	-2.6	-	-	-	-	
0507	68	302 CRES	Bimetal	Etched below liquid, spotty tarnish above No pitting	-3.0	-	-	-	-	

Table A-1 (contd)

Specimen Number	Duration of test, days	Specimen			Capsule			Propellant	
		Material	Configuration	Remarks	Weight change, mg	pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg
0485	5	347 CRES	Bimetal	Clean and bright below liquid, etched above. No pitting	-0.7	10.0	0.63	Slight decomposition Yellow color with residue	31.8
		302 CRES	Bimetal	Clean and bright below liquid, etched above. No pitting	+1.3				
0491	10	347 CRES	Bimetal Std	Etched below liquid. Severe localized corrosion	+1.2	25.1	1.7	Moderate decomposition	26.0
		304L CRES	Bimetal	Etched below liquid. Numerous, minute pits	-1.8				
0493	3	347 CRES	Bimetal Std	Bright and shiny	+2.2	< 3.5	—	Slightly discolored	—
		304L CRES	Bimetal	Tarnished above liquid. Rust spots below liquid	+3.0				
0497	10	347 CRES	Bimetal Std	Slight corrosion at contact. No pitting	+1.1	29.4	1.7	Moderate decomposition Yellow color	30.4
		321 CRES	Bimetal	Severe tarnish. No pitting	-0.7				
0611	69	347 CRES	Bimetal Std	Slight corrosion	-0.5	—	—	Not examined	—
		6AHVTi	Bimetal	Severe tarnish below liquid	-7.8				
0615	69	347 CRES	Bimetal Std	Slight corrosion	+24.7	74.5	—	Light brown color, much sediment	—
		6AHVTi	Bimetal	Severe tarnish below liquid	+8.1				
0617	69	347 CRES	Bimetal Std	Slight corrosion	+1.0	66.9	—	Light brown color, slightly turbid	—
		6AHVTi	Bimetal	Severe tarnish below liquid	+7.0				
0635	217	347 CRES	Bimetal Std	Rust color above liquid	+1.8	47.6	—	No residue, water white	—
		303 CRES	Bimetal	Slight tarnish above liquid	+0.2				
0637	302	347 CRES	Bimetal Std	Spotty rust above liquid	+1.9	63.4	—	No residue, water white	—
		303 CRES	Bimetal	Gray tarnish above liquid	-0.6				

Table A-1 (contd)

Specimen Number	Duration of test, days	Specimen			Capsule			Propellant	
		Material	Configuration	Remarks	Weight change, mg	pressure, N/cm ² at 43 C	Decomposition, %	Remarks	Halide content, mg
0641	5	347 CRES	Binetal Std	Clean and bright	+21.1	<3.5	—	Greenish yellow color, slightly turbid	—
0823	316	304L CRES	Binetal	Slight tarnish below liquid	+13.3				
				Spotty tarnish above					
0825	5	302 CRES	Slug stressed	Etched below liquid	-19.4	48.6	1.9	Moderate decomposition	1.6
				Corrosion at contact points					
0835	130	347 CRES	Fixture	Minute pits localized at interface					
				Severe corrosion					
0837	81	321 CRES	Slug stressed	Severe corrosion	-1.9	30.4	1.8	Moderate decomposition	23.5
				No pitting					
0837	81	321 CRES	Slug stressed	Severe corrosion	-3.3	118.6	—	Not examined	—
				Tarnished below liquid					
0837	81	321 CRES	Slug stressed	Spotty corrosion above	-0.5	67.1	4.1	Severe decomposition	4.3
				Etched above liquid					
1999	1063	304L CRES	Weld-stressed	Etched below liquid	-2.0	9.7	0.65	Slight decomposition	<0.2 ND ^a
				Corrosion at contact points					
2003	1179	347 CRES	Weld	Numerous, minute pits	-5.1	10.3	0.72	Slight decomposition	<0.2 ND
				Clean and bright					
3231	484	446 CRES	Weld	Faint line at interface	—	4.8	0.37	Slight decomposition	<0.2 ND
				No pitting					
0019	No record	6Al4V Ti	Slug	Clean and bright	-0.8	<3.5	—	Slight turbidity, white	—
				Faint line at interface					
0021	No record	6Al4V Ti	Slug	Clean and bright	+2.4	<3.5	—	Pale yellow, no residue	—
				Faint line at interface					

Table A-1 (contd)

Specimen Number	Duration of test, days	Specimen			Weight change, mg	Capsule pressure, N/cm ² at 43°C	Propellant		
		Material	Configuration	Remarks			Decomposition, %	Remarks	Halide content, mg
0023	No record	6Al4V Ti	Slug	Gray tarnish	+3.2	<3.5	—	Clear, water white	—
0055	39	6Al4V Ti	Slug	Dark corrosion below liquid Random, minute pits	-56.2	57.9	5.1	Severe decomposition	349
0189	1306	6Al4V Ti ELI	Slug	Bright below liquid, blue tarnish above. Pits from pretest etching	-23.3	2.4	0.2	Very little decomposition Clear, water white	<0.2 ND
0195	1525	6Al4V Ti ELI	Slug	Blue-grey tarnish Pits from pretest etching	+3.0	2.4	0.16	Very little decomposition Clear, water white	0.8
3029	909	6Al4V Ti	Slug	Clean and bright No pitting	-0.7	0.90	0.14	Very little decomposition Clear, water white	<0.2 ND
0057	69	6Al4V Ti	Slug	Flaky, black film below liquid, dark tarnish above	-51.1	~90	—	Dark green color, black solids	—
0059	95	6Al4V Ti	Slug	Flaky, black film below liquid, dark tarnish above Very numerous, minute pits	-47.1	~90	~5.5	Dark green color, black solids	~85
0061	69	6Al4V Ti	Slug	Flaky, black film below liquid, dark tarnish above	-65.5	~160	~1.5	Dark green color, black solids	~200
0065	69	6Al4V Ti	Slug	Flaky, black film below liquid, dark tarnish above	-54.6	~110	~5.1	Dark green color, black solids	~190
0555	205	6Al4V Ti	Bimetal Std	Slightly etched	-111.5	53.8	3.8	Severe decomposition No residue	6.6
		347 CRES	Bimetal	Spots above liquid, etching at interface, no pitting	+0.6				
0557	205	6Al4V Ti	Bimetal Std	Spots above liquid, clean below. Deeply etched at contact	+1.0	53.8	3.8	Severe decomposition No residue	4.6
		347 CRES	Bimetal	Spots above liquid, clean below. Minute rust pits	+0.9				
0583	392	6Al4V Ti	Bimetal Std	Spots above liquid, etched below. Numerous, minute pits	+1.8	71.0	1.9	Moderate decomposition No residue	4.1
		303 CRES	Bimetal	Very clean No pitting	-0.8				

Table A-1 (contd)

Specimen Number	Duration of test, days	Specimen			Propellant			Halide content, mg	
		Material	Configuration	Remarks	Weight change, mg	Capsule pressure, N/cm ² at 43°C	Decomposition, %		Remarks
0599	205	6Al4V Ti	Bimetal Std	Etched deeply Scattered minute pits	+2.0	54.6	3.6	Fairly severe decomposition	9.1
0781	8	304L CRES 6Al4V Ti	Bimetal Slug-stressed Fixture	Corrosion deposits below liquid, dark tarnish above Shallow pits Clean and bright	— -2.8	<3.5	—	Clear, water white	—
0787	1797	6Al4V Ti	Slug-stressed	Blue-gray tarnish, darkest at liquid interface No pitting	-0.4	6.5	0.46	Slight decomposition No residue	<0.5
0847	68	6Al4V Ti 6Al4V Ti ELI	Fixture Slug-stressed	Blue-gray tarnish Dark and etched below liquid, less severe above	-1.0	—	—	Not examined	18.5
0899	1302	347 CRES 6Al4V Ti 6Al4V Ti	Fixture Weld-stressed Fixture	Etched below liquid No corrosion below liquid Slight tarnish above Slight tarnish Minute pits localized at interface	+1.7	3.7	0.25	Very little decomposition No residue	3.1
1371	59	Nickel	Slug Krytox coated	Dull surface Pits from passivation	+0.3	49.7	1.2	Moderate decomposition	<0.3 ND
1401	722	Hastelloy-C	Slug Krytox coated	Clean and shiny Pitting from pretest treatment	+0.5	64.8	1.6	Moderate decomposition No residue, water white	<0.2 ND
1403	24	Hastelloy-C	Slug Krytox coated	Clean and shiny	-0.5	<3.5	—	Yellow color	—
1433	144	Molybdenum	Slug Krytox coated	No visible corrosion	+0.3	118.6	—	Not examined	—

Table A-1 (contd)

Specimen Number	Specimen				Capsule		Propellant		
	Duration of test, days	Material	Configuration	Remarks	Weight change, mg	pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg
1455	187	Molybdenum	Slug Krytox coated	Clean and shiny	0	58.2	4.2	Severe decomposition No residue	<0.2
1453	405	Inconel-X	Slug	Clean and shiny	-1.4	68.4	3.1	Moderate decomposition	0.8
1455	389	Inconel-X	Slug	Minor corrosion at liquid interface	-1.2	Exploded in fixture	—	Not examined	—
1457	1234	Inconel-X	Slug Krytox coated	Clean and bright with a few small spots of tarnish	+0.8	26.9	1.1	Moderate decomposition	<0.2 ND
				Pitting from pretest treatment					
1459	17	Inconel-X	Slug Krytox coated	Etched below liquid, slightly stained above	-29.8	48.3	2.3	Moderate decomposition	186
				Scattered pitting possibly due to pretest treatment					
3085	132	Tungsten carbide	Slug	Clean with very slight staining. No pitting	-1.3	64.1	4.7	Severe decomposition	<0.3 ND
3087	132	Tungsten carbide	Slug	Clean with no visible corrosion. No pitting	-37.3	62.7	3.6	Fairly severe decomposition Clear, water white	<0.2 ND
3089	132	Tungsten carbide	Slug	Clean and shiny	-1.2	154.4	—	Clear, water white	—
3103	776	LRV-448 Teflon	3 Strips	Dark brown color	+1.9% after drying	4.5	0.3	Very little decomposition	—
3109	868	EPT-10 Rubber	3 Strips	Normal appearance	+1.4% after drying	2.7	0.17	Very little decomposition Clear, water white	0.2
3163	746	EPT-10	3 Strips	Normal appearance	+0.7% after drying	2.0	0.15	Very little decomposition Clear, water white	0.3
				Slightly tarnished above liquid. No pitting	-0.4 mg				

Table A-1 (contd)

Specimen number	Duration of test, days	Specimen				Capsule			Propellant	
		Material	Configuration	Remarks	Weight change, mg	pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg	
3165	802	EPT-10	3 Strips	Normal	+1.3% after drying	2.3	0.15	Very little decomposition	0.3	
		6AHVTi	Slug	Faint brown spots. No pitting	-0.2 mg			Clear, water white		
3169	802	EPT-10	3 Strips	Normal	+2.2% after drying	6.3	0.43	Slight decomposition	0.8	
		347 CRES	Slug	Clean and shiny. No pitting	-0.2 mg			Clear, water white		
1681		None	—		—	1.2	<0.05	Reference unit	68	
1701		None	—		—	7.7	<0.05	Reference unit	>100	

ND : None detected; less than amount detectable by the analytical technique used

— : Not measured; data not available

~ : Approximately; estimated value

< : Less than; known to be less than stated value

> : Greater than; known to be greater than stated value

Table A-2. Summary of posttest analyses and results—hydrazine-hydrazine nitrate

Specimen number	Duration of test, days	Specimen			Capsule			Propellant	
		Material	Configuration	Remarks	Weight change, mg	pressure, N/cm ² at 43°C	Decomposition, %	Remarks	Halide content, mg
1885	19	304L CRES	Slug	Severely etched and corroded	-84.6	60.9	3.5	Fairly severe decomposition Bright red color, much sediment	53.0
1909	15	347 CRES	Bimetal Std	Clean in liquid, tarnished above. Pretest etching	-3.7	27.4	1.6	Moderate decomposition Pink color, no sediment	56.0
1915	1247	304L CRES	Bimetal	Clean in liquid, tarnished above. No pitting	-8.3				
		6061-T6Al	Bimetal Std	Deeply etched, thick oxide film	-44.2	6.9	0.5	Slight decomposition Turbid with gray scales	—
1933	1500	6Al4V-Ti	Bimetal	Slightly etched. No pitting	+2.9				
		6Al4V-Ti	Bimetal Std	White corrosion film	+1.6	11.4	0.6	Slight decomposition Gray and black residue	52.0
1941	15	6061-T6Al	Bimetal	Black corrosion film	-60.6				
		6Al4V-Ti	Bimetal Std	Discolored. Minute pits at interface	+6.0	82.1	6.6	Severe decomposition Pink color	36.0
1943	15	303 CRES	Bimetal	Severely etched. No pitting	-290				
		6Al4V-Ti	Bimetal Std	Etched above liquid	+1.4	88.3	6.4	Severe decomposition	55.0
		303 CRES	Bimetal	Scattered, minute pits Severe corrosion below liquid	-340				
1945	19	6Al4V-Ti	Bimetal Std	Numerous, minute pits Stained along edges Minute pits along edges	-0.7	34.7	2.3	Moderate decomposition	68.6
		304L CRES	Bimetal	Etched below liquid No pitting	-62.2				
1947	26	6Al4V-Ti	Bimetal Std	Discolored under liquid Scattered, minute pits	-1.2	44.3	3.0	Moderate decomposition Pink color	68.0
		304L CRES	Bimetal	Etched under liquid No pitting	-74.0				
1959	1247	6Al4V-Ti	Slug stressed	Dark tarnish below liquid Spotty tarnish above No pitting	+3.1	23.4	1.7	Moderate decomposition	—
		6Al4V-Ti	Fixture	Light tarnish					

Table A-2 (contd)

Specimen number	Duration of test, days	Specimen				Propellant			
		Material	Configura-tion	Remarks	Weight change, mg	Capsule pressure, N/cm ² at 43°C	Decom-position, %	Remarks	Halide content, mg
2043	78	304L CRES	Surface tension screen	Slight tarnish above liquid Scattered, minute pits	-1.7	49.2	2.8	Moderate decomposition Clear, water white	5.1
2045	2003	304L CRES	Surface tension screen	Etched and pitted below liquid, shiny above Scattered, minute pits	-6.3	>138	—	Pink color	<0.3 ND
2055	2067	None	—	—	—	<0.5	—	Reference unit Clear, water white	18

ND - None detected; less than amount detectable by the analytical technique used

— - Not measured; data not available

Table A-3. Summary of posttest analyses and results—monomethylhydrazine

Specimen number	Duration of test, days	Specimen				Capsule			Propellant	
		Material	Configuration	Remarks	Weight change, mg	pressure, N/cm ² at 48°C	Decomposition, %	Remarks	Halide content, mg	
1539	1918	FEP Teflon	3 strips	Slightly yellowed ~20% loss tensile stress	+2.4	1.7	Negligible	Almost no decomposition Clear, water white	0.5	
1633	1365	6Al4V-Ti	Bimetal Std	Clean and shiny Faint line at liquid level	+2.0	4.4	0.18	Very little decomposition Clear, water white	<0.2 ND	
		303 CRES	Bimetal	Clean and shiny Faint line at liquid level	+1.5					
1663	130	304L CRES	Slug-stressed	Clean and bright Slightly mottled Pits from pretest treatment	+0.9	3.0	0.15	Very little decomposition Clear, water white	9.8	
1677	0 (1361 days under refrigeration)	6Al4V-Ti 6Al4V-Ti	Fixture Weld-stressed Fixture	Clean and bright Clean and shiny No pitting Clean and shiny	+3.6	3.1	0.15	Very little decomposition Clear, water white	1.9	

ND None detected; less than amount detectable by the analytical technique used

Table A-4. Summary of posttest analyses and results—nitrogen tetroxide

Specimen number	Duration of test, days	Material	Configuration	Specimen			Propellant		
				Remarks	Weight change, mg	Capsule pressure, N/cm ² at 43°C	Decomposition, %	Remarks	NOCl content, mg
0002	1580	347 CRES	Slug	Clean and shiny Pits from pretest treatment	+0.3	Negligible	ND	No decomposition No residue	3.5
0011	1523	6061-T6Al	Slug	White to gray tarnish No pitting	-1.3	Negligible	ND	No decomposition No residue	3.0
0052	1580	6Al4V-Ti	Slug	Spotty, gray corrosion No pitting	+0.5	Negligible	ND	No decomposition No residue	2.7
ND None detected; less than amount detectable by the analytical technique used.									

Table A-6. Summary of detailed posttest analyses and results—hydrazine-hydrazine nitrate

Specimen number	Specimen weight		Pre-plant wt. g	Analysis of propellant ^a										Analysis of gas					
	Initial g	Change g		Fe - Cr + Ni + Mn mg	AL mg	Tl + V mg	Total metal mg	Cl + F mg	CO ₂ μg/g	H ₂ O %	NH ₃ %	Aniline %	Hydrazine Nitrate %	N ₂ + H ₂ cm ³ STP	NH ₃ cm ³ STP	N ₂ Mole %	H ₂ Mole %	NH ₃ Mole %	Ratio H ₂ /N
1985	5.827	-0.0848	21	—	—	—	64.6	53.0	—	4.5	2.1	—	23.2	250.7	531.1	28.8	1.3	69.9	1.06
1999A	2.7173	-0.0037	21	—	—	—	10.1	59.0	—	3.2	0.8	—	22.8	117.1	221.4	32.9	1.7	65.4	1.38
1999B	2.7509	-0.0083	21	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1915A	0.8270	-0.0422	21	—	—	—	44.1	—	—	2.5	0.23	0.51	23.1	38.0	63.0	29.1	7.3	63.6	0.50
1915B	1.4897	-0.0029	20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1933A	1.5961	-0.0016	20	—	—	—	—	—	—	2.2	0.35	0.55	22.7	51.1	92.0	32.0	3.7	64.3	1.56
1933B	0.9241	-0.0009	20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1941A	1.4131	-0.0060	21.17	—	—	—	277.6	36.0	—	—	1.38	—	—	316.0	1331.6	18.4	0.81	80.8	2.06
1941B	2.7337	-0.2900	21.12	—	—	—	314.9	55.0	—	—	0.77	—	—	358.7	1190.7	22.5	0.55	70.0	1.89
1943A	1.4704	-0.0014	21.12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1943B	2.7423	-0.3401	21.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1945A	1.4103	-0.0007	21.00	—	—	—	58.0	68.6	—	—	0.40	—	—	143.9	427.4	24.1	1.04	74.7	1.83
1945B	2.7854	-0.0822	21.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1947A	1.5219	-0.0012	21	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1947B	2.6804	-0.0740	21	—	—	—	71.7	68.0	—	—	0.85	—	—	183.9	539.2	24.4	1.07	74.0	1.81
1959	3.2978	-0.0031	21	—	—	—	5.6	—	—	3.1	0.62	0.60	22.8	106.0	172.0	36.8	3.1	60.1	1.70
2043	0.3127	-0.0017	21	—	—	—	1.3	5.1	—	1.5	1.7	—	23.8	202.7	470.4	28.4	1.7	69.9	1.66
2045	0.3127	-0.0063	20	—	—	—	135.0	<0.2 ND	—	1.92	0.95	0.16	20.9	—	—	—	—	—	—
2085	—	—	20	—	—	—	—	18	—	—	—	—	—	<1.2	—	—	—	—	—

^aPropellant cannot be safely distilled; remove from capsule with a syringe.^bEstimate of quantities because of accidental escape of gas.

ND = None detected; less than amount detected by the analytical technique used.

— = Not measured; data not available.

Table A-7. Summary of detailed posttest analyses and results—monomethylhydrazine

Specimen number	Specimen weight		Pro- pellant wt. %	Analysis of propellant										Analysis of gas					
	Initial, g	Change, g		Fe + Cr + Ni + Mn, mg	Al, mg	Ti + V, mg	Total metal, mg	Cl + F, mg	CO ₂ , mg/g	H ₂ O, %	NH ₃ , %	Anilic, %	Purity, %	N ₂ + CH ₄ , cm ³ STP	NH ₃ , cm ³ STP	N ₂ , Mole %	CH ₄ , Mole %	NH ₃ , Mole %	Ratio H/N
1539	1.629	-0.0024	20	—	—	—	—	0.5	—	0.29	0.10	—	99.0	6.9	5.3	55.8	—	43.3	—
1633A	1.4324	+0.0020	20	0.15	<0.03 ND	<0.08 ND	0.13	<0.2 ND	94	0.78	0.09	—	>99.0	21.7	—	51.7	48.2	—	—
1633B	2.7335	+0.0015	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1663	5.5140	+0.0009	20	0.19	—	—	0.19	9.8	58	0.77	0.10	—	>99.0	14.0	—	56.0	14.0	—	—
1677	3.4873	-0.0036	20	—	<0.03 ND	<0.09 ND	<0.1	1.9	50	0.77	0.10	—	>99.0	—	—	—	—	—	—

¹NH₃ concentration not measured in gas phase because of very slight decomposition of propellant.

²Limited analysis; capsule pressure measured, general description of specimen and propellant.

ND None detected, less than amount detected by analytical technique used.

— Not measured, data not available.

Table A-8. Summary of detailed posttest analyses and results—nitrogen tetroxide

Specimen number	Specimen weight		Pro- pellant wt. %	Analysis of propellant										Analysis of gas					
	Initial, g	Change, g		Fe + Cr + Ni + Mn, mg	Al, mg	Ti + V, mg	Total metal, mg	NOCl, mg	NO, %	H ₂ O, %	Purity, %	N ₂ + H ₂ , cm ³ STP	N ₂ , Mole %	H ₂ , Mole %	Ratio H/N				
0002	5.9661	-0.0003	35.45	0.43	—	—	0.43	3.5	0.57	—	—	—	99.4	1.3	—	—	—	—	—
0014	2.9165	-0.0013	30.36	—	1.5	—	1.5	3.0	0.34	—	—	—	99.7	ND	—	—	—	—	—
0052	3.2470	-0.0005	25.50	—	0.05	0.03	0.08	2.7	0.55	—	—	—	99.4	1.8	—	—	—	—	—

ND None detected, less than amount detectable by analytical technique used.

— Not measured, data not available.

Weight of propellant:

3 or 4 significant figures indicate propellant accuracy weighed during analysis.

2 significant figures indicate weight of propellant was estimated.

No enl. indicates no estimate was possible due to premature breakage of tube.

Appendix B
Test Units in Storage

REPRODUCING PAGE BLANK NOT FILLED

Table B-1. Test specimens in hydrazine storage (Spec. MIL-P-26536B)

Material	Slug	Bimetal contact						Bimetal separated				Stressed (Stressed to 67% of yield)		Welded	Other				Total	
		302	303	347	304	2219-T81	6-4Ti	303	347	316	6-4Ti	Slug	Weld		Self	Gold plate	Chrome plate	Anorize		Krytox 24C AC
303 CRES																				
304L	6											1		2				1		1
316	2																			9
347	1								2				2	1						2
430	2															3				6
446	2														2					5
17-4																		1		4
17-7	2																	2		1
350	1																			4
355	2																			1
356-T6 Al																		2		2
2014-T6	1											5					1	2		9
2219-T81	2																			2
2219-T86	1																			1
5052																	2	2		4
6061T6	14	2		1	3		5	1	2			4	2		3	4	3		44	
7075T6																1			1	
6Al-4V Ti	28		3			1		2	2			22	17					8		83
6Al-4V ELI	4																			4
Columbium																		2		2
EPT-10	2			2		3														11
Teflon																				
LRV-448	2																			2
N ₂ H ₄		(Controls)																	24	24
Total	72	2	3	3	3	4	5	3	4	2	4	32	21	3	3	5	8	23	24	224

Table B-2. Specimens in hydrazine—Viking Lander '75 grade material
(STM N020, July 14, 1972, Rev. 2)

Material	Slug	Bimetal contact 6-4Ti	Stressed (stressed to 67% of yield)				Welded			Brazed		Dogbone, ASTM Double fold, DB, ASTM Other Controls				Total
			Slug	Weld	Bimetal weld	Bimetal weld 17-4PH	Self	Bimetal 347	Bimetal 304L	Self	Bimetal 304L	Dogbone, ASTM	Double fold, DB, ASTM	Other	Controls	
301 Cryo								4 (Tank section & diaphragm)							4	
304L CRES 316	1		6	2	2	3	5	1		2 (Tube & coupling)					20 2	
446 15-7	2			3			4								7 3	
Inconel-X 6Al-4V Ti	2 2		2								1 (Transition joint)				2 5	
AFE-332		2 (ASTM Dog-bone, double fold)										4	6		12	
AFE-332		3 (O-rings high stress)													3	
AFE-332		3 (O-rings low stress)													3	
EPT-10		5 (Tank section)													5	
Al ₂ O ₃ (sphere)														1	1	
N ₂ H ₄ (controls)														6	6	
Argon gas (calibration units)														3	3	
Total	7	13	9	5	2	3	9	1	4	2	1	4	6	1	9	76

Table B-3. Specimens in test, hydrazine—hydrazine nitrate
(75% N₂H₄; 24% N₂H₄NO₃; 1% H₂O)

Material	Slug	Bimetal contact		Stressed (Stressed to 67% of yield)		Welded Self	Other controls	Total
		6061	6-4Ti	Slug	Weld			
6061-T6 Al			1	1		2		4
6Al-4V Ti	1	2		3	3	4		13
Hydrazine nitrate							1	1
Total	1	2	1	4	3	6	1	18

Table B-4. Specimens in monomethylhydrazine (MIL-P-27404A)

Material	Slug	Bimetal contact			Stressed (Stressed to 67% of yield)		Welded Self	Brazed Self	Controls	Total
		347	6061	6-4Ti	Slug	Weld				
303 CRES	3	2	2	1	2	2		2		14
304L	3	2	2	2	1	2	2			14
316	3	2	4	2	2	2	2			17
347	3		2	2	2	2	2			13
6061-T6 Al	3	1			2	2	1			9
6 Al-4V Ti		2	2		4	3	3			14
Teflon FEP	3									3
Teflon TFE	4									4
MMH (control)								3		3
Total	22	9	12	7	13	13	10	2	3	91

Table B-5. Specimens in nitrogen tetroxide (Spec. MSC-PPD-2B)

Material	Slug	Bimetal contact			Stressed (Stressed to 67% of yield)		Chrome Plate	Other Anodize	Krytox 240 AC	Controls	Total
		347	6061	6-4Ti	Slug	Weld					
302 CRES	5	1	1		1						8
303	5	2									7
304L	6	2			2	2		2			14
316	5										5
321	3	2			2	2					9
347	5		8	4	2		2		2		23
416	3										3
17-4	6							2			8
17-7	5							2			7
5052 Al	4										4
6061 T 6	4	2		4	4			4	4		22
7075	3										3
6 Al 4V Ti	11				17	10			3		41
Nickel	6								2		8
N ₂ O ₄ (Controls)										6	6
Total	71	9	9	8	28	14	2	4	17	6	168

Table B-6. Chemical composition of specification-type ferrous and nonferrous alloys-

Alloy	Element														Other	Specification						
	Fe	C	Mn	P	S	Si	Cr	Ni	Mo	Zn	Cb + Ta	Mg	Cu	Ti			Al	V	N	O	H	
6061	0.7		0.15		0.035	0.8	0.35			0.25		1.2	0.40	0.15	Balance					0.05 each 0.15 total	QQ-A-250/11	
Aluminum alloy																						
CRES alloys																						
17-4	Balance	0.07	1.00	0.040	0.030	1.00	17.50	5.00	0.50		0.45		5.00								MS 5604	
17-7	Balance	0.09	1.00	0.040	0.030	1.00	18.00	7.75							1.50						MIL-S-25043	
301	Balance	0.15	2.00	0.045	0.030	1.00	18.00	8.00	0.50				0.50								MIL-S-5059	
303	Balance	0.15	2.00	0.15	0.40	1.00	19.00	10.00	0.75				0.50								MIL-S-7730	
304L	Balance	0.03	2.00	0.040	0.030	1.00	20.00	11.00													MIL-S-4043	
316	Balance	0.08	2.00	0.045	0.030	1.00	18.00	14.00	3.00												MIL-S-5059	
347	Balance	0.08	2.00	0.040	0.030	1.00	19.00	13.00			1.25										MIL-S-6721	
350	Balance	0.11	1.25	0.040	0.030	0.50	17.00	5.00	3.25								0.13				MIL-S-8640	
355	Balance	0.15	1.25	0.040	0.030	0.50	16.00	5.00	3.25								0.13				MIL-S-8840	
430	Balance	0.20	1.00	0.040	0.030	1.00	18.00														QQ-S-763	
446	Balance	0.20	1.50	0.040	0.030	1.00	27.00										0.25				QQ-S-763	
Nickel alloy																						
Inconel	6.52	0.02	0.27		0.007	0.25	15.14	73.88		0.94			0.03	2.46	0.66						MIL-N-7786	
Titanium alloy																						
6Al-4V	0.50	0.08													Balance	5.50- 6.75	3.5- 4.5	0.05	0.20	0.015	0.40	MIL-T-008046

*Percent maximum.
See Refs. 7 and 8 for mechanical properties.

Appendix C
Propellant Specifications and Assays

PRECEDING PAGE BLANK NOT FILLED

Table C-1. Assays of hydrazine-hydrazine nitrate

Constituent or property	MIL-P-26536B ^a specification limits	Assay ^b of hydrazine as received (drum H-3155)	Assay of JPL-purified hydrazine	Assay of JPL-produced hydrazine-hydrazine nitrate
Hydrazine assay, % by weight	97.5 min	98.2	99.9 ^c	75.2
Other major constituent, % by weight	NA ^d	NA	NA	24.0 (N ₂ H ₅ NO ₃)
Water plus soluble impurities, % by weight	2.5 max	0.45	H ₂ O <0.02	0.4
Density at 298 K (77°F), g/cm ³	1.004 ±0.002	Not determined	Not determined	Not determined
Particulate, mg/cm ³	0.01 max	Not determined	Not determined	Not determined
Ammonia plus amines, % by weight	Not required	1.18 (NH ₃) 0.20 (C ₆ H ₅ NH ₂)	0.08 (NH ₃) <5 ppm (C ₆ H ₅ NH ₂)	0.1 (NH ₃) 0.3 (C ₆ H ₅ NH ₂)
Dissolved metals, % by weight	Not required			
Iron		0.01	Not determined because levels assumed below detection threshold	Not determined
Aluminum		None detected		
Nickel		↓		
Manganese		↓		
Cobalt		↓		
Chromium		0.003		
Copper		0.003		
Zinc		None detected		
Silicon		0.008		
Magnesium		0.002		
Sodium		0.075		
Calcium		0.009		
Barium		0.005		
Boron		0.005		
Dissolved anions, % by weight	Not required			
Chloride		None detected	None detected	Not determined
Sulfate		↓		
Nitrate		↓		
Nonvolatile residue, mg/cm ³	Not required	Not determined	Not determined	↓

^aVersion of hydrazine specification in force at start of program.

^bFrom Ref. 41.

^cAssay by titration with acid indicated 100% hydrazine; assay by titration with chloramine T, 99.9% hydrazine.

^dNot applicable.

Table C-2. Assay of monomethylhydrazine

Constituent or property	MIL-P-27404A amendment 2 specification limits	Assay of $N_2H_3CH_3$ prior to filling capsules
Monomethylhydrazine ($N_2H_3CH_3$) assay, % by weight	98.3 min	99.42
Water, % by weight	1.5 max	0.48
Particulate, milligram per liter	10.0 max	0.97
Density, grams per milliliter at 25°C (77°F)	0.870 to 0.874	0.872
Ammonia (NH_3), % by weight	Not required	0.10

Table C-3. Assay of nitrogen tetroxide

Constituent or property	MSC-PPD-2B specification limits	Assay of N_2O_4 prior to filling capsules
Nitrogen tetroxide (N_2O_4) assay, % by weight	98.50	99.36
Nitric oxide (NO) assay, % by weight	0.8 ± 0.20	0.60
Water equivalent, % by weight	0.10 max	0.06
Nitrosyl chloride (NO Cl), assay, % by weight	0.08 max	0.01
Ash, % by weight	Not required	0.01

Appendix D
Method for Determining Carbon Dioxide Content in Hydrazine

PRECEDING PAGE BLANK NOT FILLED

I. Determination of Carbon Dioxide Absorbed by Hydrazine

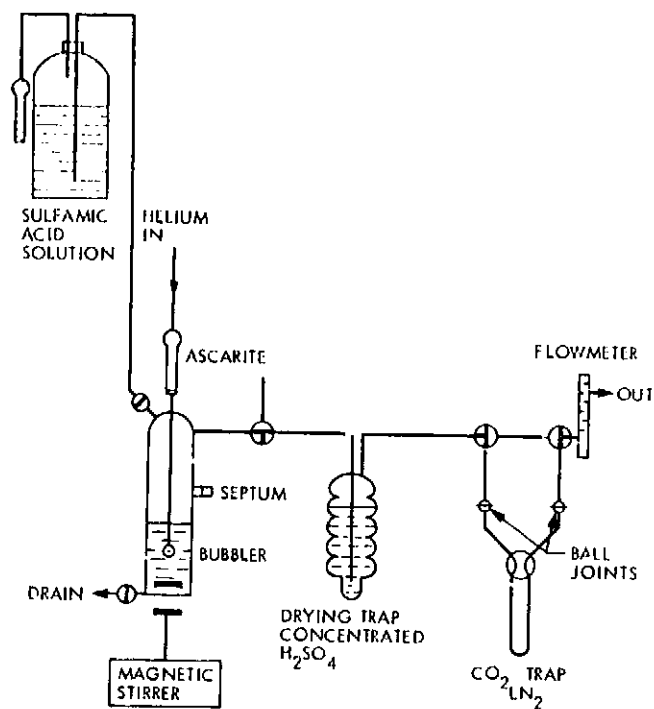
The general test setup is shown schematically in Fig. D-1. The sulfamic acid solution is prepared by dissolving 150 g of reagent grade material in 1.0 l of distilled water. To reduce the CO₂ content of the sulfamic acid, high purity helium, passed through Ascarite, is bubbled through the sulfamic acid solution via the glass frit which provides a fine gas dispersion and efficient purging. The helium gas is passed through the sulfamic acid delivery tube for about 16 hours at 50–60 cm³/min. The exit end of the helium gas from the sulfamic acid bottle is protected against air and CO₂ with an Ascarite tube. This Ascarite tube is replaced with a new one after the helium purge. With the precautions outlined, the blank CO₂ is under 2.0 ppm.

The apparatus is standardized by means of a NaHCO₃ solution prepared by dissolving 0.381 g of dried NaHCO₃ in distilled water. The solution is stored in glass, and air exposure is minimized. This solution provides 0.20 mg CO₂ per milliliter. Its CO₂ content is 200 ppm by weight.

The column is 6.0-mm diam tubing, 3.66 m long (0.24-in. diam, 12-ft long), filled with 60-80 mesh F & M Polypack No. 5. This packing gives good separation of CO₂ at ambient temperature. The peaks are sharp, permitting direct reading of the heights and eliminating the need for peak area measurements. The column is bent into a number of 0.7-m (2 ft) sections arranged close together and contained in a glass jacket. The filament-type thermal conductivity detector unit is kept at ambient temperature in a glass dewar to minimize temperature fluctuations. A 1.0 mV recorder records the detector output. Helium flow is 60 cm³/min.

The first step in the analysis is the determination of the blank; the CO₂ picked up from the reagents and the system. The flow of the high purity helium purge gas after passage through Ascarite, is adjusted to 50 cm³/min by means of a flowmeter in the system. A 60-ml sulfamic acid solution is run into the unit via the stopcock. The stirrer is adjusted to give vigorous constant stirring. Once set the helium flow and stirring are kept fixed through the whole run.

After addition of the sulfamic acid, the helium gas is passed through the traps for 30 min to purge the system of air. The CO₂ trap is then immersed in liquid nitrogen to the top level of the glass beads. Flow of helium is



GAS CHROMATOGRAPH

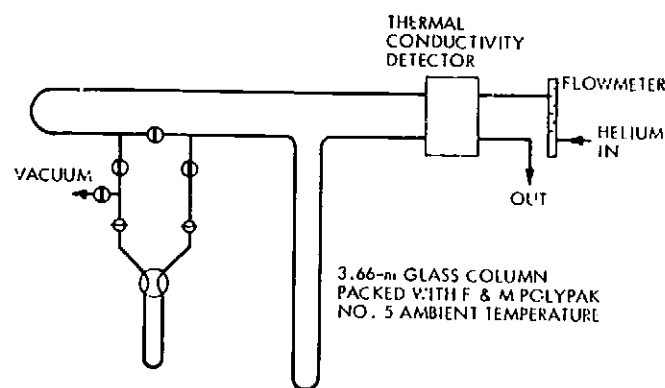


Fig. D-1. Apparatus for analysis of CO₂ in hydrazine

continued for 20 min after which time the stopcock on the CO₂ trap is turned to isolate the loop on the trap.

The trap, immersed in liquid nitrogen, is removed and transferred to the gas chromatograph sampling system. The stopcock on the CO₂ trap is turned so as to evacuate the noncondensable gases in the trap and then turned to isolate the loop containing the frozen CO₂.

The next step is to flow the helium gas through the branched leg of the sampling system. During this opera-

tion the liquid nitrogen is removed, and the CO₂ trap thawed with warm water. After a few minutes, the stopcock is turned so as to flush the CO₂ with helium into the chromatographic column for separation and assay. The blank run is repeated until consistent low values are obtained.

The standardization run is made in the same manner as the blanks, except that after a 5-min preliminary purge with helium, 0.50 ml of standard NaHCO₃ solution is injected into the vigorously stirred sulfamic acid via the septum on the sulfamic acid unit. The released CO₂ is frozen out in the CO₂ trap immersed in liquid nitrogen. The trapped CO₂ from the standard solution is transferred to the gas chromatographic sampling system. This yields a peak height for a standard of 100 ppm CO₂.

The CO₂ in hydrazine is similarly determined. A 1.0-ml sample is injected into the sulfamic acid solution via the septum, and the released CO₂ is swept out of the solution for a period of 20 min. The hydrazine injections should be made rapidly and with a minimum exposure to air. The sulfamic acid solution is sufficient to neutralize 1.0 ml

of hydrazine and should therefore be discarded after each hydrazine analysis. If another sample is to be run, the sulfamic acid unit is refilled, and the blank and the standard determinations are made as before.

II. Calculation for Carbon Dioxide Content

Parts per million carbon dioxide

$$\frac{\text{peak sample} - \text{peak blank}}{\text{peak standard} - \text{peak blank}} \times 100$$

For hydrazine, where the density can be taken as 1.0, a density correction term is not applied. The error due to this omission is about 1%, well within the $\pm 10\%$ precision for the CO₂ determination when the values are under 20 ppm.

III. Conclusion

The method described provides meaningful results for the determination of CO₂ in hydrazine or the methyl-substituted derivatives.

PRECEDING PAGE BLANK NOT FILLED

Appendix E
Data Summary Sample Format

HYDRAZINE COMPATIBILITY DATA SUMMARY: TITANIUM
6AL-4V ELI

I. TEST SPECIFIMEN CHARACTERIZATION

Material(s)	Configuration	Specimen Number (S/N)
<u>6AL-4V ELI</u>	<u>SLUG STRESSED</u>	<u>0787</u>
	<u>DWG 10040406 A</u>	
<u>6AL-4V</u>	<u>DWG 10026715 A</u>	<u>STRESS FIXTURE</u>

S/N	Specification	Assay	Temper
<u>0787</u>	<u>MIL-T-9046</u>	<u>0.023C, 0.09 Fe, 0.01N,</u>	<u>ANNEALED</u>
<u>⊕</u>	<u>TYPE III, COMP C</u>	<u>5.1AL, 4.1Va, 0.012H</u>	<u>CONDITION</u>
<u>FIXTURE</u>	<u>HEAT No G-1863</u>	<u>0.10 O₂</u>	

	Length	Width	Thickness	Weight
	cm (in.)	cm (in.)	cm (in.)	g
<u>0787</u>	<u>7.5989 (2.9917)</u>	<u>1.2598 (0.4960)</u>	<u>0.076 (0.030)</u>	<u>3.2086</u>

Hardness	Surface Finish: ID/Opposite Sides
<u>0787</u> <u>NOT APPLICABLE</u>	<u>0.3/0.3 μm (12/12 μin.)</u>

Welding Method	
Special Surface Preparation	<u>BY PSI PER JPL F5505029</u>
Cleaning and Surface Treatment	<u>BY PSI PER JPL F5505029</u> <u>(ISOPROPYL ALCOHOL)</u>

II. TEST MILESTONES

	Date	Period (days)	Environment
Capsule Sealed	<u>13 NOV 1968</u>		
Test Started	<u>25 MAR 1970</u>	<u>496</u>	<u>222K (-60°F)</u>
Test Stopped	<u>24 FEB 1975</u>	<u>1797</u>	<u>316.5K (110°F)</u>
Analysis Started	<u>12 MAR 1975</u>	<u>16</u>	<u>253K (-4°F)</u>

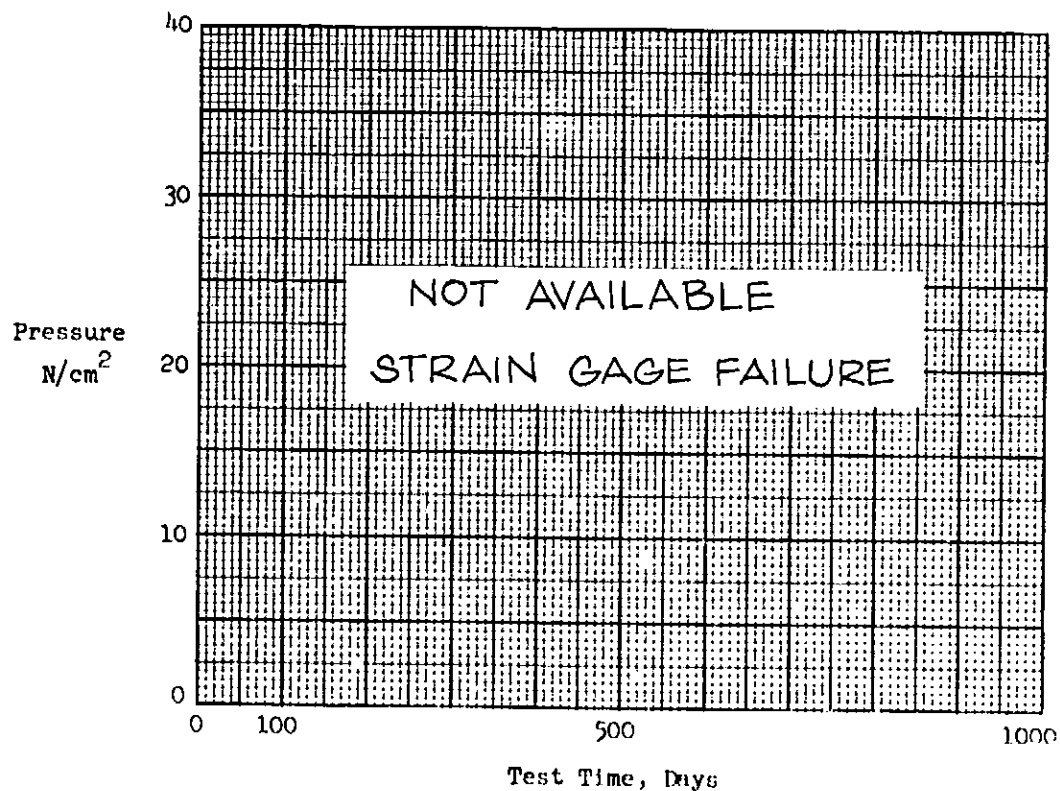
III. POST-TEST ANALYSIS RESULTS

A. Gas Analysis

Gas	Volume cc (STP)	Percentage of Decomposition Total
N ₂	24.6	21.1
H ₂	1.7	1.5
NH ₃	89.9	77.4
Decomp. Total		
Ar		
—		
Total	116.0	

Final capsule pressure at 43°C (110°F) = 6.5 N/cm² (9.4 psia)

TEST CAPSULE PRESSURE HISTORY



B. Liquid Analysis

Liquids and Solutes	Initial Value*	Final Value
Main Constituents, %		
N ₂ H ₄	98.93	98.82
H ₂ O	0.33	0.73
C ₆ H ₅ NH ₂	0.25	0.25
NH ₃	< 0.10	< 0.10

Dissolved Metals, mg		
Fe		
Cr		
Mn		
Ni		
Al		0.02
Ti		< 0.03
V		< 0.01
Na		
Si		
Co		
W		

Dissolved Anions, mg		
F		< 0.2
Cl		0.3
Carbazate (as CO ₂)		

	* REF. DRUM NUMBER 3155	

< Indicates element is not detectable at concentration given

Total Metals in Solution Limited Analysis
 Initial Hydrazine Weight 21.47 g
 Total Hydrazine Decomposed 0.46 %

Contamination
 Halide Content
< 0.5 mg

C. Specimen Analysis

Property	S/N	Initial Value	Final Value	Measured Change, mg	Solute-Indicated Change, %
Weight, g	0787	3.2086	3.2086	-0.4	
	FIXTURE		24.9713		
Thickness					
Hardness		NOT	NOT		
		APPLICABLE	APPLICABLE		N/A

Surface Properties

Area:

S/N	Liquid-Exposed cm ²	Vapor-Exposed cm ²	Total cm ²
0787	12.479	6.819	19.2989
FIXTURE	17.759	14.163	31.922

NOTE: S/V RATIO: SLUG, 0.624 cm⁻¹; WITH FIXTURE 1.52 cm⁻¹

Films:

S/N	Location	Thickness	Color
0787	LIQUID (L)	2.0 μ	OXIDE FILM BUILDUP
FIXTURE	VAPOR (V) INTERFACE	2.0 μ	OXIDE FILM BUILDUP
	OTHER SURFACES	0.2 μ	BLUE GRAY TARNISH

S/N	Area	Composition	Pitting	Remarks
0787	NONUNIFORM	NOT DETERMINED	NONE	
	(NOT MEASURED)			

Identified Corrosion Mechanisms

IV. DOCUMENTATION

See SEM photos.

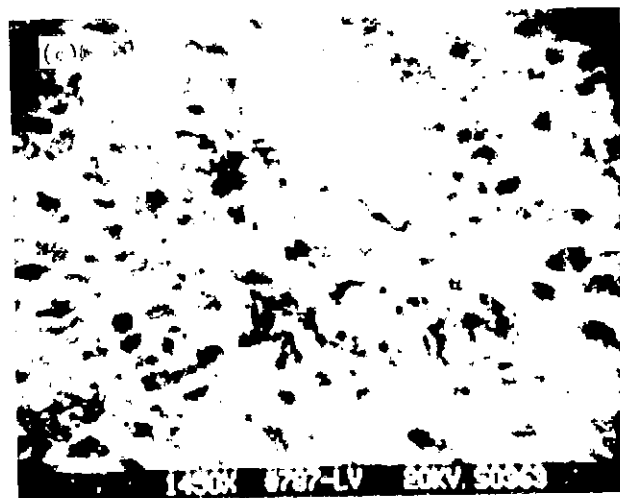
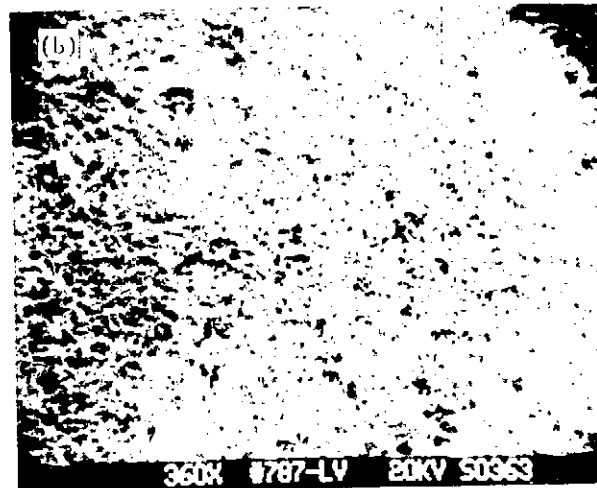


Fig. E-1. Sample of liquid-vapor interface (a) at 135x, (b) at 360x, and (c) at 1450x.