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MCR-72-26 Copy No. \_\_\_\_\_

MATERIAL COMPATIBILITY  
WITH  
SPACE STORABLE PROPELLANTS

DESIGN GUIDEBOOK

March 1972

(NASA-CR-127057) MATERIAL COMPATIBILITY  
WITH SPACE STORABLE PROPELLANTS. DESIGN  
GUIDEBOOK P.E. Uney, et al (Martin  
Marietta Corp.) Mar. 1972 123 p CSCL 21I

N72-26678

Unclas  
G3/27 30162

Prepared for  
Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, California 91103

Contract No. HF-556439  
Under NAS 7-100



**MARTIN MARIETTA**

DENVER DIVISION

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Prepared by

P. E. Uney and D. A. Fester

Approved



Dale A. Fester  
Program Manager

MARTIN MARIETTA CORPORATION  
P.O. Box 179  
Denver, Colorado 80201

FOREWORD

This report is submitted by Martin Marietta Corporation, Denver, Colorado, in accordance with the requirements of JPL Contract No. HF-556439, dated 21 September 1971. The work was administered by the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, with Mr. Robert F. Lem as the JPL Technical Manager. Mr. Dale A. Fester of the Advanced Fluid Technology Section, Propulsion Department, was the Martin Marietta Program Manager.

ABSTRACT

An important consideration in the design of spacecraft for interplanetary missions is the compatibility of storage materials with the propellants. Serious problems can arise because many propellants are either extremely reactive or subject to catalytic decomposition, making the selection of proper materials of construction for propellant containment and control a critical requirement for the long-life applications.

To aid in selecting materials and designing and evaluating various propulsion subsystems, available information on the compatibility of spacecraft materials with propellants of interest was compiled from literature searches and personal contacts. The compatibility of both metals and non-metals with hydrazine, monomethyl hydrazine, nitrated hydrazine, and diborane fuels and nitrogen tetroxide, fluorine, oxygen difluoride, and Flox oxidizers was surveyed. These fuels and oxidizers encompass the wide variety of problems encountered in propellant storage. As such, they present worst case situations of the propellant affecting the material and the material affecting the propellant. This includes material attack, propellant decomposition, and the formation of clogging materials.

CONTENTS

	<u>Page</u>
Foreword . . . . .	11
Abstract . . . . .	111
Contents . . . . .	iv
I. Introduction . . . . .	1
II. Hydrazine ( $N_2H_4$ ) . . . . .	5
A. Compatibility Summary . . . . .	5
B. General Discussion . . . . .	9
III. Monomethyl Hydrazine (MMH) . . . . .	27
A. Compatibility Summary . . . . .	27
B. General Discussion . . . . .	30
IV. Nitrated Hydrazine Fuels . . . . .	37
A. Compatibility Summary . . . . .	37
B. General Discussion . . . . .	40
V. Diborane ( $B_2H_6$ ) . . . . .	45
A. Compatibility Summary . . . . .	45
B. General Discussion . . . . .	49
VI. Nitrogen Tetroxide ( $N_2O_4$ ) . . . . .	57
A. Compatibility Summary . . . . .	57
B. General Discussion . . . . .	63
VII. Fluorine ( $F_2$ ) . . . . .	85
A. Compatibility Summary . . . . .	85
B. General Discussion . . . . .	89
VIII. Oxygen Difluoride ( $OF_2$ ) . . . . .	103
A. Compatibility Summary . . . . .	103
B. General Discussion . . . . .	105
IX. Flox ( $F_2+O_2$ ) . . . . .	109
A. Compatibility Summary . . . . .	109
B. General Discussion . . . . .	110
X. References . . . . .	113

I. INTRODUCTION

An important consideration in the design of spacecraft for interplanetary missions is the compatibility of storage materials with the propellants. Serious problems can arise because many propellants are either extremely reactive or subject to catalytic decomposition, making the selection of proper materials of construction for propellant containment a critical requirement.

Under Contract NAS7-754, Investigation of Space Storable Propellant Acquisition Devices, information on the compatibility of both metals and non-metals with nitrogen tetroxide, oxygen difluoride, diborane, hydrazine, monomethyl hydrazine, and nitrated hydrazine propellants was compiled to aid in selecting materials and evaluating the propulsion systems of interest. This information was included in two separate Martin Marietta reports:

- 1) Uney, P. E.: Compatibility of Storage Materials with Various Rocket Propellants. SR 1660-69-20, Martin Marietta Corporation, Denver, Colorado, November 1969; and
- 2) Uney, P. E.: Compatibility of Storage Materials with Various Rocket Propellants. SR 1660-69-20A, Martin Marietta Corporation, Denver, Colorado, January 1970.

It was the purpose of this program to revise and update the information contained in these reports and to add information on the compatibility of various materials with Flox and fluorine. The resulting compilation was to be incorporated into a material compatibility design guidebook having a common format for each propellant of interest. The results are presented in this document.

A chapter is devoted to the compatibility of materials with each of the eight propellants. The four fuels are discussed first. Chapter II discusses hydrazine compatibility, Chapter III discusses monomethyl hydrazine compatibility, nitrated hydrazine fuels are discussed in Chapter IV, and diborane information is presented in Chapter V. The four oxidizers are then discussed in Chapters VI through IX, with nitrogen tetroxide in Chapter VI, fluorine in Chapter VII, oxygen difluoride in Chapter VIII, and Flox in Chapter IX. Finally, the references for the entire report are listed in Chapter X.

The information presented in this report was gathered through literature searches and personal contacts with government agencies, universities, and industry. No experimental effort was involved in this program; all information presented is based on a critical review of the compiled data.

Most of the material compatibility information was compiled from studies made over a time period of more than a decade. The time span included was roughly from 1959 through 1971. In reviewing the various studies, it became apparent that it is difficult to compare results obtained from earlier studies with more recently acquired data. Up to about the middle of the time span, long term storage was usually concerned with a matter of weeks or months, while later studies have focused on storage times of years. Much of the older data was obtained through short term exposure of the material to the propellant and the resulting rate was extrapolated to the desired time, usually a year. This approach generally resulted in material corrosion or propellant decomposition rates which were too high. Later data has shown that after a short induction period, the initially high rates decrease to much lower values. Another problem encountered, is that much of the compatibility information is conflicting. The reasons for this are numerous and varied. They include:

- 1) Different investigators;
- 2) Differing sample preparation methods;
- 3) Differing cleaning techniques and fluids;
- 4) Varied compatibility testing methods and procedures;
- 5) Propellant purity variations arising from different manufacturers, changed specifications, and the wide range of contaminants allowed by a given specification;
- 6) Varying standards for determining what constitutes compatibility.

Therefore, the material compatibility ratings presented reflect our interpretation of the data. These ratings are summarized in tabular form in the first section of each chapter. This summary is then followed by a general discussion of the data on which the ratings are based.

No correlation of the effects of time or temperature on material compatibility is available other than the general relationships that the extent of a reaction varies directly with time and the reaction rate is a function of

temperature. Thus, the effects of any reaction become more pronounced for longer periods of time at a given temperature or for shorter times at elevated temperatures. Extrapolation of the data presented to a 10-year life requirement would be fraught with uncertainties. However, it is felt that the data are representative of the material compatibility to be expected for a storage period of one to two years.

II. HYDRAZINE

## A. COMPATIBILITY SUMMARY

The compatibility of both metals and non-metals with neat  $N_2H_4$  is summarized in Table 1, as determined by interpreting available compatibility information. Specific references used in this determination are listed in the table. Compatibility of a material with  $N_2H_4$  was based on the criteria that the material be essentially unaffected by  $N_2H_4$  exposure (negligible corrosion for metals and negligible loss of physical properties for non-metals) and that it should not significantly affect the rate of  $N_2H_4$  decomposition. Listing of a material in the table was based, in general, on the existence of specific compatibility data for that material with  $N_2H_4$ ; however, certain materials were included even though no such data were available. A compatibility rating for such a case was determined by use of either compatibility data with a sister material (similar alloy) or a sister propellant (MMH or a hydrazine-blend fuel). In some instances, two compatibility ratings were assigned to the same material due to conflicting data. Also, where compatibility was determined for a specific use, this is indicated in the remarks section of the table.

In establishing a compatibility rating for a material with hydrazine, the primary mechanism on which that rating is based is of interest. The compatibility rating for metals with  $N_2H_4$ , as shown in Table 1, is primarily an indication of the degree to which the metal affects the propellant, since non-contaminated  $N_2H_4$  has little effect on metals. On the other hand, the compatibility rating for non-metals with  $N_2H_4$  is based on either the extent that the material affects the propellant or the extent that the propellant affects the material, or both.

Table 1 N<sub>2</sub>H<sub>4</sub> Summary Compatibility Chart

Material	Rating					References	Remarks
	1	2	3	4	5		
<u>Metals</u>							
1) Aluminums							
a. Aluminum alloys in general	A	A,B				1,2,3,4,5,6,7,10,13,14	Ratings based on non-contaminated N <sub>2</sub> H <sub>4</sub> , i.e., no Cl <sub>2</sub> or CO <sub>2</sub> contaminants.
b. Pure	A					2	
c. 1100	A					4,5,7	
d. 2014	A		A			4,5,6,7,14	Conflicting data
e. 2021	A	A				6	
f. 2024	A	B				4,5	
g. 2219	A					1,2,4,5,6,7	
h. 3003	A					4,5	
i. 5052	A					4,5	
j. 6061	A	A	A			4,5,13,10,14	Conflicting data
k. 356	A	A				4,5,13	
2) Steels							
a. Stainless Steels in General							
b. 301 Cryoformed		Aa	A,B			1,2,3,4,5,6,7,8,14	
c. 304		Aa	Bb			1,2,6	
d. 316		Aa	Ab	A		2,3,4,5,8	a. for short term use (<6 mo.)
e. 321		Aa	Ab			2	b. long term use (>6 mo.)
f. 347		Aa	A			2,3,4,5,14	
g. 410		Aa	Bb			2,7	
h. 430		Aa	Bb			1,2,4,5	
i. 440C		Aa	Bb			1,2,4,5	
j. 17-4 PH or 17-7 PH		Aa	Ab			1,2,4,5,6	
k. AM350 or AM355		Aa	A,C			1,6,8,83	
l. A-286		Aa	Bb			1,2,6	
m. Maraging steels			C			29,83	
n. Non-stainless steels				B,C		1,2,4,5,84	

Table 1 (Continued)

Material	Rating					References	Remarks
	1	2	3	4	5		
3) Titaniums							
a. Titanium alloys in general	A, B					1, 3, 4, 5, 6, 8, 10, 14	
b. 6Al-4V	A					4, 5, 6, 8, 10, 14	
c. 5Al-2.5Sn	A					4, 5	
d. A-70	A					14	
4) Miscellaneous Metals							
a. Pure iron				A, C		1, 2, 4, 5, 84	
b. Pure nickel				A, C		1, 2, 9, 83, 84	Poor corrosion resistance
c. Zinc			A, C			4, 5, 83	
d. Brass				A, B, C		1, 4, 5, 84	
e. Bronze				A, B, C		1, 4, 5, 84	
f. Copper				A, C		1, 4, 5, 84	
g. Magnesium					A		Not enough data Conflicting data
h. Lead		B, C	A			1, 4, 5, 28	
i. Cobalt				A, C		1, 4, 5, 83	
j. Molybdenum				A, C		1, 4, 5, 83	
k. Tantalum	A					1, 4, 5	
l. Silver		C				83	Limited data
m. Gold				A, C		9, 83	
n. Platinum		A				4, 5, 13	
o. Tin		A, C				1, 4, 5, 83	
p. Zirconium	A					1, 4, 5	
q. Chromium						1, 4, 5, 83, 84	Conflicting data
r. 82/18 Au/Ni braze		A, C	B, C	A		9	
s. Monel			B			1, 2	
t. Inconel			B			1, 2	
u. Hastelloy Alloys			B			1, 2	
<u>Non-Metals</u>							
1) Polymers							
a. TFE Teflon		A				4, 5, 17	Rated for general use (no specific application, except as noted). Teflon is highly permeable.
b. FEP Teflon		L				4, 5, 17	

Table 1 (Concluded)

Material	Rating					References	Remarks
	1	2	3	4	5		
1) Polymeric (Cont'd)							
c. Kel-F		A		A		4, 5, 17	
d. Saran						4, 5	
e. Natural rubbers		A	A			4, 5	
f. Polyethylene						4, 5, 17	
g. Butyl rubbers		A	A			4, 5, 19, 20, 23	
h. Mylar				A		4, 5	
i. Nylon		A	A			4, 5	
j. Rulon (PTFE)		A				13, 27	
k. EPR's in general		A				4, 13, 18, 19, 20, 21, 23, 27	Conflicting data Rated for no carbon black filler.
1. EPR 132		A				20, 21	Same as above.
m. EPR's w/carbon black filler				A		20, 21, 23, 27	
n. EPR SR722-70						20, 22	
o. EPR E515-8			A			20, 21	
p. EPT's in general		A, B	A			23, 24, 26	Same as above.
q. EPT-10	A	A				23, 24, 26	Same as above.
r. AF-E-102						25	
s. AF-E-332	A					26	
2) Lubricants							
a. Lubricants in general							
b. Graphite		A				5	
3) Miscellaneous non-metals							
a. Asbestos		A				5	
b. Metal oxides in general				A		4, 5, 16	
1 - Compatible							A - Rating based on data on the specific material with the specific propellant
2 - Probable Compatibility							B - Rating based on data on a similar or sister material
3 - Doubtful Compatibility							with the specific propellant
4 - Incompatible							C - Rating based on data on the specific material but with a sister propellant
5 - Unable to Rate							D - No specific data

## B. GENERAL DISCUSSION

Hydrazine is a highly reactive and toxic propellant. It is considered thermodynamically unstable and exists in a state of continuous decomposition. The decomposition rate is a function of both temperature and the presence of a catalyst. At ambient temperatures ( $\approx 70^{\circ}\text{F}$ ) and in the absence of a catalyst, the average decomposition rate of  $\text{N}_2\text{H}_4$  is minimal. The attack of storage materials is usually considered a problem only for non-metals since practically all metals show excellent corrosion resistance to neat  $\text{N}_2\text{H}_4$ . However,  $\text{N}_2\text{H}_4$  has become corrosive to metals when certain contaminants, such as  $\text{CO}_2$  and  $\text{Cl}_2$  have been added. Therefore, for long term storage of uncontaminated  $\text{N}_2\text{H}_4$ , the major concern is the degree that the metal being considered accelerates the  $\text{N}_2\text{H}_4$  decomposition rate. For long term storage with non-metals, on the other hand, both catalytic and material attack must be considered.

### 1. Compatibility with Metals

According to Eberstein and Glassman the decomposition rate of  $\text{N}_2\text{H}_4$  tends to increase when the  $\text{N}_2\text{H}_4$  is in contact with metals having incomplete d-subshells (Ref 1). This is due to the relatively weak nitrogen to nitrogen bond in the  $\text{N}_2\text{H}_4$  molecule. Eberstein and Glassman state that metals in the atomic number groups 24 to 29, 42 to 47, and 74 to 79 (transition metals with incomplete d-subshells) would act as catalysts for hydrazine decomposition. Some metals which fall into this category are nickel, chromium, iron, molybdenum, copper, gold, platinum, silver and manganese. Aluminum, titanium, magnesium and zinc fall outside this group. From this, stainless steel would appear unacceptable for  $\text{N}_2\text{H}_4$  storage, while 6061 aluminum, 2219 aluminum, and 6Al-4V titanium would seem acceptable.

Tests conducted by Rocketdyne confirm the compatibility of  $\text{N}_2\text{H}_4$  with high-purity aluminum but also indicate that some stainless steels might be compatible (Ref 2). The testing was conducted at  $338^{\circ}\text{F}$  with liquid propellant-grade  $\text{N}_2\text{H}_4$  in contact with high-purity iron, nickel, and aluminum, and 304, 316, 321, and 347 stainless steels. All metal surfaces were cleaned with concentrated nitric acid prior to immersion in the Pyrex glass containers.

Containers with no metal sample served as controls. Decomposition rates compared to those with glass were greater by about 200 times with nickel, 130 times with 316 stainless steel, 100 times with iron, 40 times with 347 stainless steel, but only 10 times with 304 and 321 stainless steels. The decomposition rate with the aluminum was the same as the control samples. Since these tests were conducted at elevated temperature, the decomposition rates observed are considerably higher than would be expected under normal storage conditions ( $\approx 70^{\circ}\text{F}$ )\*. It would seem, therefore, that 304 and 321 stainless steels might be candidates for long term storage of  $\text{N}_2\text{H}_4$ .

Based on compatibility tests performed over the past decade at Martin Marietta, Caudill and O'Brien (Ref 3) state that chemically clean 304 and 321 stainless steels are compatible with  $\text{N}_2\text{H}_4$  at temperatures below  $120^{\circ}\text{F}$ . However, both also state that aluminum or titanium alloys are better storage materials since they exhibited compatibility even at  $275^{\circ}\text{F}$ .

TRW and DMIC surveyed material compatibility data and recommended materials for  $\text{N}_2\text{H}_4$  use (Ref 4 and 5). For these reports, a metal was considered applicable for long term service with  $\text{N}_2\text{H}_4$  if it had a corrosion rate less than one mil/yr, would not promote  $\text{N}_2\text{H}_4$  decomposition, and was not considered shock sensitive when in contact with  $\text{N}_2\text{H}_4$ . Compatibility recommendations for long term storage with  $\text{N}_2\text{H}_4$ , at temperatures below  $75^{\circ}\text{F}$ , are presented in Tables 2 and 3. As can be seen by the recommendations, a great number of stainless steels, as well as such metals as gold, platinum, silver, nickel alloys and chromium, are considered compatible with  $\text{N}_2\text{H}_4$ . This is in direct opposition to the Eberstein and Glassman theory of  $\text{N}_2\text{H}_4$  decomposition since these metals fall into the atomic number groups considered to be catalytic.

\* Many compatibility evaluations are conducted at elevated temperatures to accentuate the effects of reactions which may be occurring. This approach generally increases the reaction rates to provide comparative results in a shorter time, e.g., the relative degree to which various materials act as catalysts for the propellant of interest is more readily obtained.

Table 2 Metals Compatible with  $N_2H_4$  (Ref 4 and 5 )

Aluminum Alloys	Stainless Steels	Miscellaneous Metals
1100	410	Chromel-A
2014	416	Chromium Plating
2017	430	Gold
2024	440C	Hastelloy-C
3003	302	Inconel
4043	304	Inconel-X
5052	316	K-Monel
5456	317	Monel
6061	321	Nichrome Braze
6066	347	Platinum
715	17-4 PH	Silver
356	17-7 PH	Silver Solder
40E	AM 350	Stellite-21
	AM 355	Tantalum
		Tin
		Titanium, 5Al-2.5Sn
		Titanium, 6Al-4V
		Zirconium

Table 3 Metals Incompatible with  $N_2H_4$  (Ref 4 and 5 )

Cadmium	Zinc	Iron*
Cobalt	Brass*	Molybdenum* -
Lead	Bronze*	Mild Steel*
Magnesium	Copper*	6Al-4V Ti**

\*The authors stated that these metals were considered unacceptable because their Oxides act as catalysts for decomposition of hydrazine at elevated temperatures.

\*\*Based on one reference showing excessive decomposition at 110°F with 50/50  $N_2H_4$ /UDMH.

Giving further support to the hypothesis that certain stainless steels are compatible with  $N_2H_4$ , but disagreeing with certain of the recommendations made by DMIC and TRW, is preliminary data on  $N_2H_4$  storage presented by Branigan of the Air Force Rocket Propulsion Laboratory (Ref 6). Based on a storage period of 17 months at a temperature of approximately  $110^\circ F$ , AFRPL found no pressure rises (indication of  $N_2H_4$  decomposition) in storage tanks constructed of 301 cryoformed and A-286 stainless steels; 18% nickel-maraging 200 steel; 2014-T62, and 2021-T81 aluminums; and 6Al-4V titanium. Pressure rises were observed in storage tanks constructed of AM-350 and 17-7PH stainless steels.

In tests run at the Naval Weapons Center, the compatibility of different tankage materials with various hydrazine fuels, including neat  $N_2H_4$ , was investigated (Ref 7). Small 5.3-cu-in. storage containers were fabricated of 347 stainless steel, 2014-T6 Al, and 1100-0 Al. After filling approximately half-full with  $N_2H_4$ , the containers were stored for 4 weeks at  $100^\circ F$  to screen out problem containers (leaking, high pressure rises, etc.). This was then followed by storage for 48 weeks at the  $165^\circ F$  test temperature. The results showed about the same rate of pressure increase for the aluminum containers, while the pressure rise rates in the 347 stainless steel containers were from three to four times those with aluminum. These results indicate that 347 stainless steel is probably not a good material for long term storage of  $N_2H_4$  and that aluminum is a preferable material.

More data, indicating the catalytic nature of stainless steels with  $N_2H_4$ , is reported by the United Aircraft Research Laboratories, UARL, (Ref 8). Using a technique which measured gas evolution rates at constant temperature and pressure, UARL tested various metal samples for compatibility with  $N_2H_4$ . The samples consisted of small specimens of AM-355 stainless steel, 304 stainless steel, and 6Al-4V titanium. The tests were run at both  $160^\circ F$  and  $120^\circ F$ , except for the 304 stainless steel which was run at  $160^\circ F$  only. Test pressure was 1 atmosphere. Prior to immersion in the  $N_2H_4$ , the samples were polished, cleaned with trichloroethylene, detergent, and acetone in an ultrasonic cleaner, and then dried in  $GN_2$ . For the  $120^\circ F$  tests, the AM-355 samples gave a gas evolution rate 5 times that of the  $N_2H_4$  control sample, while the

6Al-4V titanium specimen gave a rate only  $1\frac{1}{2}$  times that of the control sample. For the  $160^{\circ}\text{F}$  tests, however, the AM-355 specimen had a gas evolution rate 17 times the control samples rate, the 304 specimen rate was 50 times greater than the control sample rate, and the 6Al-4V titanium specimen had the same gas evolution rate as that of the control sample. These data indicate that the catalytic effect on  $\text{N}_2\text{H}_4$  is far greater with 304 and AM-355 stainless steels than it is with 6Al-4V titanium. In fact, the titanium material may exert no catalytic effect.

Gold, nickel, and 82/18 wt % gold/nickel brazing alloy were found to be incompatible with  $\text{N}_2\text{H}_4$  in tests conducted at AFRL (Ref 9). Samples of the materials were immersed for up to 24 hr in test capsules filled with  $\text{N}_2\text{H}_4$  maintained at  $140^{\circ}\text{F}$ . Decomposition of the  $\text{N}_2\text{H}_4$  was determined by measuring the number of moles of  $\text{NH}_3$  formed. The capsules containing the samples showed excessive  $\text{NH}_3$  production. Thus, these results are also in agreement with the theory of Eberstein and Glassman.

Results concurring with the theory of Eberstein and Glassman were reported by Ng at Picatinny Arsenal and by NWC (Ref 83 and 84). In tests run with mixed hydrazine fuel at  $160^{\circ}\text{F}$  for up to 2 years in duration, Ng found excessive pressure rise rates for test samples of 18% Ni maraging steel, AM355 and Inco 718 steels, pure molybdenum, and for chromium, gold, nickel, and cobalt plated on 18% Ni maraging steel (Ref 83). However, 301 cryoformed stainless steel and tin and zinc plated 18% Ni maraging steel produced only moderate pressure rise rates while near zero rates were reported for samples of pure aluminum, 6Al-4V titanium, and 18% Ni maraging steel plated with cadmium or silver. The zinc plated maraging steel corroded severely. NWC exposed pure aluminum, titanium, iron, nickel, copper, and chromium to the same mixed hydrazine fuel for up to 94 days at  $165^{\circ}\text{F}$  (Ref 84). Excessive pressure rise rates occurred with iron, nickel, and copper, while near zero rates were found with titanium and aluminum. After an initially high pressure rise rate for the first 12 days of storage with chromium, the rise rate dropped to zero for the rest of the storage period.

Although corrosion of materials is generally not considered to be a problem with  $N_2H_4$  storage, it has been found that  $N_2H_4$  contaminated with either  $CO_2$  or  $Cl_2$  will corrode certain metals. TRW found that  $N_2H_4$  doped with  $CO_2$  and  $H_2O$  is corrosive to stainless steels (Ref 10). The tests consisted of using both artificially conditioned and normal hydrazine in contact with various metal samples to check compatibility. Two specimens of 6061-T6 aluminum, 6Al-4V titanium, and 347 stainless steel were placed in contact with hydrazine conditioned with approximately 1%  $NH_3$ , 1%  $CO_2$  and 3%  $H_2O$ . A third specimen of each material was placed in contact with the reference hydrazine. Half of each specimen was covered with liquid, and the other half was exposed to the vapor above the liquid. Glass capsules were employed as test containers. All samples were thoroughly cleaned but not passivated prior to testing. The 347 stainless steel samples were also honed with aluminum grit. The tests were conducted at  $120^\circ F$  with temperature and pressure monitored at regular intervals. Almost immediately after test initiation, the two 347 stainless samples showed signs of reactivity, and venting at regular intervals was required to protect the capsules and pressure gages.

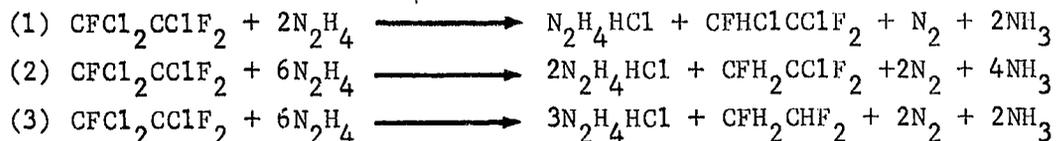
After 166 hr, the conditioned hydrazine in contact with the 347 stainless samples had turned red in color and a crystalline solid was deposited on both specimens and in the bottom of the tubes. Due to this build-up of the crystalline solid, the tests were terminated after 188 hr of testing. The stainless steel specimens were removed from their test capsules, cleaned, and examined. Extensive pitting was found over the entire surface of the samples. Analysis of the hydrazine liquid revealed large amounts of chromium, nickel and iron in solution. After five months of storage at  $120^\circ F$  and an additional month at ambient temperature, there were no apparent signs of specimen corrosion or propellant discoloration with the aluminum and titanium samples.

The results obtained by TRW can probably be explained by work done at Rocket Research where 303 and 304 stainless steel fittings were exposed to hydrazine samples under different atmospheres (Ref 11). Three series of tests were conducted with duplicate samples of both 303 and 304 fittings used in each series. In the first test series, the samples were immersed in hydrazine using

a nitrogen atmosphere. In the second test series, the samples were immersed in hydrazine under a nitrogen-carbon dioxide atmosphere (97%  $N_2$ , 3%  $CO_2$ ). In the third test series, a 97% hydrazine-3% water mixture was used in conjunction with a 97%  $N_2$ -3%  $CO_2$  atmosphere. The six 303 and six 304 stainless steel fittings were cleaned by successive immersions in trichlorethylene, water, and methanol and water. This was followed by a three minute soak in propellant grade hydrazine, thorough rinsing with distilled water, and drying at  $230^\circ F$  for one hour. Glass sample jars, previously cleaned with detergent, rinsed with distilled water, and oven dried were used to hold the samples. The fittings were placed in these jars and 75 ml of hydrazine or hydrazine-water mixture were added (sufficient to cover the fittings) while either a nitrogen or a nitrogen-carbon dioxide purge was maintained to exclude air. The jar mouth was covered with 2-mil polyethylene film before capping and sealing with vinyl tape. The sealed bottles were then maintained at  $160 \pm 5^\circ F$  for 11 days. The significant result from these tests was the deterioration of both the fittings and the hydrazine in contact with the nitrogen-carbon dioxide atmosphere. In addition to the dulling of fittings and discoloration of the hydrazine, the hydrazine (or hydrazine-water mix) became filled with gas bubbles which developed into a frothy scum in some instances. Since the corrosion of the fittings and the decomposition of the  $N_2H_4$  occurred in both the pure  $N_2H_4$  and the  $N_2H_4 - H_2O$  mix samples, the effect of  $H_2O$  in the corrosion process appears negligible. According to Rocket Research,  $CO_2$  reacts rapidly with hydrazine to form carbamic acid ( $H_3N_2CO_2H$ ) which in turn reacts with excess  $N_2H_4$  to form a salt ( $H_3N_2CO_2(N_2H_5)$ ) which is soluble in hydrazine. It apparently is this salt which is responsible for the stainless steel corrosion. No corrosion was observed in the samples using the  $N_2$  atmosphere only.

In addition to  $N_2H_4$  contaminated with  $CO_2$  being corrosive to stainless steels, SRI has found that  $N_2H_4$  contaminated with  $Cl_2$  is corrosive to titanium (Ref 12). Test capsules containing  $N_2H_4$  and 6Al-4V titanium test specimens, that had been in storage at JPL to determine the compatibility of various materials with  $N_2H_4$ , were analyzed for both corrosion and propellant decomposition. The storage temperature was  $110^\circ F$ . Prior to storage initiation, the test

capsules had been degreased using Freon TF in accordance with JPL specification GMZ-50521-GEN-A. Upon analysis of the test capsule contents, SRI found both excessive  $N_2H_4$  decomposition and severe corrosion of the Ti specimens. A detailed analysis of the  $N_2H_4$  revealed large concentrations of both chloride and carbon impurities. Also, the titanium specimens had chloride concentrations 200 times greater than that found in virgin 6Al-4V titanium. The high chloride and carbon impurities led SRI to hypothesize that the decomposition and corrosion was due to the reaction of  $N_2H_4$  with Freon TF. It was felt that the Freon TF had not been completely removed from the test capsules before they were filled with  $N_2H_4$ . To verify this hypothesis, they mixed  $N_2H_4$  and Freon TF and found that hydrazine monohydrochloride ( $N_2H_4HCl$ ) was formed. This salt will make  $N_2H_4$  acidic and corrosive to metals. SRI proposed the following reactions as the means for the creation of the  $N_2H_4HCl$  salt:



As the above reactions show,  $N_2$  and  $NH_3$  production is a product of the  $N_2H_4$  - Freon TF reaction which explains the observed  $N_2H_4$  decomposition. Since SRI did not detect the products  $\text{CFHClCClF}_2$ ,  $\text{CFH}_2\text{CClF}_2$ , and  $\text{CFH}_2\text{CHF}_2$  but did find chloride and carbon concentrations in the capsules, it was felt that some further reaction had also occurred.

The results of the SRI analysis indicate that the use of degreasing or cleaning solvents containing  $Cl_2$  should be avoided as a means of cleaning metals prior to use with  $N_2H_4$ . Although only titanium specimens were analyzed, hydrazine containing  $N_2H_4HCl$  would also be corrosive to other storage metals such as aluminums and stainless steels. Therefore, chlorinated solvents, such as Freon TF, trichlorethylene, methylene chloride, etc., should not be used with any metal (Al, Ti, stainless steels, etc.) slated for service with  $N_2H_4$  unless all traces of these degreasing agents can be removed prior to use.

Although both aluminum and titanium materials seem, from the data presented so far, to be excellent storage materials for  $N_2H_4$ , some evidence exists showing certain aluminums and titaniums to be incompatible with hydrazine fuels. In

a series of JPL tests analyzed by SRI, various metals were tested for long term storage with  $N_2H_4$  and Aerozine-50 (Ref 13). The tests were run at a constant temperature of  $110^{\circ}F$  for periods up to 4 years. For this study, a material was rated compatible if the fuel decomposition rate was no greater than the decomposition rate of the fuel alone (determined by control samples) and the corrosion rate of the metal sample was not greater than  $3 \mu in/yr$ . Prior to testing, the platinum, aluminum and titanium samples were subjected to a cleaning and pickling passivation process which consisted of a detergent rinse followed by pickling in an aqueous solution of HF and  $HNO_3$ . The samples were then dried with  $N_2$ . The tests were conducted in glass test capsules cleaned in accordance with JPL specification GMZ-50521-GEN-A. Platinum and aluminum samples were tested in neat  $N_2H_4$  and 6Al-4V titanium was tested in Aerozine-50. Based on the compatibility criteria employed, SRI concluded from the test results that platinum and 6061-T6 aluminum were compatible with  $N_2H_4$  over the entire 4-yr test period while 356-T6 aluminum was rated compatible after one year but incompatible after two years. Also, 6Al-4V titanium was rated incompatible with Aerozine-50 after one year. There was no evidence of corrosive attack on the specimens except for the occurrence of some staining.

In evaluating these results, it is apparent that the criteria employed for assessing compatibility is much more stringent than that employed in other material compatibility studies. It appears that in many cases a material was rated as incompatible when only one of the samples tested had a higher final capsule pressure than the control sample. When the average normalized final storage pressure at  $110^{\circ}F$  for the metal-containing samples is compared to the corresponding pressure for the control samples, it appears that none of the above materials should be rated incompatible with the test propellants for the stated time periods.

In tests run at McDonnell, the compatibility of various metal tankage materials with  $N_2H_4$  at spacecraft sterilization temperatures ( $275^{\circ}F$ ) was investigated (Ref 14). The 6Al-4V titanium, 6061-T6 and 1100 aluminums, and 321 stainless steel test metals were fabricated into capsules and tensile test



In a recently completed program, Battelle evaluated the effects of radiation on the compatibility of storage materials with hydrazine (Ref 15). Various specimens of 1100-0 and 6061-T6 aluminum, 347 stainless steel, and 6Al-4V titanium in contact with hydrazine were exposed to cobalt-60 gamma radiation. In one series of tests,  $N_2H_4$  was stored in capsules made from the four metals tested. With no irradiation, the average rate of gas buildup over the 980-hr storage period was  $5 \times 10^{-9}$ ,  $6 \times 10^{-9}$ ,  $6 \times 10^{-9}$ , and  $4 \times 10^{-9}$  moles per gram of liquid per hour for 1100-0 Al, 6061-T6 Al, 347 S.S. and 6Al-4V Ti, respectively. When exposed to 0.52 megarads/hr over 288 hr, the respective average rates increased to  $6.6 \times 10^{-7}$ ,  $8.1 \times 10^{-7}$ ,  $6.6 \times 10^{-7}$ , and  $8.0 \times 10^{-7}$  moles per gram of liquid per hour. These results indicate little difference between alloys but do show an increase in decomposition rate with irradiation. After completion of the gas evolution studies, the interior surfaces were examined. Only very thin films were observed by electron diffraction.

The data obtained in the referenced studies indicate that the preferable materials for long term storage of hydrazine are 6Al-4V titanium and various alloys of aluminum. The 300 series stainless steels are considerably less desirable and iron, nickel, and gold are incompatible. These results are generally in agreement with the theory of Eberstein and Glassman on hydrazine compatibility. However, Vango has proposed another theory on the compatibility of metals with hydrazine (Ref 16). He states that the decomposition observed in  $N_2H_4$  compatibility tests is due to the presence of metal oxides or metal ions in solution with the propellant. He has found, for instance, that neither pure molybdenum nor pure iron in their reduced state promote hydrazine decomposition. Vango further contends that the observed promotion of  $N_2H_4$  decomposition by stainless steels is probably due to the tenacious protective oxide coating formed during passivation with  $HNO_3$ .

It appears that some of the reported data can be explained by the Vango theory while some of the data seems in opposition. Since the Rocketdyne samples were cleaned with  $HNO_3$ , the oxide layer on the iron, nickel and stainless steels could have caused hydrazine decomposition. However, aluminum oxide evidently does not promote decomposition since the aluminum was found to be compatible. Also, an oxide decomposition mechanism does not seem to explain the incompatibility of gold, observed by AFRPL, since gold oxide is difficult to form.

In actuality, both the Vango theory and the Eberstein and Glassman theory seem to apply. Both theories appear to complement each other with the net result being that titanium and aluminum alloys exert the least, if any, catalytic effect in decomposing hydrazine. The stainless steels, while being more catalytic in decomposing hydrazine, might find limited application where needed, however. Finally, metals such as iron, molybdenum, nickel, and gold are not desirable for long term storage with hydrazine and must be rated as incompatible. The results of the previously discussed studies also tend to support the following conclusions:

- 1) In preparing systems for long term storage of hydrazine, care must be taken to provide a truly clean system. In particular, the introduction of contaminants by the cleaning process itself must be precluded;
- 2) Because contaminants such as  $\text{Cl}_2$ ,  $\text{CO}_2$ , other compounds, or metal ions appear to promote hydrazine decomposition, a purified hydrazine may be necessary for long term storage applications. A wide variety of contaminants could be present in propellant-grade hydrazine;
- 3) Care must be taken to keep all hydrazine systems pressurized with only an inert gas blanket to prevent the introduction of contaminants such as  $\text{CO}_2$ .

## 2. Compatibility with Non-Metals

According to reports written by DMIC, TRW, and AFRPL (Ref 5, 4 and 17), only a few non-metals are considered suitable for  $\text{N}_2\text{H}_4$  applications. Von Doehren states that Teflon, Kel-F, and polyethylene are suitable for general use with  $\text{N}_2\text{H}_4$  (Ref 17). DMIC rated Teflon, butyl rubber compound 805-70, Graphitar 2 and 50, and Denlanian as suitable storage materials with  $\text{N}_2\text{H}_4$  below  $140^\circ\text{F}$ , while rating polyethylene, graphite, SBR rubber, asbestos, and Kel-F suitable below  $75^\circ\text{F}$  (Ref 5). Non-metals such as nylon, Saran, Mylar, and natural rubber were rated as unsuitable. DMIC based compatibility on the premise that a material would have a volume change less than  $\pm 25\%$ , would not change visually, and would not decompose the propellant in question. TRW rated Teflon, butyl rubber,

Kel-F and EPR (ethylene propylene rubber) as suitable materials for  $N_2H_4$  service below  $140^{\circ}F$  (Ref 4). Polyethylene was rated suitable only for service below  $80^{\circ}F$ . If a non-metal gave satisfactory service for general use, it was considered compatible. These three reports based their ratings on available compatibility data, in the period 1964 to 1967.

Although Teflon seems to be one of the better storage materials for  $N_2H_4$ , it is very permeable to  $N_2H_4$ . According to O'Brien and Bolt (Ref 18), Teflon is generally not used, to a large extent, as a storage material in propellant management systems due to its high permeability with hydrazine type fuels. O'Brien and Bolt both recommended either butyl rubber or EPR formulations as storage materials for  $N_2H_4$  and stated that both of these materials give good results if properly manufactured. It should be noted that both NASA and JPL have mainly used either butyl rubber or EPR on their missions for hydrazine-type fuel storage to date. Reliance on EPR as a storage material seems justified, for  $N_2H_4$  storage, by tests conducted at JPL (Ref 19). JPL ran both  $N_2H_4$  permeability rate and  $N_2H_4$  decomposition rate tests on butyl rubber and EPR samples. The tests lasted up to one year at a test temperature of  $110^{\circ}F$ . The butyl rubber showed permeability rates between 0 and  $0.001 \text{ mg/in.}^2/\text{hr}$  and a fuel decomposition rate of 0.1%/day, while the EPR samples showed permeability rates between 0.001 and  $0.4 \text{ mg/in.}^2/\text{hr}$  and a maximum fuel decomposition rate of 0.0038%/day.

Some compatibility test data on PTFE, which disagrees with the ratings given by DMIC, TRW, and AFRPL on Teflon in general, have been reported by SRI (Ref 13). As part of the JPL long term storage tests reported on earlier under metals compatibility, various metal test bars coated with different non-metals were stored in liquid  $N_2H_4$  for periods up to 4 years. Test specimens included a polytetrafluoroethylene (PTFE) resin, Rulon, coated on a 6061-T6 aluminum test bar and EPR bonded on a 6Al-4V titanium test bar. In addition, a sample of EPR alone was tested. The results were conflicting. Based on pressure rise data, SRI concluded that the metal-EPR and metal-Rulon samples were incompatible with  $N_2H_4$ .

However, the EPR samples without a metal gave pressure rise rates which SRI felt made this sample compatible with  $N_2H_4$ . SRI also reported that the EPR had unbonded from the 6Al-4V titanium but that its properties suffered little from the exposure to  $N_2H_4$ . Because of these results, SRI felt that EPR was probably compatible with  $N_2H_4$  but 6Al-4V Ti may not be. No good explanation of why the Rulon coating exhibited incompatibility was given; SRI postulated that impurities contained in the Rulon may have been responsible.

More data on the compatibility of ethylene-propylene elastomers (EPR rubbers) with  $N_2H_4$  have been reported by both TRW and Aerospace Corporation (Ref 20 and 21). Howell of TRW states that the compatibility of EPR depends significantly upon the compounding variations used for each EPR formulation (Ref 20). EPR compounds using carbon black as filler have significantly higher decomposition rates than those using the silicate filler, Silene D. Also, butyl rubbers may not be as compatible as some of the other EPR formulations. Howell further states that the purity and exact quantity of ingredients as well as curing time and temperatures also significantly affect compatibility. Therefore, an EPR considered compatible with  $N_2H_4$  may be incompatible unless stringent controls are maintained to see that no variations in purity or composition or in curing time or temperature occur for the particular EPR being considered.

EPR/ $N_2H_4$  compatibility data presented by Aerospace Corporation seems to substantiate the data presented by Howell (Ref 21). In a series of tests, Aerospace measured both gas evaluation rates and property changes of various EPR formulations while immersed in 97% pure anhydrous  $N_2H_4$  at 70°F. Their results indicate that EPR 132 is compatible with  $N_2H_4$  as long as no carbon black filler is used in its formulation.

Further data on the compatibility of ethylene propylene elastomers with  $N_2H_4$  has been reported by SRI, APCO, and Martin Marietta (Ref 22 thru 24). SRI analyzed a prototype spacecraft tank which had been subjected to intermittent testing with  $N_2H_4$  and  $GN_2$  at temperatures and pressures up to 150°F and 1500 psi, respectively (Ref 22). A bonded EPR (Stillman Rubber Co., SR722-70) expulsion diaphragm was contained within the JPL test tank. One side of the diaphragm had been exposed to  $GN_2$  while the other side had been exposed to  $N_2H_4$  during testing. Upon analysis of the diaphragm, SRI found:

- 1) Materials had been leached out of the SR722-70 EPR material during hydrazine exposure. However, on the basis of an accelerated 24 hour decomposition test, the leached out materials seemed to have no effect on  $N_2H_4$  decomposition;
- 2) Embrittlement of the diaphragm material occurred;
- 3) No increase in permeability of the diaphragm material, due to  $N_2H_4$  exposure, was found.

Accessory Products Company (APCO), conducted a compounding study to improve both the compatibility and permeability of ethylene propylene copolymers (EPR) and terpolymers (EPT) with  $N_2H_4$  (Ref 23). Ten compounds were formulated for the study. One was simply EPR 132. Four others contained HAF carbon black as a filler while the others used either Icecap KE clay, Silene D, or a mixture of both as fillers. Curing agents for the various formulations included peroxide, resin, and sulfur. On the basis of mechanical property tests conducted on the 10 formulations, the non-carbon black fillers gave lower tensile strengths. Also it was found that the terpolymer formulations gave greater hardness values than the copolymer formulations.

Hydrazine immersion tests were conducted at JPL. Compatibility was determined on the basis of pressure rise (low  $N_2H_4$  decomposition). Test temperature was 125°F. In addition to the 10 formulations, two additional commercial EPR (Parker E515-8 and Stillman SR722-70) and one commercial butyl (Fargo FR6-60-26) were also tested. After 60 days of testing, only four of the test polymer containers had pressure increases less than 30 psi. These were the peroxide cured EPR compounds ( $\Delta P \approx 25$  psi) and the sulfur cured EPT compounds ( $\Delta P \approx 10$  psi). These four formulations contained no carbon black. All of the tests with the other polymers had to be terminated before 60 days due to excessive pressure build up ( $\Delta P = 50$  psi). On the basis of this first series of tests, the EPT compounds were reimmersed for an additional 328 days with little additional  $N_2H_4$  decomposition. This led APCO to believe that a passivation process probably had occurred during the first part of the testing.

The 10 formulations were also tested for permeability and weight gain. Low permeation was associated with high hydrazine adsorption. The hydrated silica and clay fillers appeared to have a high affinity for hydrazine adsorption while simultaneously showing excellent compatibility. For example, peroxide-cured EPT had a weight gain of 23% after 286 hours and yet had no detectable permeation at the end of 760 hours of exposure. Conversely, sulfur-cured EPT had a weight increase of only 5% while the permeation test was discontinued at 141 hours when the rate had already risen to 0.334 mg/in.<sup>2</sup>/hr.

Martin Marietta has conducted mechanical property and propellant decomposition tests with the EPT-10 diaphragm material proposed for the Viking lander propellant tanks (Ref 24). The major concern was the effect that sterilization at 275°F would have on the compatibility of the terpolymer with N<sub>2</sub>H<sub>4</sub>. Testing is still in progress. Preliminary results indicate that sterilization does not significantly effect the compatibility of EPT-10 with N<sub>2</sub>H<sub>4</sub>. Although dry heat sterilization considerably altered the mechanical properties of EPT-10, these properties again returned to the as-cured values after soaking in N<sub>2</sub>H<sub>4</sub>. A passivation process seems to occur upon immersion after dry heat sterilization. High pressure rises have been recorded for the first twenty days of immersion. After this time, near-zero pressure rise rates have been observed.

The most recent compatibility information on ethylene-propylene rubbers with N<sub>2</sub>H<sub>4</sub> has been reported by TRW (Ref 25). TRW conducted a compounding study for the Air Force to develop a superior rubber for seats in N<sub>2</sub>H<sub>4</sub> thruster valves. This study centered around the use of peroxide-cured ethylene-propylene rubbers reinforced with TRW polyurethane resin, Hyst1. Laboratory tests were used to screen candidate compounds. Prime candidate compounds were evaluated further by long-term tests in hydrazine valves at elevated temperatures. As a result of this work, three compounds were developed with mechanical and chemical properties superior to the Stillman SR724-90 EPR control material. The newly developed materials were shown to be highly compatible with hydrazine. Maintenance of mechanical properties in elevated temperature hydrazine during rapid valve cycling short-term tests and during slower valve cycling long-term tests was considered excellent. The newly developed materials maintained their shape,

thickness and sealing properties after all of the in-valve tests. On the basis of these tests, Compound 102-1, a peroxide-cured composite of EPT, Hyst1, and fumed silica was selected as the prime  $N_2H_4$  valve seat material. The Air Force designation for this compound is AF-E-102.

Due to the success in developing AF-E-102, the Air Force further funded TRW to develop a similar compound (EPT plus Hyst1) for use as a polymeric bladder or diaphragm material (Ref 26). This new material was to demonstrate both lower permeability and  $N_2H_4$  decomposition over state-of-the-art expulsion bladder materials. TRW chose EPT-10 as a reference for comparison. On the basis of compounding studies, TRW chose an EPT/Hyst1 covulcanizate, designated AF-E-332, as their prime candidate. In both static immersion tests and permeability tests, the new compound has showed itself superior to EPT-10.

Just recently, the European Space Research Organization (ESRO) has presented additional non-metal compatibility information with  $N_2H_4$  (Ref 27). Static immersion tests were run at 40, 60, and 80°C to measure both  $N_2H_4$  decomposition and material attack. From the results, Butyl, EPR, and PTFE were considered to have good resistance to  $N_2H_4$  attack and not to cause excessive  $N_2H_4$  decomposition if carbon black is not employed as a filler material.

III. MONOMETHYL HYDRAZINE

## A. COMPATIBILITY SUMMARY

The compatibility of both metals and non-metals with MMH is summarized in Table 4. Specific references used in this determination are listed in the table. Compatibility of a material with MMH was based on the same criteria used for neat  $N_2H_4$ . The ratings for metals are based primarily on the degree to which the material affects the propellant. For non-metals, both the extent that the material affects the propellant and the extent that the propellant affects the material are reflected in the ratings.

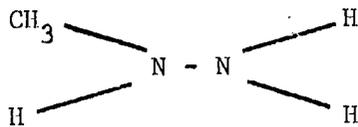
Table 4 MMH Summary Compatibility Chart

Material	Rating					References	Remarks
	1	2	3	4	5		
Metals							
1) Aluminums							
a. Aluminum alloys in general	A, B					28, 29	
b. 1100	A					28	
c. 2014	A					28, 29	
d. 2024	A					29	
e. 2219	A					28	
f. 6061	A					28	
2) Steels							
a. Stainless steels in general		A, B				28, 29, 30	
b. 301 cryoformed		B, C				28, 29, 30, 83	
c. 304		A				28	
d. 316			A			28	
e. 321		A				28	
f. 347		A				28, 29, 30	
g. 17-7 PH or 17-4 PH		A				28	
h. A-286		A				28, 30	
i. Carpenter 20 Cb.		A				28	
j. Ni maraging steels		A				29	
3) Titaniums							
a. Titanium alloys in general	B, C					6, 8, 14, 28, 29	
b. 6Al-4V	A					28, 29	
c. 5Al-2.5Sn	B, C					6, 8, 14, 28, 29	
4) Miscellaneous Metals							
a. Nickel		A	B, C			1, 2, 28, 29, 83, 84	Conflicting data
b. Hastelloy C		A				28	
c. Hastelloy W		A				30	
d. Monel		A	B, C			1, 2, 28, 29, 83, 84	Conflicting data
e. Molybdenum				B, C		28, 29, 83	



## B. GENERAL DISCUSSION

Like its hydrazine sister fuel, monomethylhydrazine ( $\text{CH}_3\text{N}_2\text{H}_3$  or MMH) is a highly reactive and toxic propellant. Its molecular structure is the same as hydrazine's structure except for having a hydrogen atom replaced by a methyl radical, i.e.,



Therefore, it shares many characteristics with  $\text{N}_2\text{H}_4$ . Like hydrazine, MMH is in a constant state of decomposition; but, at ambient temperatures and when not exposed to catalytic materials, the decomposition rate is minimal. Also, metal corrosion is usually not a problem in MMH storage while catalytic decomposition can be. Further, non-metals can be a source of catalytic decomposition as well as being subject to attack.

MMH is generally considered less reactive or more stable than hydrazine; materials showing compatibility with  $\text{N}_2\text{H}_4$  will be either as compatible or more compatible with MMH. Conversely, materials causing catalytic decomposition of MMH would also be catalytic to  $\text{N}_2\text{H}_4$ . However, with non-metals, no such relative ranking of reactivity can be made.

#### 1. Compatibility with Metals

Since MMH has the same nitrogen to nitrogen bond as  $\text{N}_2\text{H}_4$ , it would seem that the metals considered catalytic to  $\text{N}_2\text{H}_4$  would also promote decomposition of MMH. Therefore, metals in the atomic number groups 24 to 29, 42 to 47, and 74 to 79 and alloys of these metals, such as stainless steels, would be expected to be incompatible with MMH, while metals such as titanium, aluminum, and their alloys should be compatible. As with  $\text{N}_2\text{H}_4$ , however, there exists data showing stainless steels and even some nickel alloys to be compatible with MMH.

At Martin Marietta, the applicability of different propulsion system components for use with MMH at sterilization temperatures ( $275^\circ\text{F}$ ) was investigated (Ref 28). Prescreening, screening, and long term (1 year) storage tests were conducted. Small material samples were exposed to MMH at  $275^\circ\text{F}$  for periods

up to 120 hours in the prescreening tests. The metal samples included 6061-T6 and 1100-0 aluminum, 321 and 316 stainless steel, 6Al-4V titanium, pure nickel, and pure lead. Before testing, the samples were cleaned by successive immersions in HCl and HNO<sub>3</sub>/HF and then passivated in a 25/75 mixture of MMH and H<sub>2</sub>O at 275°F for a period of 76 hours. The test containers were fabricated of 304 stainless steel. The results of these tests indicated that all the metals, except 316 stainless steel, were compatible with MMH. No corrosion was observed on any of the samples. The decomposition with 316 stainless steel was attributed to the high molybdenum content of this material.

The screening tests consisted of exposing metal strips to 275°F MMH for periods of 300 and 600 hours in glass containers. All samples were cleaned and passivated before testing using the same method employed for the pre-screening tests. The following metals were tested for 300 hours and were found to be compatible (no corrosion or MMH decomposition observed):

Stainless Steel

304, 321, 347, 17-4 PH, 17-7 PH, A-286, Carpenter 20 Cb

Aluminum

1100-0, 2014-T6, 2219-T87

Hastelloy C

6 Al-4V Titanium

All of these materials plus pure nickel and 6061-T6 aluminum were included in the 600-hr tests. Again, no corrosion or MMH decomposition was observed with any of the metals.

Four 15-in. diameter spherical tanks constructed of 6Al-4V titanium were used in the long term storage tests. A simulated capillary screen trap device was installed inside each tank. This device consisted of a sample of 165 x 800 mesh, 304L stainless steel screen sandwiched by Monel rivets between 0.5-in. thick 304L stock riveted to a 6Al-4V titanium strip which was welded to the tank interior wall. The tanks were cleaned and passivated using the previously described procedure. After filling with MMH to 5% ullage, the tanks were subjected to the six 275°F sterilization cycles and then stored at ambient

temperature for up to one year. Three of the tanks were opened, one every four months for examination. The fourth tank was held as a control specimen. During this 12-month storage, no metal corrosion or MMH decomposition was observed.

Aerojet-General immersed various metal samples in MMH to determine the decomposition effects (Ref 29). Sealed glass-manometer and sealed glass-ampule tests were used. The former method provided continual pressure monitoring, while the latter was designed to permit periodic analyses of both the liquid and gas phases by gas chromatography. The metals evaluated were 347 stainless steel, 2014-T6 and 2024 aluminum, two nickel maraging steels, and 6Al-4V titanium. One of the maraging steels contained 18% nickel and 4% molybdenum and the other contained 20% nickel and 1.5% titanium. To eliminate surface impurities, each metal coupon was sanded with silicon carbide paper (No. 240-A), polished with crocus cloth, washed with detergent, rinsed with water, rinsed with acetone, and dried under an argon atmosphere at 248°F for 6 hours. After complete immersion of the samples in MMH, the glass-manometer tests were run at 77 and 158°F while the glass ampule tests were run at only 158°F.

The 77°F manometer tests lasted approximately 24 weeks. Minor MMH decomposition may have occurred with the maraging steel sample containing molybdenum; however, no reaction was observed with any of the other samples. The tests conducted at 158°F were terminated after approximately 12 weeks. Both of the maraging steel samples showed significant pressure increases with time with only small changes noted with the other materials. The incompatibility of MMH with both of the maraging steel samples was also evident from the chromatographic results. Also, the sample containing molybdenum showed the greatest reactivity.

As the data presented so far indicate, most stainless steels seem compatible with MMH. Adding further support are test results reported by Bell Aerosystems (Ref 30). Bell evaluated the compatibility of stressed stainless steel test specimens with MMH. The first test series consisted of exposing various test bars to liquid MMH while stressed in bending to 25% of yield strength. The bars consisted of A-286 parent metal, A-286 welded to A-286 with Hastelloy W,

A-286 welded to 347 stainless with Hastelloy W, and A-286 welded to 347 by meltdown. To contain the test bars and MMH, 300 series stainless steel test tanks were employed. After stressing the test bars within the storage tanks, the tanks were leak checked, purged with dry  $\text{GN}_2$ , and then filled with MIL-P-27404 MMH using a closed system. The tanks were pressurized with nitrogen to 150 psig and maintained at  $150 \pm 5^\circ\text{F}$ . Pressure and temperature were monitored during testing and the propellant analyzed before and after test. All specimens had been cleaned, passivated, and macroscopically inspected at 60X prior to testing to assure surface integrity. The cleaning and passivation procedure consisted of pickling the samples in nitric-hydrofluoric acid followed by passivation in nitric-dichromic acid. Test specimens were also weighed and dimensionally measured before and after storage. Post storage specimen evaluation consisted of corrosion rate determination, macroscopic evaluation at 60X magnification, metallographic examination up to 500X to determine the extent of any corrosion attack or cracking, plus an evaluation of whether any of the MMH had severely decomposed. After six months of storage, Bell stated that no MMH decomposition or metal corrosion was detected.

The second test series was identical to the first except that three test temperatures (70, 125, and  $150^\circ\text{F}$ ) and three stress levels (0, 40, and 90% of yield strength) were used. Again, after six months of testing, no corrosion or MMH decomposition was reported.

As with hydrazine, the titanium and aluminum alloys appear to be the preferable metals for use with MMH. However, the data from the previously discussed studies also indicate that most stainless steels can be used with MMH if proper surface preparation is provided prior to use. Molybdenum, chromium, iron, nickel, and copper should be considered as questionable.

## 2. Compatibility with Non-Metals

Data on the compatibility of MMH with non-metals is scarce. Based on Aerojet tests reported by CPIA (Ref 31), only high density polyethylene was rated as a good storage material (weight change  $<0.5\%$  and no elasticity change) for MMH service below  $160^\circ\text{F}$  and for exposures less than 4 weeks.

Teflon, natural rubber, silicone rubber and Neoprene were rated as only intermediate storage materials (weight change <2.5% and change of elasticity of 25 to 40%) for the same service. Butyl rubber was considered usable only below 95°F and Kel-F showed poor compatibility.

Although CPIA found no MMH decomposition with the non-metals they reported on, there exists evidence which shows that at least one non-metal considered by CPIA, may increase MMH decomposition rates. In a series of tests conducted by Aerojet (Ref 29), various non-metals were immersed in MMH and UDMH to determine any catalytic effects on fuel decomposition. The tests were run at both room temperature and 158°F for periods up to 3 months. The non-metals tested were Teflon, polyethylene and Kel-F. The results showed that although none of the samples showed excessive fuel decomposition at room temperatures, Kel-F did show excessive fuel decomposition rates at 158°F.

Further tests on the compatibility of MMH with non-metals were conducted at an even higher temperature by Martin Marietta to determine the effects of a sterilizing process on various non-metals when immersed in MMH (Ref 28). Teflon (TFE and FEP), B591-8 butyl rubber, and E515-8 EPR were tested with 275°F MMH for periods up to 88 hours. The Teflon samples gave the best results. For the first 28 hours, the Teflon samples showed no effect. After 88 hours, the TFE samples showed an approximate loss in strength of 2.6% with an increase in elongation of 10%, while the FEP samples had a .7% loss in strength with a 10% increase in elongation. No fuel decomposition was observed. Considerable MMH decomposition was apparent with the butyl rubber samples after the first 24 hours. Also, a 20% volume increase plus a hardness loss of 10-12 Shore A was observed. EPR samples fared better. After the first 24 hours, the MMH became discolored as if exposed to air, indicating decomposition, and lost 5 Shore A in hardness with a 7% volume increase.

From the data presented so far, Teflon seems to be fairly compatible with MMH. However, problems have been encountered when applying Teflon to systems employing MMH. JPL found stress cracking in expulsion bladders made out of a certain type of Teflon laminate (Ref 32). In a series of tests, JPL stretched to failure test specimens of the standard Teflon laminate planned as the bladder material for the Mariner Mars 1971 spacecraft. The specimens were

tested while immersed in various solvents including  $N_2O_4$  and MMH. The standard laminate was composed of an outer "durability" layer of FEP 120 Teflon over an inner "permeability reducing" layer of TFE 30 Teflon. Failure originated in solvent stress cracks resulting from exposure of the low molecular weight FEP 120 to the propellants or referee propellants. To solve the solvent stress cracking problem, FEP 9511 Teflon was substituted for the FEP 120 material. The FEP 9511 with its higher molecular weight is less sensitive to solvents. In addition, the 9511 material was sandwiched between inner and outer layers of a new TFE/FEP codispersion of 80% TFE 30 and 20% FEP 9511. This material showed improved properties for bladder application, produced no solvent stress cracking and was used for the MM '71 flight bladders. More detail concerning the compatibility of this material is contained in Chapter VI. The results obtained with  $N_2O_4$  also apply to MMH.

IV. NITRATED HYDRAZINE

## A. COMPATIBILITY SUMMARY

Table 5 summarizes the compatibility of both metals and non-metals with nitrated  $N_2H_4$  fuels as determined from available data. The specific references employed are indicated. As with both  $N_2H_4$  and MMH, the compatibility of a material with  $N_2H_4 - N_2H_5NO_3$  mixtures was based on the criteria that the material be essentially unaffected by propellant exposure and not cause a significant increase in the rate of propellant decomposition. Inclusion of a material in the table was determined in the same manner as for  $N_2H_4$  and MMH. Dual ratings have been employed as well as ratings for specific applications.

The compatibility ratings presented in Table 5 for both metals and non-metals is a relative measure of the extent that the specific material is affected by the propellant and the extent that the propellant is affected by the material. Both mechanisms are of concern with materials exposed to nitrated hydrazine fuels since both material attack and propellant decomposition can occur.

Table 5 Nitrate<sup>d</sup> N<sub>2</sub>H<sub>4</sub> Fuels Summary Compatibility Chart

Material	Rating					References	Remarks
	1	2	3	4	5		
<u>Metals</u>							
1) Aluminums							
a. Aluminum alloys in general			A, B			13, 15, 35	Rated for less than 24% N <sub>2</sub> H <sub>4</sub> NO <sub>3</sub> . Greater percentages of N <sub>2</sub> H <sub>4</sub> NO <sub>3</sub> form shock sensitive mixtures.
b. 1100			A		15	Corrosion testing is needed	
c. 2024			B		15		
d. 2219			B		15		
e. 6061		A	A		13, 15	Conflicting data	
2) Steels							
a. Stainless steels in general				A, B		2, 15, 16, 34, 35	
b. 301 cryoformed				B		2, 15, 16, 34	
c. 304				B		2, 15, 16, 34	
d. 316				B		2, 15, 16, 34, 35	
e. 321				A		2	
f. 347				A		15	
g. 400 series in general				B		2, 15, 16, 34, 35	
h. Maraging Steels				B		2, 15, 16, 34, 35	
i. Non-stainless steels				B		2, 15, 16, 34	
3) Titaniums							
a. Titanium alloys in general		A, B				13, 15, 35	Corrosion testing is needed
b. 6Al-4V		A				13, 15	
c. 5Al-2.5Sn		A				13	
d. 6Al-6V-2Sn		A				13	

Table 5 (Concluded)

Material	Rating					References	Remarks
	1	2	3	4	5		
4) Miscellaneous Metals							
a. Nickel and its alloys				A, B, C		1, 2, 9, 35, 83, 84	
b. Copper and its alloys				A, C		1, 4, 5, 35, 84	
c. Monel				A, B, C		1, 2, 9, 35, 83, 84	
d. Pure iron				A, B, C		1, 2, 4, 5, 35, 84	
Non-Metals							Rated for general service.
1) Polymers							
a. Teflon		A		A		35	
b. Kel-F				A		35	
c. Nylon				A		35	
d. Polyethylene				A		35	
e. Natural Rubbers						15	
f. Butyl Rubbers			A				
g. EPR's in general w/o carbon black		A				15	
h. EPR's in general w/carbon black		A		C		20, 21, 23	
i. Buna N						35	
j. Saran				A		35	
k. Mylar				A, C		4, 5, 35	
2) Other Non-Metals in general			A			35	
1 - Compatible	A - Rating based on data on the specific material with the specific propellant						
2 - Probable Compatibility	B - Rating based on data on a similar or sister material with the specific propellant						
3 - Doubtful Compatibility	C - Rating based on data on the specific material but with a sister propellant						
4 - Incompatible	D - No specific data						
5 - Unable to Rate							

## B. GENERAL DISCUSSION

One method of increasing the reactivity of neat  $N_2H_4$  is by the addition of hydrazine nitrate ( $N_2H_5NO_3$ ). This higher reactivity, although advantageous to increased engine performance, creates greater storage problems than those associated with neat  $N_2H_4$  alone. As stated earlier, neat hydrazine exists in a continuous state of decomposition. The addition of hydrazine nitrate increases — this instability or tendency for decomposition. Therefore, materials which have only slight or negligible catalytic effect on the decomposition of neat  $N_2H_4$  can become active catalysts with nitrated hydrazine. Also, the addition of the nitrate produces an acidic solution which is corrosive to metals. At least one report has noted severe corrosion of stainless steels when immersed in nitrated hydrazine. Therefore, for long term storage of hydrazine-hydrazine nitrate mixtures with both metals and non-metals, both propellant decomposition and material corrosion become concerns.

In addition to the above mentioned problems, Garrett AiResearch reported that certain nitrated hydrazine mixtures exhibit shock sensitive characteristics (Ref 33). Mixtures containing more than 23%  $N_2H_5NO_3$  are considered shock sensitive. They further add that even mixtures containing lower than 23% nitrate must be treated with extreme care since the decomposition of these mixtures is very energetic, releasing large amounts of heat. However, shock sensitivity tests conducted by JPL showed that the upper limit of  $N_2H_5NO_3$  which can be added to neat  $N_2H_4$  without creating a shock sensitive mixture is 24% (Ref 34).

### 1. Compatibility with Metals

Most metals considered as catalysts with  $N_2H_4$  would probably be unsuitable for long term service with nitrated hydrazine mixtures due to their increased reactivity compared to neat  $N_2H_4$ . Data supporting this contention, has been reported by Rocketdyne (Ref 2 ). As part of the  $N_2H_4$  tests previously discussed in Chapter II, Rocketdyne doped neat  $N_2H_4$  with 1% ammonium nitrate ( $NH_4NO_3$ ) to determine the effect this would have on the decomposition of hydrazine. The addition of  $NH_4NO_3$  was felt by Rocketdyne to be equivalent to adding  $N_2H_5NO_3$  to the hydrazine since the ammonium nitrate reacts with hydrazine

to produce hydrazine nitrate and ammonia. The decomposition of the resulting solution was compared against that of neat  $N_2H_4$  in Pyrex containers at a temperature of  $262^\circ F$ . Also compared were the decomposition rates of the neat  $N_2H_4$  and the doped  $N_2H_4$  when in contact with 321 stainless steel specimens. It was found that the addition of hydrazine nitrate did not increase decomposition rate in the glass containers. However, in the presence of the 321 stainless samples, the decomposition rates of hydrazine containing hydrazine nitrate were approximately 100 times those of the neat hydrazine after six hours.

In addition to the above data showing stainless steels to be very active decomposition catalysts for mixtures of  $N_2H_4$  and  $N_2H_5NO_3$ , evidence also shows that these mixtures are corrosive to stainless steels. JPL has found that stainless steels not only cause severe decomposition of  $N_2H_4/N_2H_5NO_3$  mixtures but also are severely corroded by these mixtures (Ref 16). Specifically, Vango has observed that the  $N_2H_4/N_2H_5NO_3$  mixtures almost immediately turn pink when stainless steel test specimens are introduced (Ref 16). This is indicative of metal ions being released into solution, i.e., metal corrosion. In clarifying this corrosion phenomena, Toth stated that the degree of stainless steel corrosion observed seems to be proportional to the concentration of  $N_2H_5NO_3$  in the mixture (Ref 34).

Why hydrazine containing  $N_2H_5NO_3$  should become corrosive to metals can be explained by considering the chemistry involved when this soluble salt is added to  $N_2H_4$ . Neat hydrazine by itself is considered a weak base and thus not corrosive to metals. However, by the addition of soluble salts to neat  $N_2H_4$ , the resultant mixture can be either more basic or acidic, depending on the nature of the salt. In general, the addition of a salt formed from a strong base and a weak acid results in a basic solution. Conversely, if a salt formed from a weak base and a strong acid are added to a pure liquid, the resultant solution will be acidic. Applying this guide to neat  $N_2H_4$ , the observed corrosion reported with either doped or contaminated  $N_2H_4$  can be explained.

The TRW and Rocket Research tests showed that when  $CO_2$  reacts with  $N_2H_4$  a hydrazine soluble salt  $[H_3N_2CO_2(N_2H_5)]$  is formed (Ref 10 and 11). This

salt is a product of carbazic acid ( $\text{H}_3\text{N}_2\text{CO}_2\text{H}$ ) and the weak base, hydrazine. Therefore, the resultant solution of this salt and  $\text{N}_2\text{H}_4$  would be slightly acidic and somewhat corrosive to metals. As the TRW and Rocket Research test results showed, stainless steels were corroded by this solution. SRI showed that  $\text{Cl}_2$  reacts with  $\text{N}_2\text{H}_4$  to form  $\text{N}_2\text{H}_5\text{Cl}$ . This salt is formed from the strong acid,  $\text{HCl}$ , and the weak base,  $\text{N}_2\text{H}_4$ . Thus, the resulting solution is acidic and corrosive to metals (Ref 12).

Based upon the above considerations, a solution of  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{H}_5\text{NO}_3$  should be acidic and corrosive to most metals, including stainless steels, since  $\text{N}_2\text{H}_5\text{NO}_3$  is formed from a strong acid,  $\text{HNO}_3$ , and a weak base,  $\text{N}_2\text{H}_4$ .

As part of the long term  $\text{N}_2\text{H}_4$  compatibility tests analyzed by SRI for JPL (previously discussed in Chapter II), SRI also analyzed JPL tests conducted to determine the compatibility of different titanium and aluminum alloys with nitrated hydrazine monopropellant fuel containing 75%  $\text{N}_2\text{H}_4$ , 24%  $\text{N}_2\text{H}_5\text{NO}_3$ , and 1%  $\text{H}_2\text{O}$  (Ref 13). The test procedures and techniques used were identical to those described earlier. Test metals were 6061-T6 aluminum and 6Al-4V, 5Al-2.5Sn, and 6Al-6V-2Sn titanium alloys. The samples were first subjected to a cleaning and pickling type passivation process consisting of a detergent rinse followed by a pickling solution of  $\text{HF}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ . One 6061-T6 aluminum sample was passivated with  $\text{NaOH}$  instead of the acid solution. The samples were dried with  $\text{N}_2$ . Testing was conducted in glass capsules cleaned in accordance with JPL specification GMZ-50521-GEN-A. Some of the glass test capsules contained specimens of two different metals.

SRI concluded that 6061-T6 aluminum was probably compatible with the nitrated hydrazine as were the titanium alloys. They found that some corrosion such as etching and pitting was evident with some of the samples in both alloy groups; however, these samples were in poor condition (spotted or stained) before storage. Upon assessment of the results presented by SRI, it is concluded that all of the materials tested should really be rated as compatible.

In addition to using neat  $\text{N}_2\text{H}_4$  in their radiation exposure tests, reported in Chapter II, Battelle also ran the same tests with the nitrated hydrazine monopropellant (Ref 15). For the tests run in the small storage capsules,

Battelle again found that the exposure to radiation greatly increased decomposition. However, for both the irradiated and non-irradiated samples, the decomposition rates of the nitrated hydrazine were far in excess of those for the neat  $N_2H_4$ . Also, the 347 stainless steel capsules had a rate approximately twice those of the other capsules (1100-0 Al, 6061-T6 Al, and 6Al-4V Ti) for the irradiated tests and about 6 to 7 times those of the other capsules for the non-irradiated tests. Battelle also found, upon opening the test capsules after storage, that the nitrated  $N_2H_4$  had turned a dark red-violet color in the 347 stainless capsule and that a brownish film had formed on the metal surface. For the 6Al-4V titanium capsule, no change in either propellant or capsule surface was observed; for the aluminum capsules, etching by the nitrated  $N_2H_4$  was found.

Based on the available data, the alloys of aluminum and titanium are the best materials for long term service with nitrated hydrazine mixtures. However, in view of corrosion considerations stated earlier, even these metals may not be applicable for use with nitrated hydrazine mixtures. It can be concluded, though, that all ferric metals including stainless steels are totally unacceptable with nitrated hydrazine.

## 2. Compatibility with Non-Metals

Data on the compatibility of non-metals with nitrated hydrazine mixtures are very limited. A compilation and an evaluation of experimental data obtained from available literature were presented by JPL on the compatibility of materials with mixtures of hydrazine, hydrazine nitrate, and water (Ref 35). Polyethylene, Teflon, and glass were evaluated as acceptable for general service. Based on the test results presented, it appears that Buna N rubber would also be acceptable.

As part of the previously discussed radiation exposure tests conducted by Battelle, the functional operation of spacecraft components was conducted in nitrated hydrazine monopropellant containing 75%  $N_2H_4$ , 24%  $N_2H_5NO_3$ , and 1%  $H_2O$  (Ref 15). One such component was a 347 stainless filter containing an EPR O-ring seal. The nitrated hydrazine was flowed through the filter which was

irradiated by Cobalt 60 gamma radiation. Visual examination after testing showed that the O-ring seal was affected by the exposure. Because of this result, Battelle conducted additional tests to investigate the compatibility of both EPR and Butyl O-rings with the nitrated propellant in and out of the radiation field. They found that the Butyl O-rings softened, distorted, and reacted with the propellant, while the ethylene-propylene O-ring distorted only in the radiation field to conform to its retaining cavity and did not return to its original shape. However, the EPR O-ring did not appear to soften or react with the propellant.

As part of these new additional tests, the effects of radiation, propellant, and stress on EPR flat stock were also evaluated in an effort to differentiate these factors in the operation of EPR seals or diaphragms. Flat and folded specimens were exposed to radiation and to room storage in and out of the propellant. No measurable effects were observed on either the flat or folded specimens in room storage. However, all folded specimens took a permanent set when exposed to a gamma radiation dose of 33.4 megarads and slight welding occurred where the folds contacted.

From the limited available information, it would seem that only Teflon, polyethylene, and EPR and Buna N rubbers are applicable for use with nitrated hydrazine propellants. In actual practice, however, use of an all metal system appears advisable with these mixtures.

V. DIBORANE

## A. COMPATIBILITY SUMMARY

The compatibility of both metals and non-metals with  $B_2H_6$  is summarized in Table 6. The ratings are based on the information presented in the specific references cited. Compatibility of a material with  $B_2H_6$  was based on negligible material change (corrosion for metals, loss of physical properties for non-metals) and no significant increase in the rate of decomposition of the  $B_2H_6$ . When ratings have been determined for specific applications, this is indicated in the remarks section of the table.

In comparison to other fuels, diborane appears relatively easy to store from a materials standpoint. Decomposition is primarily based on thermal considerations. Therefore, the ratings presented in Table 6 reflect the degree to which the propellant affects the material.

Table 6 B<sub>2</sub>H<sub>6</sub> Summary Compatibility Chart

Material	Rating					References	Remarks
	1	2	3	4	5		
Metals							
1) Aluminums							
a. Aluminum alloys in general	A, B, C					38	
b. 1100	B					38	
c. 2024	B, C					38	
d. 2219	B					38	
e. 6061	A					38	
f. 356	A					38	
2) Steels							
a. Stainless steels in general	A, B					38	
b. 301 Cryoformed	B					38	
c. 304	A					38	
d. 316	B					38	
e. 321	B					38	
f. 347	A					38	
g. 18-8 PH	A					38	
h. Low carbon steel	A					38	
i. Maraging steels	A					38	
3) Titaniums							
a. Titanium alloys in general	A, B, C					38	
b. 6Al-4V	A					38	
c. 5Al-2.5Sn	B, C					38	
							Rocketdyne stated that some researchers had found this alloy to be incompatible with boron hydrides.

Table 6 (Continued)

Material	Rating					References	Remarks
	1	2	3	4	5		
4) Miscellaneous Metals							
a. Monel	A					38	
b. Nickel alloys	A					38	
c. Copper	A					38	
d. Hastelloy	C					38	
e. Brass	A					38	
f. Magnesium alloys		A				38	Rocketdyne states that one researcher has found magnesium to be incompatible
g. Tin			A			37	
h. Platinum		A				37	
i. Chromium		A				37	
Non-Metals							
1) Polymers							
a. Saran		A				38	Rated for general use except as noted. Temperature effects not considered.
b. Kel-F or equivalent CTFE		A				38	
c. Teflon or equivalent TFE		A				38	
d. 50/50 polyethylene/polyisobutylene		A					
e. Polyethylene		A				38	
f. Viton		A				36	
g. Mylar		A				38	
h. Nylon		A				38	
i. Natural rubbers		A				38	
j. Neoprene				A		38	
k. Nordel 1145 EPT				A		38	
l. W-970 silicon elastomer				A		38	
m. CIS-4 polybutadiene elastomer				A		38	
n. Hycar 1072 Nitrile		A				38	



Table 6 (Concluded)

Material	Rating					References	Remarks
	1	2	3	4	5		
1) Polymeric (Cont'd) o. TRW compound 215-3		Ac		Ad		40	c. for general use d. for expulsion device use
p. Silicone rubber				A		38,41	
2) Lubricants a. Fluorolube FS		A				38	
b. Dow-Corning low temp. silicone grease		A				38	
c. Ordinary oil & grease				A		38	
d. Graphite	A					38	
e. Paraffin		A				38	
f. Vaseline		A				38	
g. Perfluorocarbon lubricants		A				38	
h. Silicone greases in general		A				38	
3) Miscellaneous Non-Metals a. Asbestos	A					38	
b. Permatex				A		38	
c. Metal Oxides in general				A		38	
d. Carbon		B				38	
e. Silica (SiO <sub>2</sub> )	A					38	
1 - Compatible	A - Rating based on data on the specific material with the						
2 - Probable Compatibility	specific propellant						
3 - Doubtful Compatibility	B - Rating based on data on a similar or sister material with						
4 - Incompatible	the specific propellant						
5 - Unable to Rate	C - Rating based on data on the specific material but with a sister propellant						
	D - No specific data						

## B. GENERAL DISCUSSION

Diborane is considered a highly reactive and toxic space storable propellant. Although its heat of formation is positive, it does not exhibit any decomposition problems when stored at temperatures below  $-112^{\circ}\text{F}$ . As storage temperatures are increased above  $-112^{\circ}\text{F}$ , however,  $\text{B}_2\text{H}_6$  no longer remains stable and storage problems arise due to thermal decomposition. According to Callery Chemical (Ref 36), thermal decomposition of  $\text{B}_2\text{H}_6$  is not in itself a serious storage problem unless storage temperatures are raised above  $-20^{\circ}\text{C}$  ( $-4^{\circ}\text{F}$ ). Callery gives decomposition rates of only 0.2% per year for  $\text{B}_2\text{H}_6$  stored at  $-4^{\circ}\text{F}$ , while for storage temperatures of  $77^{\circ}\text{F}$ , they report decomposition rates in the order of 10% per month.

In investigating propellant clogging of propulsion systems, TRW investigated flow blockage problems in  $\text{B}_2\text{H}_6$  systems due to the formation of decomposition products (Ref 10). According to TRW,  $\text{B}_2\text{H}_6$  decomposes slightly when storage temperatures are raised above dry ice temperature ( $-78^{\circ}\text{C}$  or  $-112^{\circ}\text{F}$ ). The products are higher molecular weight boranes (tetraborane, pentaborane, hexaborane, etc.), polymeric boron hydrides  $(\text{BH})_x$ , and hydrogen:  $\text{B}_2\text{H}_6 \rightarrow \text{B}_4\text{H}_{10} + \text{B}_5\text{H}_9 + \text{B}_{10}\text{H}_{14} + (\text{BH})_x + \text{H}_2$ . Although the  $\text{H}_2$  does not present a storage problem, the other products can. Both the higher weight boranes and the polymeric boron hydrides will exist to some extent as dissolved impurities which could perturb  $\text{B}_2\text{H}_6$  flow properties. Because of increased decomposition above  $-4^{\circ}\text{F}$ , the possibility of flow blockage problems would be even further increased.

It seems from the above evidence that storage of liquid  $\text{B}_2\text{H}_6$  above  $-112^{\circ}\text{F}$  could present problems. For most rocket propellant applications, however, the storage temperatures of  $\text{B}_2\text{H}_6$  are generally below  $-160^{\circ}\text{F}$ . Therefore, for long term storage of  $\text{B}_2\text{H}_6$  below  $-160^{\circ}\text{F}$ , the major problem is not one of thermal decomposition but one of either material attack or catalytic decomposition.

When considering compatibility problems like material attack (corrosion of metals or dissolving or physical property changes of non-metals), the diborane sister fuel, pentaborane ( $\text{B}_5\text{H}_9$ ), is of interest. Pentaborane, like diborane is also a highly reactive and toxic propellant. According to Callery Chemical and TRW,  $\text{B}_2\text{H}_6$  and  $\text{B}_5\text{H}_9$  behave almost identically in regard to material

attack on either metals or non-metals (Ref 37 and 4 ). In fact, Callery states than any material compatible with  $B_5H_9$  should be as compatible or even more compatible with diborane. However, this general guide of using  $B_5H_9$  data to predict  $B_2H_6$  compatibility evidently does not apply for non-metals. Rocketdyne rated many non-metals such as Mylar, Nylon, and Saran as being compatible with  $B_2H_6$ , but they also showed that these same non-metals had been found unsatisfactory for use with  $B_5H_9$  (Ref38 ).

#### 1. Compatibility with Metals

Information on the compatibility of metals with  $B_2H_6$  is limited. In addition, most of this information consists of only material recommendations, based either on practical handling experiences or on other author's recommendations. Very few laboratory studies have been performed. The most recent information available on the compatibility of metals with  $B_2H_6$  is presented in the Rocketdyne "Diborane Handbook" which presents a compilation of the available compatibility data (through 1969) and recommendations based on this data (Ref 38).

In short term storage tests to determine metal corrosion by  $B_2H_6$  or  $B_2H_6$  decomposition by metals, TRW (as reported by Rocketdyne) exposed various metal alloys and stainless steel oxides to both liquid and gaseous  $B_2H_6$ . For the metal alloys storage tests, liquid  $B_2H_6$  was stored in contact with 6061-T6 aluminum, 347 stainless steel, and 6Al-4V titanium specimens contained in cylinders fabricated from the respective metals. After 45 days of storage at  $-108^\circ F$ , analysis of the liquid and vapor phases by mass spectroscopy showed minimal decomposition. Examination of the metal specimens showed minimal (almost no) corrosions with the following order: 347 stainless steel < 6Al-4V titanium < 6061-T6 aluminum.

For the stainless steel oxide storage tests, oxide particles smaller than 325 mesh were prepared by burning 304 SS shim stock in gaseous oxygen. The oxide was exposed to both gaseous and liquid  $B_2H_6$  in 347 stainless steel containers for a period of 30 days at  $-108^\circ F$  and at  $-4^\circ F$ . TRW concluded that very little  $B_2H_6$  decomposition took place since no higher boron hydrides were found after storage. However, examination indicated that some of the metal

oxides had been reduced to pure metal. Rocketdyne felt that this could present a potential problem (cold-welding) with rubbing or sliding surfaces exposed to  $B_2H_6$  unless these metal surfaces are deoxidized prior to exposure.

In another series of tests reported by Rocketdyne, Thiokol-RMD measured the decomposition of  $B_2H_6$  stored in stainless steel cylinders at various temperatures. In one test, liquid  $B_2H_6$  was stored in a stainless steel cylinder at  $32^\circ F$  for a period of 197 days with no pressure rise observed. In another test,  $B_2H_6$  gas was stored for 3 months in a stainless steel cylinder at  $32^\circ F$ . This time an 11-psi pressure increase (318 to 330 psia) occurred. However, the validity of these results were questioned because the pressure measurement system had been exposed to ambient temperatures. In a third test, gaseous  $B_2H_6$  was stored in a stainless steel cylinder at  $77^\circ F$  for 4 months. In this case, a 480-psi pressure rise occurred. At the end of the test period, chemical analysis of the cylinder contents showed only 50 to 60% of the original  $B_2H_6$  remaining (between 40 and 50% decomposition). Remembering the fact that  $B_2H_6$  can decompose as much as 10% per month at  $77^\circ F$  as stated earlier, this decomposition is probably due to temperature rather than catalytic effects.

On the basis of these results and the other information compiled, Rocketdyne rated the following metals compatible (no corrosion or catalytic decomposition) with either liquid or gaseous  $B_2H_6$ :

Aluminum	Brass
Low Carbon Steel	Copper
Chrome-Moly Steel	Lead
18-8 Stainless Steel	Monel and K-Monel
300 Series Stainless Steel	Nickel
6Al-4V Titanium	Soft solder

It was recommended that maraging steel and magnesium not be used with  $B_2H_6$  and that metal oxides be minimized. As stated earlier,  $B_5H_9$  compatibility data is of value as a general guide to determining which metals might be suitable for service with  $B_2H_6$ . However, no metal was classified incompatible with  $B_5H_9$ .

In a report on the treatment of metal surfaces for use with space storable propellants, SRI hypothesized that embrittlement and moisture problems may exist with  $B_2H_6$  storage (Ref 39). Since hydrogen may be liberated by  $B_2H_6$  decomposition, titanium embrittlement problems might occur. Since  $B_2H_6$  is easily hydrolyzed by water to form both hydrogen and boric acid, moisture should be precluded from  $B_2H_6$  systems. The hydrogen, in titanium systems, is not wanted because of embrittlement problems. The boric acid, although not considered very reactive, could turn into an acid sludge (according to SRI) which is a particularly effective clogging agent. It should be noted, however, that no titanium embrittlement problems due to  $B_2H_6$  storage have been encountered.

Tin is not recommended for  $B_2H_6$  systems. Houghof Callery Chemical stated that tin might react with  $B_2H_6$  to form volatile tin hydrides (Ref 37). Although the possibility of this reaction is better at high temperatures, there is a rare possibility of this happening in liquid  $B_2H_6$ . Hough also stated that, based on his experience at Callery, metals like chromium and platinum are compatible with  $B_2H_6$ .

In conclusion, there would seem to be no major problems in storing liquid  $B_2H_6$  with any metal as long as the storage temperatures are below  $-112^{\circ}F$  and moisture is precluded. However, the normal approaches employed in the design of low-temperature systems should be followed.

## 2. Compatibility with Non-Metals

As was the case with metals, very little information is available on the compatibility of non-metals with  $B_2H_6$ . The most recent collection of information on non-metal compatibility also exists in the Rocketdyne "Diborane Handbook" which was used as the prime source of information (Ref 38).

In tests reported by Rocketdyne, Thiokol-RMD exposed various plastics and lubricants to gaseous  $B_2H_6$  at  $75^{\circ}F$  for a period of 24 hours to 96 hours, depending on the non-metal tested. Glass capsules were used to hold both the  $B_2H_6$  and samples. No effect was observed on Saran, Kel-F, and 50/50 polyethylene/polyisobutylene and only a slight effect was observed with a Dow-Corning low temperature silicone grease and with Fluorolube FS. On the basis of these results, RMD felt that  $B_2H_6$  will be compatible with organic substances which have no functional groups or are completely saturated.

Further test data is reported by Rocketdyne. In studies carried out by Aerojet-General, Nylon and Kel-F seals were irradiated in test fixtures containing liquid  $B_2H_6$  at  $-108^\circ F$  (Ref 38). Based on the test results, it was concluded that both seals were compatible under the test conditions.

Rocketdyne also summarized tests run by TRW to evaluate elastomers with both gaseous and liquid  $B_2H_6$  (Ref 38). These TRW tests were conducted for JPL to identify and characterize elastomers suitable for use as  $B_2H_6$  expulsion bladders. In the first test series, three unfilled cured elastomers were exposed to  $B_2H_6$ . The elastomers were peroxide-cured Nordel 1145 EPT (DuPont), zinc oxide and peroxide cured Hycar 1072 Nitrile (Goodrich Chemical Company), and peroxide cured W-970 Silicon (Union Carbide). Test temperatures were  $-109^\circ F$  ( $B_2H_6$  liquid) and  $32^\circ F$  ( $B_2H_6$  gas). Based on the results, the Nordel 1145 EPT was eliminated from further testing. In the second test series, W-970 Silicone and Hycar 1072, filled or reinforced with Silica were exposed to liquid  $B_2H_6$ . Also included was CIS-4 1203 polybutadiene filled with  $SiO_2$ . Only the Hycar 1072 appeared compatible. Permeability tests were then conducted with both filled and unfilled Hycar 1072 Nitrile using either helium or diborane gas. Both the filled and unfilled Hycar 1072 seemed acceptable.

On the basis of the above results and other compiled information, Rocketdyne rated the following non-metals as compatible with either liquid or gaseous  $B_2H_6$  (temperature effects not considered):

General Non-Metals

Saran

Viton A, Fluorel, or equivalent asbestos graphite (Garlock or equivalent)

Tetrafluoroethylene (TFE, Halon TFE, Teflon, or equivalent)

Polychlorotrifluoroethylene (Kel-F, Halon CTF, or equivalent)

50/50 polyethylene/polyisobutylene

Polyethylene

C2

Mylar

Hycar rubber

Hycar 1072 butadiene/acrylonitrile elastomer, unfilled and  $\text{SiO}_2$ -filled

Pure dry asbestos or tetrafluoroethylene-impregnated asbestos

JM-76

Nylon

Glyptal

Crane lead seal

Shellac-graphite paste

#### Lubricants

Perfluorocarbon lubricants

Fluorolube FS

Vaseline

Paraffin

Graphite

High vacuum silicone grease

DC 33 silicone grease

"T-film" (Eco Engineering)

The following non-metals were considered incompatible with  $\text{B}_2\text{H}_6$ :

Natural rubbers

Neoprene

Leak-lock

Permatex

Ordinary oil and grease

Nordel 1145 EPT elastomer, unfilled and  $\text{SiO}_2$ -filled

W-970 silicon elastomer, unfilled and  $\text{SiO}_2$ -filled

CIS-4 polybutadiene elastomer, unfilled and  $\text{SiO}_2$ -filled

The compatible rating listed for the Hycar 1072 Nitrile elastomer was based on the previously discussed TRW results. Since this prior study, TRW conducted an additional program to develop a polymer for use in a  $\text{B}_2\text{H}_6$  expulsion bladder (Ref 40).

The Hycar 1072 had been shown to be compatible with  $B_2H_6$  while the CIS-4 polybutadiene was not. However, the Hycar 1072 became stiff and non-elastomeric at low temperature while the CIS-4 did not. Since a homopolymer of butadiene is analogous to a nitrile polymer with 0% acrylonitrile (ACN) and Hycar 1072 contains between 25-30% ACN, TRW concluded that the ACN stabilized the Hycar 1072 against any attack by  $B_2H_6$  but was also the agent responsible for the low temperature embrittlement. Therefore, TRW sought to find a nitrile polymer with the right percent of ACN so that an elastomeric bladder material with the proper properties for  $B_2H_6$  service could be developed. The result was a silica-reinforced, sulfur-cured butadiene copolymer having low acrylonitrile content. This material was termed compound 215-3.

A series of tests was conducted with the material to determine its applicability with  $B_2H_6$ . These included dynamic compatibility, expulsion, storage, and permeability tests. Specimens stressed to failure while immersed in 70°F propellant produced no evidence of chemical reaction. In small scale  $B_2H_6$  expulsion tests at approximately -49°F, the compound 215-3 was not stiffened and showed no evidence of chemical attack. Specimens stored with  $B_2H_6$  at -4°F for 48 days showed a slow attack of the base polymer. This appeared to be a surface phenomenon and was attributed to the sulfur curing agent since a similar compound cured with peroxide showed excellent compatibility. Based on the degradation data and measured permeability, a loss in strength of 23% per year and a propellant loss of 10.4% per year were calculated for a 10-inch diameter compound 215-3 bladder containing  $B_2H_6$  at -4°F. Based on these results, it appears that various butadiene copolymers should be compatible with  $B_2H_6$ . However, the exact composition for best performance appears highly dependent on the application and service conditions and exposure duration.

An independent evaluation of silicone rubber with  $B_2H_6$  was made at the University of Utah which agreed with the incompatible rating resulting from TRW tests. After exposure to  $B_2H_6$  at 250°F for 4000 seconds, excessive fuel decomposition was shown in comparison to a  $B_2H_6$  control sample (Ref 41).

VI. NITROGEN TETROXIDE

## A. COMPATIBILITY SUMMARY

The compatibility of both metals and non-metals with  $N_2O_4$  is summarized in Table 7, as determined by interpreting available compatibility information. Specific references used are listed in the table. Compatibility of a material with  $N_2O_4$  was based primarily on the criteria that the material be essentially unaffected by  $N_2O_4$  exposure (negligible corrosion for metals and negligible loss of physical properties for non-metals). However, also taken into consideration was the potential for formation of clogging agents when exposed to  $N_2O_4$ . This was a prime consideration for iron-based metals since the data indicate serious flow decay problems can occur with  $N_2O_4$ /ferric metal systems. As for the other propellants, listing of a material in the table was based, in general, on the existence of specific compatibility data for that material with  $N_2O_4$ ; some materials were included due to their importance even though no specific data were available. In some instances, two compatibility ratings were assigned to the same material due to conflicting data. Also, where compatibility was determined for a specific form of  $N_2O_4$  or for a specific use with  $N_2O_4$ , this is indicated in the remarks section of the table.

The ratings presented in Table 7 primarily are based on the extent to which the propellant affects the material. However, consideration is given to the material affecting the propellant in those cases where the potential for forming metal adducts, or clogging agents, exists.

Table 7 N<sub>2</sub>O<sub>4</sub> Summary Compatibility Chart

Materials	Rating					References	Remarks
	1	2	3	4	5		
<u>Metals</u>							
1) Aluminums							
a. Aluminum alloys in general		A, B				5, 28, 42, 43, 44, 45, 48, 50 51, 52, 53, 54, 57, 58	H <sub>2</sub> O content must be limited. Ratings based on dry N <sub>2</sub> O <sub>4</sub> (<0.1% H <sub>2</sub> O). Also flow decay problems may exist. Use of high temperatures (>160°F) is also not recommended.
b. 1100		A				5, 28, 44	
c. 2014		A				28, 44, 45, 53, 57, 58	
d. 2021			A			54	
e. 2024		A				43, 53, 58	
f. 2219		A				28, 44, 53, 54	
g. 3003	A					5, 43, 58	
h. 5052	A					5, 43, 58	
i. 6061		A		A		5, 28, 44, 48, 53, 58	Conflicting data
j. 7075		A				5, 43, 44, 53	
k. 356		A				5, 44, 52	
l. Anodized aluminum alloys	A, B					58	
2) Steels							
a. Steels in general			A, B			28, 30, 46, 48, 49, 50, 52, 53, 54, 58	Practically all steels are incompatible at high temperatures (>200°F). Severe iron adduct problems are usually encountered. H <sub>2</sub> O also increases corrosion.
b. Stainless steels in general			A, B			Same as above.	Earlier summaries listed stainless steels as compatible. However, later studies indicate doubtful compatibility due to iron adduct problem, except as noted.

Table 7 (Continued)

Materials	Rating					References	Remarks
	1	2	3	4	5		
2) Steels (Cont'd)							
c. 300 series in general			A, B			28, 46, 48, 49, 50, 58	
d. 301 cryoformed			A, B			28, 30, 46, 48, 49, 50	
e. 304			A, B			28, 30, 48, 49, 50	
f. 316			A, B			28, 48, 49, 50	
g. 321			A, B			28, 48, 49, 50	
h. 347			A, B			28, 30, 48, 49, 50	
i. 400 series in general							
j. 410		A, B				42, 52, 58	
k. 416		A				52, 54	
l. 430		A				52	
m. 440C		A				52, 58	
n. A-286		A	A			52	Conflicting data
o. AM350 or AM355			A			28, 30	
p. 17-4PH or 17-7PH			B			28, 48, 49	
q. 1018 or 1020 steels			A			28	
r. 19-9DL			A, B			48, 49, 53	
s. Maraging steels						52	
t. Carpenter 20Cb		A				28	
u. HY-140 steel		A				28	
3) Titaniums						58	
a. Titanium alloys in general	A, B					5, 28, 42, 44, 48, 55, 56, 57, 58	Some shock sensitivity reported
b. 6Al-4V	A					5, 28, 44, 48, 57	All titanium alloys subject to stress corrosion in Mil Spec N <sub>2</sub> O <sub>4</sub> . Ratings based only on NASA Spec. N <sub>2</sub> O <sub>4</sub> .
c. 5Al-2.5Sn	A					58	
d. 75A	A					5	
e. 65A	A	A				5	
f. B120VCA	A					44	
g. Pure	A					28	
h. 8Al-1Mo	A					58	

Table 7 (Continued)

Materials	Rating					References	Remarks
	1	2	3	4	5		
4) Miscellaneous Metals							
a. Beryllium	A					58	
b. Columbium	A					58	
c. Tantalum	A					5, 58	
d. Tungsten	A					58	
e. TZM-alloy			A			58	
f. L-605 Cobalt Alloy			A			58	
g. Nickel (pure)				A		28	
h. Magnesium alloys				A		43, 52	
i. Zinc				A		5	
j. Copper				A		5, 43	
k. Brass				A		5	
l. Bronze				A		5	
m. Tin				A		5	
n. Inconel		A				28, 43, 58	Conflicting data
o. Pure Molybdenum		A		A		52	
p. Hastelloy alloys				A		28, 30, 52	
q. Kovar metal				A		52	
r. Pure lead				A		28	
s. Monel				B		28, 58	
t. Gold		A				5	
u. Platinum		A				5	
v. Silver				A		5	
w. Zirconium				A		5	
x. Pure iron				B		28, 48, 49, 50, 58	
y. Chromium				A		58	
<u>Non-Metals</u>							
1) Polymers							
a. FEP Teflon		A				4, 5, 28, 32, 42, 43, 44	Rated for general use (no specific application except as noted) Teflon is highly permeable. FEP 9511 probable, FEP 120 doubtful Teflon is highly permeable.
b. TFE Teflon		A				4, 5, 28, 32, 42, 43, 44, 59	Teflon is highly permeable.

Table 7 (Continued)

Materials	Rating					References	Remarks
	1	2	3	4	5		
1) Polymers (Cont'd)							
c. Kel-F				A		4, 5, 42, 43, 44	
d. Polyethylene				A		4, 5, 42, 43, 44	
e. Polypropylene				A		4, 5, 43	
f. Nylon				A		4, 5, 43	
g. Mylar				A		4, 5, 43	
h. Saran		A				4, 5, 43	
i. Kynar				A		4, 5, 43, 44	
j. Lexan				A		4, 5, 43	
k. Plexiglas				A		4, 5, 43	
l. Isobutylene copolymers				A		4, 5, 43	
m. EPR rubbers				A		4, 5, 28, 43, 44	
n. Butyl rubbers				A		4, 5, 28, 43, 44	
o. Fluoro-rubbers				A		4, 5, 43	
p. Silicone rubbers				A		4, 5, 43, 44	
q. Buna N				A		4, 5, 43	
r. Neoprene				A		4, 5, 43	
s. Natural rubbers				A		4, 5, 43	
t. Polyurethanes				A		4, 5, 43, 44	
u. Rulon (PTFE)		A				4, 5, 43	
v. Fluon-fluorinated hydrocarbon		A				52	
w. Carboxy nitroso rubber (CNR)		A				59	
2) Lubricants						26, 60	
a. Graphite		A				4, 5, 43	
b. Fluorolube		A				4, 5, 43	
c. Halocarbon grease				A		4, 5, 43	
d. Kel-F grease			A			52	
e. LOX safe		A				4, 5, 43	
f. Molykote Z		A				4, 5, 43	

Table 7 (Concluded)

Materials	Rating					References	Remarks
	1	2	3	4	5		
3) Miscellaneous Non-Metals							
a. Epon resins				A		4, 5, 43	
b. RTV silicones				A		4, 5, 43	
c. Polyesters				A		4, 5, 43	
d. Most ceramics				A		4, 5, 43	
e. Al <sub>2</sub> O <sub>3</sub>	A					52, 58	
f. Beryllium oxide	A					58	
g. Carbon		B				4, 5, 43	
h. Asbestos		A				4, 5, 43	
1 - Compatible	A - Rating based on data on the specific material with the						
2 - Probable Compatibility	specific propellant						
3 - Doubtful Compatibility	B - Rating based on data on a similar or sister material with						
4 - Incompatible	the specific propellant						
5 - Unable to Rate	C - Rating based on data on the specific material but with a						
	sister propellant						
	D - No specific data						

## B. GENERAL DISCUSSION

Nitrogen tetroxide is a highly reactive and toxic oxidizer. It is stable with respect to decomposition and forms an equilibrium mixture of  $N_2O_4$  and  $NO_2$  ( $N_2O_4 \rightleftharpoons 2NO_2$ ). At ambient temperatures, this equilibrium mixture is practically all  $N_2O_4$ . As temperature increases, the equilibrium mixture shifts in the direction of  $NO_2$ . The major problem in long term storage of  $N_2O_4$  concerns the relatively high reactivity which manifests itself in corrosion problems for metals and dissolving or loss of material properties problems for non-metals.

Two propellant specifications have been used to designate propellant grade nitrogen tetroxide. These specification grades are differentiated by the amount of nitric oxide (NO) corrosion inhibitor contained in the  $N_2O_4$ . If the NO content is less than 0.4%, the  $N_2O_4$  is termed "brown" or Military Specification (MIL-P-26539A or B)  $N_2O_4$ . If the NO content is between 0.4 and 0.8%, the  $N_2O_4$  is termed "green" or NASA Specification (MSC-PPD-2A or B)  $N_2O_4$ . The terms "brown" and "green" arise from the colors of the liquid. Until the 1966-67 time period the Military Specification  $N_2O_4$  was the primary grade in use. At about this time, however, problems arose due to the occurrence of stress corrosion of titanium alloys with brown  $N_2O_4$ . Most of these stress corrosion problems were circumvented by the addition of more NO to the propellant. For this reason, the green NASA Specification  $N_2O_4$  has essentially replaced the brown Military Specification  $N_2O_4$  for aerospace applications from about 1967 on.

### 1. Compatibility with Metals

According to reports written by AFRPL, Aerojet-General and Bell Aerosystems (Ref 17, 42 and 43), most metals seem to be compatible with 60 to 120°F  $N_2O_4$  if the moisture content is small (<0.1%). Moisture results in corrosion due to the formation of nitric acid ( $HNO_3$ ) when  $H_2O$  reacts with  $N_2O_4$ . According to VonDoehren (Ref 17), carbon steels, aluminum, nickel, Inconel, and stainless steels are all compatible with dry  $N_2O_4$ . However, if the  $N_2O_4$  is wet, 300 series stainless steels suitable for  $HNO_3$  storage

should be used. Aerojet states that 300 and 400 series, 17-4 PH, 17-7 PH, AM350, and AM355 stainless steels and titanium are all good for wet  $N_2O_4$  storage, while nickel, mild steel, and aluminum are safe only for storage of dry nitrogen tetroxide (Ref 42).

Bell, in general, agrees with the conclusions drawn by RPL and Aerojet concerning  $N_2O_4$  compatible metals (Ref 43). However, Bell does state that the purer aluminum alloys, i.e., 5052, 3003, etc., show better compatibility than the aluminum alloys containing large percentage of other metals such as 2024 and 7075. They also point out that 2024 is more desirable than 7075 since the zinc-bearing 7075 has shown higher corrosion rates than the copper-bearing 2024 in wet  $N_2O_4$ . This differentiation between the compatibility of the various aluminum alloys does not become apparent until  $N_2O_4$  contains greater than 0.3%  $H_2O$ . Concerning other metals, Bell states that titanium and Inconel show excellent corrosion resistance even with very wet  $N_2O_4$ . Carbon steels and nickel alloys (except Inconel) were considered acceptable for dry  $N_2O_4$  service only, while magnesium and copper alloys were considered totally unacceptable even for very dry  $N_2O_4$ .

The AFRPL, Aerojet, and Bell reports represent the  $N_2O_4$  compatibility thinking as of 1961. The opinions expressed in the AFRPL and Bell reports were based on the current available compatibility data existing at the time, obtained by industry wide surveys. The Aerojet opinions were based on personal experience with handling  $N_2O_4$ . However, none of these reports present any exact  $N_2O_4$  compatibility test results.

Further data on compatibility of metals with  $N_2O_4$  is reported by DMIC (Ref 5). In 1965, DMIC rated various metals for service with dry  $N_2O_4$  (considered as having a moisture content < 0.2%). A metal was considered compatible if it showed a corrosion rate of < 1 mil per year. All ratings were temperature dependent. For service at temperatures up to 130°F, 2024, 3003, 5052, 6061, 5086, and 7075 aluminum, 304, 410, and 347 stainless steel, mild, 1020, and A-286 steel, and 6Al-4V and 75A titanium were rated as compatible. For service below 100°F, compatible metals included most stainless steels, 356 aluminum, electroless nickel, and 65A titanium. At temperatures below 80°F, 1100 and 4043 aluminum, pure and cast iron, and tin were considered

compatible. At temperatures below 60°F, gold, all titaniums, platinum, 2014 and 2219 aluminum, magnesium, nickel, Inconel, and tantalum were considered compatible. Metals considered totally unacceptable for  $N_2O_4$  storage at any temperature were copper, brass, bronze, silver, zirconium, and zinc. DMIC used both the Aerojet and Bell reports discussed earlier as references.

The results reported by RPL, Aerojet-General, Bell, and DMIC are supported by tests conducted by Martin Marietta and JPL. Martin Marietta tested different metals with  $N_2O_4$  having varying  $H_2O$  content for periods up to one year at a constant temperature of 60°F (Ref 44). Aluminum alloys (356-T6, 1100, 2014-T6, 6061-T6, 2219-T81, 5456-H321, and 7075-T6) were tested in dry  $N_2O_4$  ( $H_2O < 0.1\%$ ) and no corrosion was observed. Titanium alloys 6Al-4V and B120VCA were tested in very wet  $N_2O_4$  (2 to 20%  $H_2O$ ) and no serious corrosion occurred. Also, wet  $N_2O_4$  ( $H_2O > 0.1\%$ ) was tested with 304, 321, 1020, and A-286 stainless steels and no corrosion was observed.

The JPL tests consisted of using 2014-T6 aluminum canisters filled with  $N_2O_4$ , containing from 0.1 to 0.2%  $H_2O$ , to determine storage compatibility (Ref 45). The tests lasted approximately 2 months at temperatures ranging from 40 to 110°F. Some of the canisters were passivated with  $N_2O_4$  prior to the tests; all were chemically cleaned. Upon inspection after the tests, pits approximately 0.0002-in. deep were observed.

From the test results and recommendations presented above, it would seem that stainless steels are one of the better storage materials for  $N_2O_4$ . More recent data, however, indicate stainless steels may be incompatible with  $N_2O_4$ , at least under certain conditions. According to Caudill, stainless steels have a tendency to form a sludge like corrosion product (adduct) when in contact with  $N_2O_4$  (dry or wet), even at ambient temperatures (Ref 46). Further clarification of this phenomena can be found in reports published by Rocketdyne, TRW, Aerospace Corporation, and Martin Marietta. In a series of tests, Rocketdyne analyzed the formation, make up, and hazards of  $N_2O_4$ /stainless steel adducts (Ref 47). According to Rocketdyne,  $N_2O_4$  will react with iron based alloys to form either a solid precipitate adduct,  $NOFe(NO_3)_4$ , or a viscous gel type adduct in  $N_2O_4$ . The adduct form (gel or solid) is dependent on the  $H_2O$  content of the  $N_2O_4$ . If the  $H_2O$  content is low, the solid precipitate is formed; conversely, the gel adduct is formed in wet  $N_2O_4$ . The

amount of adduct formed, or the amount of metal corroded, is based on the solubility of the adduct in  $N_2O_4$  which is a function of temperature. At ambient temperatures, the amount of adduct is on the order of ppm. It was reported that a  $N_2O_4$  stainless steel storage vessel would become saturated with either of the adducts within 3 weeks at ambient temperatures. From these data, there would seem to be no serious corrosion problem at ambient temperatures with storage vessels manufactured from stainless steels. However, when considering the total propulsion system, a drop in temperature during flow operations could cause adduct precipitation and flow blockage in the feed system. Although Rocketdyne states that only flow diameters of approximately 0.001 in. would be affected, serious valve actuation and filter problems could occur. Also, at elevated temperatures, a corrosion problem with the storage tanks themselves would exist since the solubility of the adducts in  $N_2O_4$  would be increased.

Part of the Rocketdyne conclusions were based on earlier work of TRW and Aerospace Corporation. The objective of the TRW work (Ref 48) was to determine the influence of minor  $N_2O_4$  impurities on metal corrosion and to try to relate these corrosive impurities to the build up of potential gelants which cause  $N_2O_4$  flow blockage problems. Corrosion tests were run to accomplish this objective. Three metal alloys, 6061-T6 aluminum, 347 stainless steel, and 6Al-4V titanium were stored in both neat and doped  $N_2O_4$  at 165°F for up to 4 months. The impurities consisted of  $H_2O$ , chloride (as NOCl),  $O_2$ , chloride plus  $O_2$ , and chlorine. These impurities are either known to exist in propellant grade  $N_2O_4$  or can be inadvertently introduced into the oxidizer fairly easily. The metal specimens were cleaned prior to immersion in the test oxidizers. After storage, both the metal specimens and test fluids were analyzed.

From a corrosion standpoint, the aluminum samples were affected the most. Especially severe were the  $H_2O$  contaminated samples. The  $Cl_2$  and NOCl doping did not seem to effect the corrosion of the aluminum samples significantly. The 347 stainless steel fared slightly better than the 6061 aluminum. The most severe attack occurred with the  $O_2$ ,  $H_2O$ , and  $O_2/NOCl$  doped  $N_2O_4$  test fluids. The 6Al-4V titanium was least affected. No pitting or general corrosion occurred even with the doped  $N_2O_4$  fluids.

On the basis of the posttest fluid analysis, TRW concluded that the clogging in  $N_2O_4$  flow systems probably occurs with "as-received"  $N_2O_4$  and is not enhanced by the addition of the test contaminants since the amount of metals dissolved in the  $N_2O_4$  did not change significantly during the tests. However, the formation of gelatinous material occurred more often with the 347 samples even though the aluminum specimens corroded more. In fact, the gelatinous material was formed with the 347 samples stored in neat  $N_2O_4$ .

In addition to the corrosion tests, TRW also conducted flow tests with neat and doped  $N_2O_4$  to try to characterize the observed clogging behavior of  $N_2O_4$  through capillary passages and filters. The doping consisted of adding iron and zinc to NASA Specification Grade (MSC-PPD-2A)  $N_2O_4$ . A 316 stainless steel flow apparatus was employed for the tests. Both 0.010-in. and 0.005-in. diameter capillaries were used with neat  $N_2O_4$ , and flow blockage by a gelatinous material was observed. However, reproducible clogging behavior and flow blockage was observed only in the lower pressure regimes with the 0.005-in. capillary. Partial blockage and build-up of material, which subsequently was blown past the capillary section, was noted in the 0.010-in. capillary, and at higher pressures in the 0.005-in. capillary. TRW states that a gel material will ultimately block the flow if the pressure differential is not too excessive. The pressure differentials given were 50 psia for the 0.005-in. capillary and 10 to 25 psia for the 0.010-in. capillary. Blockage was also observed to occur between 50 and 90 seconds after the start of the runs.

For the filter tests, both neat and doped  $N_2O_4$  were employed as test fluids with 2 micron nominal (10 micron absolute) cartridge filters. Again flow blockage occurred. Analysis of the residue removed from the neat  $N_2O_4$  filter revealed that the material was inorganic and identical to a hydrated metal nitrate such as  $Fe(NO_3)_3 \cdot 9H_2O$ . This hydrated metal nitrate was subsequently analyzed by x-ray emission to determine relative concentrations of metals; iron was the only metallic component detected in the residue. Analysis of the clogging residue for the doped  $N_2O_4$  filter tests revealed that the materials were gel-like solvated complex nitrates of both zinc and iron. TRW further stated that this analysis also implied that zinc will form gel-like nitrates more readily than iron. Therefore, dissolved zinc in  $N_2O_4$  should be minimized.

The purpose of the work conducted by Aerospace Corporation (Ref 49) was to isolate and analyze materials which might cause  $N_2O_4$  flow blockage. Obtaining a stainless steel filter from SLC-IV West at Vandenberg AFB, Aerospace

identified nitrosyl tetranitratoferrate (NTNF or  $\text{NOFe}(\text{NO}_3)_4$ ) as the agent causing  $\text{N}_2\text{O}_4$  flow blockage. In addition to isolating NTNF as the clogging agent, Aerospace also formed NTNF by reacting  $\text{N}_2\text{O}_4$  with iron powder in the laboratory using ferric chloride as a catalyst. On the basis of these results, Aerospace states that the reaction between steels and  $\text{N}_2\text{O}_4$  to form NTNF is limited by the solubility of NTNF in  $\text{N}_2\text{O}_4$  (same conclusion Rocketdyne came to, as reported earlier). The reaction between  $\text{N}_2\text{O}_4$  and iron stops when the concentration of NTNF reaches 1 to 2 ppm. However, flow restriction can occur even at these low concentrations. Upon contact with moisture, Aerospace states that NTNF is readily converted to hydrated ferric nitrate, and nitric and nitrous acids.

Martin Marietta has also investigated flow blockage of  $\text{N}_2\text{O}_4$  systems (Ref 50). The clogging problem was first noted during the loading of a Titan IIIB when severe pressure drop was recorded across a 40 to 60 micron filter. Upon examination, a brownish viscous oil was found trapped in the filter. Exposure of this oily residue to ambient air resulted in a rapid transformation into a reddish brown crystalline hydrate. Chemical analysis of the crystalline residue indicated the primary constituents to be metals in the approximate proportions: 79% iron; 12% chromium; 7% nickel; 1% manganese.

Flight data on the Titan III Transtage led to the postulation of a shift in engine mixture ratio during flight. The possibility of a flow decay with  $\text{N}_2\text{O}_4$  was investigated, and a series of tests was run to determine if accumulation of ferric nitrate adduct on the filter in the Transtage  $\text{N}_2\text{O}_4$  tank outlet line could account for the apparent mixture ratio shift.  $\text{N}_2\text{O}_4$  was flowed through a 2-in. diameter section of 60 mesh stainless steel screen at a flowrate of 18 gpm for approximately 400 seconds. The results indicated that although it was possible to collect some viscous precipitate on the Transtage  $\text{N}_2\text{O}_4$  tank outlet screen, the effect on pressure drop and flowrate was not large enough to be a likely cause of the apparent inflight flow reduction. As a result of a marked increase in gel formation due to  $\text{N}_2\text{O}_4$  cooling, however, Transtage loading procedures were modified to preclude cooling of the  $\text{N}_2\text{O}_4$  after loading in the vehicle.

From the above discussion on  $\text{N}_2\text{O}_4$  flow decay, it would seem that ferric metals are undesirable as storage materials for  $\text{N}_2\text{O}_4$  due to the formation of NTNF. However, a similar flow decay problem also exists with  $\text{N}_2\text{O}_4$ /aluminum systems. In addition, to investigating  $\text{N}_2\text{O}_4$  flow decay associated with ferric

nitrate gels, Martin Marietta also investigated flow decay problems reported with aluminum systems (Ref 50). During gas desorption tests conducted as part of the mixture ratio shift investigation, a reduction in  $N_2O_4$  flowrate through the aluminum Transtage injector was observed. Upon examination of the injector, large quantities of a white crystalline material were found. This material was an aluminum nitrate salt which was soluble in water but relatively insoluble in  $N_2O_4$ . It formed when the injector was exposed for varying periods of time to unlimited quantities of  $NO_2$  vapor plus humid air.

Analysis showed that the salt was a hydrated aluminum nitrate:  $Al(NO_3)_3 \cdot (H_2O)_9$  (Ref 51). This salt will be formed when aluminum is exposed to  $N_2O_4$  containing some  $H_2O$  ( $NO_2$  + moist air not needed). Therefore, an analogous situation probably exists between the formation of the hydrated ferric nitrate in  $N_2O_4$ /ferric metal systems and the formation of the hydrated aluminum nitrate in  $N_2O_4$ /aluminum systems. The amount of hydrated aluminum nitrate formed is based on the solubility of this salt in  $N_2O_4$ , which is very low at ambient conditions. However, as temperature increases, more salt will be formed (aluminum corroded) to keep the  $N_2O_4$  saturated. Therefore, in addition to clogging problems, a serious corrosion problem could also occur in  $N_2O_4$ /aluminum systems at higher temperatures.

From the data presented so far, titanium appears to be the only metal which exhibits long term compatibility with  $N_2O_4$ , dry or wet. Both supporting but also opposing this contention are the results of compatibility tests conducted fairly recently (1967-1969) by JPL, Bell Aerosystems, and Rocketdyne. To determine the long term compatibility of various metal alloys with  $N_2O_4$ , JPL immersed small cylindrical specimens of approximately 18 different metal alloys in dry  $N_2O_4$  ( $H_2O < 0.1\%$ ) at  $110^\circ F$  for periods up to 4 years (Ref 52). Glass test capsules were employed as containers. Prior to immersion, all specimens were cleaned and passivated in accordance with JPL specifications. Upon completion of the immersion tests, SRI analyzed the results. The only incompatible alloys were A-231C magnesium, pure molybdenum, Hastelloy B and 356-T6 aluminum. Type 347, 19-9 DL, 410, 416, 430 and 440C stainless steels--and most of all of the cobalt and nickel based alloys (except Hastelloy B) were found compatible with the dry  $N_2O_4$ . The 6Al-4V titanium specimens fared almost as well as the

stainless steel samples and were also considered compatible. The titanium corrosion rates were  $< 3 \mu\text{in/yr}$ ; the attack was limited to staining or thin coating with no etching or pitting. However, it should be noted that any difference occurring between titanium and the other materials could have resulted from the test apparatus. Kovar metal (54% Fe, 29% Ni, and 17% Co) tubing was used to connect Bourdon tube pressure gages to the glass test capsules. SRI found severe corrosion of this tubing after testing. Therefore, the recorded corrosion of many of the metal alloys may not have been due to the incompatibility of the alloys but due to contaminants introduced by the corrosion of the Kovar tubing. Specifically, SRI states that the severe corrosion of the 356-T6 samples was probably due to Kovar corrosion contaminants since large quantities of iron, nickel and cobalt salts were detected in the 356-T6 test capsules. However, the corrosion of the Hastelloy B, A-231C magnesium, and molybdenum specimens was not felt by SRI to have been caused by the corrosion of the Kovar tubing.

The Bell Aerosystems  $\text{N}_2\text{O}_4$  compatibility tests were part of the same test series conducted with MMH, reported on earlier under MMH compatibility (Ref 30). These tests were run to determine the reliability of rocket propulsion materials used to store  $\text{N}_2\text{O}_4$  and MMH under the influence of both high temperature and applied stress. Two test phases were conducted; the first phase used Military Specification Grade or "brown"  $\text{N}_2\text{O}_4$  while the second phase used NO inhibited  $\text{N}_2\text{O}_4$  similar to NASA Specification Grade or "green"  $\text{N}_2\text{O}_4$ . In each case, the  $\text{N}_2\text{O}_4$  was dry ( $\text{H}_2\text{O} < 0.1\%$ ).

Only stainless steels were tested in the initial phase. The test specimens consisted of bars constructed of various stainless steels: ---

- A286/A286 Welded with Hastelloy W
- A-286 Parent Metal
- A-286/347 Welded with Hastelloy W
- 304L/304L Meltdown Weld
- 347/304L Meltdown Weld .
- Cryofomed 301 Stainless Steel
- A286/347 Meltdown Weld

Testing was accomplished by immersion in 150°F liquid  $N_2O_4$  while stressed in bending to 25% of yield strength. The containers were constructed of 300-series stainless steel. After two months of testing, discoloration and intergranular corrosion occurred with all of the test bars. In particular, the welded A286 specimens cracked in the weld heat affected zones and the Hastelloy W weldments suffered from severe intergranular corrosion. After four months of testing, severe blackening and sludging (build up of sludge like material) of the specimens occurred. Although the intergranular attack did not deepen, penetrations became more numerous. Also, the cryoformed 301 samples developed cracks on the tension side. Propellant analysis showed that the dissolved  $O_2$  content had decreased during testing. On the basis of this fact and the other results obtained, Bell came to the following conclusions concerning storage of Military Specification Grade  $N_2O_4$  with stainless steels:

- 1) MIL-P-26539B (oxygenated) nitrogen tetroxide is not suitable for long term (greater than four months) storage in types 347 and A286 stainless steel thin walled containers (0.030-in. or less);
- 2) Type A286 stainless steel with a nitric-hydrofluoric pickled surface is more susceptible to intergranular corrosive attack by oxygenated nitrogen tetroxide than a nitric acid passivated surface. This attack is accelerated by applied stress and can cause a fracture;
- 3) The cryoformed 301 stainless steel is susceptible to surface cracking in oxygenated  $N_2O_4$ , when stressed;
- 4) Hastelloy W weldments are more susceptible to corrosion in oxygenated nitrogen tetroxide than meltdown welds.

For the second phase, approximately 0.2 to 0.4% NO inhibitor was added to MIL-P-26539B Specification  $N_2O_4$  to form a green  $N_2O_4$ . The test techniques and procedures were identical to those of the earlier phase except that three test temperatures (70°F, 125°F, and 150°F) and three stress levels (0%, 40%, and 90% of yield strength) were used. Also, only A286/A286 (Hastelloy W weld), A286/347 (meltdown weld), and 347/347 (meltdown weld) specimens were used. After six months of testing, the specimens appeared unaffected.

For the Rocketdyne compatibility tests, both stress corrosion and long term storage were assessed (Ref 53). For the stress corrosion tests, tensile specimens of three metal alloys stressed to 2/3 of ultimate strength were stored in both brown and inhibited (or green)  $N_2O_4$  at ambient temperatures for up to 45 days. The specimens were notched cylindrical tensile bars of 2219-T6 aluminum, 347 stainless steel and 250 maraging steel. Both the containers used to hold the specimens and  $N_2O_4$  and the frames used to stress the specimens were constructed of the same materials as the specimens. Prior to testing, all the specimens were consecutively cleaned by degreasing in acetone, vacuum annealed at  $1400^{\circ}F$  for 4 hours, solution treated in air at  $1743^{\circ}F$  for one hour, and aged in air at  $1000^{\circ}F$  for 8 hours. None of the samples failed during testing. The ultimate strength of the 2219-T6 aluminum alloy and the 250 maraging steel decreased as a result of exposure to specification grade MIL-P-26539B  $N_2O_4$ . There was no change in the 347 stainless steel ultimate strength with either the Military Specification or NASA Specification  $N_2O_4$ .

For the long term storage, small discs of ferric and aluminum alloys were immersed in both dry ( $H_2O < 0.1\%$ ) and wet ( $H_2O \approx 0.33\%$ ) MIL-P-26539A (brown)  $N_2O_4$ . The stainless steel alloys used consisted of 304L, 316, 321, AM 350 and 440C. The aluminum alloys were 6061-T6, 7075-T73, TENS-50, 2014-T6, and 2024. 1018 carbon steel was also tested. Two test temperatures were employed. For tests run at ambient temperature, test duration was 21 months, while for tests run at  $158^{\circ}F$ , test duration was only one month. Prior to testing, all test samples were cleaned with a soap solution, rinsed with water and acetone, and weighed. Test containers used in the tests were made out of stainless steel for the ferric samples and aluminum for the aluminum alloy samples. From the results, Rocketdyne stated that 304, 316, 321, and AM 350 stainless steels and 2014, 2024, and 7075 aluminum seem to be compatible with either dry or wet Military Specification  $N_2O_4$  at ambient temperature,

while 440C and 1018 steel and Tens-50 and 6061 aluminum seem incompatible. Of the materials tested, only 7075 aluminum appeared compatible with dry or wet  $N_2O_4$  at  $158^\circ F$  since all of the other metal specimens showed significant weight losses.

Further stress corrosion testing was conducted by Boeing to determine the fracture toughness and flaw growth characteristics of various metal alloys in  $N_2O_4$  (Ref 54). As-welded specimens of 2219-T851 aluminum, base metal and weldment specimens of 2021-T81 aluminum, and base metal specimens of 410 stainless steel were tested. Only the 2021-T81 samples showed very low threshold stress intensity values. For the base metal samples, a threshold stress intensity of  $10 \text{ ksi } \sqrt{\text{in}}$  was found; the corresponding value for the weldments was  $9 \text{ ksi } \sqrt{\text{in}}$ . These low values indicated to Boeing that 2021 aluminum might cause functional problems if used as a  $N_2O_4$  storage pressure vessel material.

As shown by the stress corrosion tests conducted by Bell, stainless steels are subject to stress corrosion in Military Specification  $N_2O_4$  (Ref 30). In the same report, Bell also stated that titanium was subject to stress corrosion. In fact, Bell used 6Al-4V titanium sample bars to check out their test apparatus. Three specimens were stressed to 90 ksi (bending stress) while immersed in "brown"  $N_2O_4$  at  $150^\circ F$ . After 135 hours, all three specimens failed, thus verifying to Bell the quality of their test apparatus for the stainless steel testing. TRW, in a report rating materials for use with  $N_2O_4$ , also states that titanium is incompatible with Military Specification or "brown"  $N_2O_4$  due to stress corrosion, while NASA specification or "green"  $N_2O_4$  is perfectly compatible with titanium (Ref 4). The conclusions were based on  $N_2O_4$  handling experience as of 1967.

DMIC has reported on the shock impact sensitivity of titanium alloys with various oxidizers (Ref 55 and 56). Commercially pure titanium, exposed to  $32^\circ F$   $N_2O_4$  for 24 hr, ignited 50% of the time when impacted at 60 to 70 ft-lb by a flat striker pin. The energy level dropped to 40 to 50 ft-lb after 384-hour exposure. Without prior exposure, the level was 201 ft-lb for 50% ignition.

These data suggest an increase in sensitivity with contact time. Galling or machining either pure or 6Al-4V titanium in contact with  $N_2O_4$  produced no reaction. Shearing 75A and 6Al-4V titanium in liquid  $N_2O_4$  resulted in evidence of ignition on the freshly exposed surfaces. Titanium tubes filled with  $N_2O_4$  showed evidence of reaction when impacted with a .30-06 slug but no signs of reaction when impacted with a .22 slug. In all reaction cases, only small fused areas on the surface were noted. In no instance did the reaction propagate, even though there was sufficient  $N_2O_4$  to consume most or all of the specimen. No reactions were observed when commercially pure or 6Al-4V titanium were ruptured under tension in gaseous  $N_2O_4$  at pressures up to 535 psia with a temperature of 257°F.

Further impact testing of titanium alloys in  $N_2O_4$  has been reported by McDonnell Douglas (Ref 57). They conducted ABMA open cup impact tests with 6Al-4V titanium (ELI) and 2014-T6 aluminum in Military Specification  $N_2O_4$ . The results showed that neither of the alloys were impact sensitive in  $N_2O_4$ . For the 6Al-4V tests, 0.025-in. thick Ti discs were impacted at 69 ft-lbs at 68°F using both 6Al-4V titanium cups and striker pins; no reactions occurred in 20 tests. For the aluminum alloy tests, 40-mil 2014-T6 discs were impacted at 70 ft-lbs at 82°F using 17-4 PH stainless steel striker pins and 1100-0 cups; no reactions occurred in 20 tests.

In a program to evaluate the effects of sterilization on the materials and components of a propulsion subsystem, Martin Marietta found titanium to be the only material compatible with  $N_2O_4$  at elevated temperatures (Ref 28). Prescreening, screening, and long term storage tests were conducted with dry (.03%  $H_2O$ ) NASA Specification  $N_2O_4$  at sterilization temperatures (275°F). In the prescreening tests, samples of 6061-T6 and 1100-0 aluminum, 321 and 316 stainless steel, 6Al-4V titanium, pure nickel, and pure lead were exposed to  $N_2O_4$  at 275°F for periods up to 120 hours. Before testing, the samples were cleaned and passivated by immersion in HCl followed by immersion in  $HNO_3/HF$ . The test containers used to hold the samples and  $N_2O_4$  were fabricated of 304 stainless steel. These tests indicated that the ferric based alloys were incompatible with  $N_2O_4$  at 275°F. Iron based adducts were formed on all of the

ferric based metal samples as well as on the test containers. The rate of formation of this adduct appeared to be approximately linear with time and seemed to increase as the amount of alloying agents increased. Nickel and molybdenum appeared to contribute to adduct formation. No residual contamination (adduct) formed on the aluminum and titanium samples.

The screening tests exposed metal strips to 275°F NASA Specification  $N_2O_4$  for periods of 300 and 600 hours in glass containers. All samples were cleaned and passivated before testing using the same procedure employed for the pre-screening tests. The metals tested were:

Stainless Steel	Titanium
304, 321, 347	Pure, 6Al-4V
17-4 PH, 17-7 PH	Aluminum
Carpenter 20 Cb	1100-0, 2014-T6
A-286	2219-T8, 6061-T6
Maraging Steel	Hastelloy C
Pure Nickel	Pure Lead

The results of the 300-hr tests verified those of the prescreening tests. Only the aluminum alloys, Hastelloy C, and the titanium didn't corrode. All the ferric alloys were attacked immediately and formed the tar-like adduct. In the 600-hr tests, only the 6Al-4V and pure titanium didn't corrode. The aluminum alloys showed severe pitting and intergranular corrosion and the tar-like adduct was formed with the stainless steels. The nickel specimen was severely attacked and formed a heavy deposit of nickel nitrate. The maraging steel sample was the only specimen to fracture as well as corrode which indicated the occurrence of stress corrosion. The Carpenter 20 Cb and Hastelloy C specimens exhibited only minor corrosion.

Four 15-in. diameter spherical tanks constructed of 6Al-4V titanium were used in the long term storage tests. A sample of Teflon laminate and a welded titanium specimen were installed in each tank. Prior to filling with  $N_2O_4$ , the tanks were cleaned and passivated using the procedure outlined earlier.

After filling to 5% ullage, the tanks were subjected to the 275°F sterilization temperature and then stored at ambient temperature for up to one year. Three of the tanks were opened for examination, one every four months. The fourth tank was held as a control specimen. During this 12-month storage, no metal corrosion was observed.

Additional 600 hour, 275°F compatibility tests were conducted by Martin Marietta using metal alloys not considered previously (Ref 58). Some of the metal alloys tested earlier were also included with protective coatings to evaluate protection potential. Test procedures were the same as those described previously.

The test results are summarized in Table 8 . Bare 2024-T3 aluminum was incompatible; formation of corrosion products plus intergranular attack occurred with this alloy. The alloys considered as only marginally compatible were the chrome plated 321, the precipitation hardened AMS 5538, and the austenitic 21-6-9 stainless steels; the TZM high temperature alloy; and the L-605 cobalt alloy. The stainless steels suffered from only light attack but formed the gelatinous iron adduct. The TZM alloy suffered from both light surface attack and formation of a smut-like material while the cobalt alloy only corroded slightly forming a white, loosely adherent product. No adduct was formed with either the 430 stainless steel or the HY-140 steel specimens. Since these alloys do not contain large amounts of nickel, this led to the feeling that nickel may be a major contributor in the formation of the adduct. Primary conclusions were:

- 1) Anodic coating of aluminum alloys can ensure almost 100% protection against  $N_2O_4$ ;
- 2) Commercially pure aluminum cladding of structural aluminum alloys provides excellent protection with only a slight amount of corrosion products being formed. The formation of corrosion products was so small the material may be classified as compatible;
- 3) Tantalum and columbium were unaffected by the propellant;
- 4) Chromium plating affords excellent protection to stainless steels (only 321 stainless steel was tested). This protection could be afforded to any metallic material.

Table 8 Materials Compatibility (Exposed to  $N_2O_4$  at 275°F for 600 Hours)  
(Ref 58)

Material	Results*
1. 2014-T6 Aluminum, Chromic Acid Anodized	C
2. 2014-T6 Aluminum, Sulfuric Acid Anodized	C
3. 6061-T6 Aluminum, Chromic Acid Anodized	C
4. 6061-T6 Aluminum, Sulfuric Acid Anodized	C
5. 2021-T6 Aluminum, Sulfuric Acid Anodized	C
6. 6061 Aluminum Screen, Chromic Acid Anodized	C
7. 2024-T3 Aluminum, Pure Aluminum Clad	C
8. 2024-T3 Aluminum, Clad Stripped	NC
9. 430 Stainless Steel	C
10. 321 Stainless Steel, Chrome Plated	MC
11. AMS 5538 Stainless Steel	MC
12. 21-6-9 Stainless Steel	MC
13. HY-140 Steel	C
14. Titanium 5Al-2.5 Sn	C
15. Titanium 8Al-1 Mo	C
16. Beryllium	C
17. Columbium DP14	C
18. Columbium CB752	C
19. Tantalum, Pure	C
20. Tungsten, Pure	C
21. TZM Titanium-Zirconium-Molybdenum	MC
22. L-605 Cobalt	MC

\*C - compatible; MC - marginally compatible; NC - not compatible.

## 2. Compatibility with Non-Metals

DMIC, Bell Aerosystems, and TRW rated various non-metals for service with  $N_2O_4$  ( $H_2O < 0.2\%$ ) based on available compatibility data for the 1961-1967 time period (Ref 5,43, and 4). These reports are not independent of one another since DMIC referenced the Bell report and TRW referenced both the DMIC and Bell reports. In each case, a non-metal was considered compatible if it had a volume change of less than 25%, a durometer reading change of less than  $\pm 3$ , showed no visual change, and did not affect the  $N_2O_4$ . The ratings are presented in Table 9. As can be seen, only FEP Teflon was rated compatible at 160°F. All elastomers were considered incompatible as well as most ceramics.

The compatibility ratings made by Bell, DMIC, and TRW (presented in Table 9) were determined, in part, from compatibility tests conducted by both Martin Marietta and Aerojet-General as part of the Titan II program. For the Martin Marietta tests, non-metals were tested with 60°F  $N_2O_4$  having various  $H_2O$  contents for periods up to one year (Ref 44). Teflon TFE samples, tested in dry  $N_2O_4$ , showed no visible changes; close inspection revealed up to a 0.73% increase in elongation, a 2.4% increase in volume, and a 3% increase in weight. The addition of up to 1%  $H_2O$  to the  $N_2O_4$  showed no effect on the TFE samples. Teflon FEP samples, after immersion in dry  $N_2O_4$ , showed a 2.6% increase in elongation, a 4% increase in volume, and a 5% increase in weight. The addition of water to the  $N_2O_4$  resulted in a 4.8% volume increase of the FEP compared to the 4% increase with dry  $N_2O_4$ . Kynar samples were only tested in dry  $N_2O_4$ . They showed a definite loss in hardness plus a 0.24% increase in elongation. All other common non-metals tested were totally incompatible. Kel-F samples were attacked immediately and began cracking. All rubbers (natural, butyl, silicone, and EPR) were severely attacked and polyethylene samples oxidized immediately and turned brittle.

For the Aerojet tests, the non-metals were immersed in dry  $N_2O_4$  at test temperatures of approximately 75°F (Ref 42). After 70 days of immersion, a 2 to 3% volume increase, a weight gain of 0.5%, a hardness loss of 20%, an 11% increase in elongation, and a loss in strength of 11.5% occurred with TFE

Table 9 Compatibility Rating Summary for Selected Non-Metals with  $N_2O_4$  (from Ref 4, 5, and 43)

Non-Metal	Compatible for Service Below			Incompatible
	160°F	85°F	60°F	
1) <u>Plastics</u>				
TFE Teflon			X	
FEP Teflon	X			
Teflon-Glass		X		
Teflon-Graphite			X	
Teflon-Asbestos			X	
Armalon 7700			X	
Fluorobestos			X	
Fluorogreen			X	
Kel-F				X
Kel-F 300				X
Genetron GCX-38			X	
Genetron XE-2B			X	
Alcar 191			X	
Polyethylene				X
Polypropylene				X
Irradiated Raythenen			X	
Nylon				X
Mylar				X
Saran		X		
Kynar				X
Lexan				X
Tedlar			X	
Plexiglas				X
Teslar 30			X	
Isobutylene-Copolymers				X
Polyethylene+Isobutylene Polymer (Formula 53)		X		
2) <u>Elastomers</u>				
EPR Rubbers				X
Butyl Rubbers				X
Fluoro Rubbers				X
Fluoro-Silicone Rubbers				X
Buna N				X
Neoprene				X
Natural Rubber				X
Polyurethane				X
3) <u>Lubricants</u>				
XC 150			X	
Molykote Z			X	
Microseal 100-1			X	
LOX Safe		X		
Graphite		X		
Graphitar			X	
CCP-72			X	

Table 9 (Concluded)

Non-Metal	Compatible for Service Below			Incompatible
	160°F	85°F	60°F	
3) <u>Lubricants</u> (Continued)				
Fluorolube MG6DO		X		
Fluoroethane G		X		
Krytox 240		X		
Drilube 703			X	
Electrofilm 66-C			X	
Halocarbon Grease				X
4) <u>Sealants and Potting Compounds</u>				
Reddy Lube 100	X			
Reddy Lube 200	X			
Waterglass-Graphite			X	
Oxylube Sealant		X		
Teflon Tape		X		
Crystal M&CF			X	
4-3			X	
Proseal 333			X	
Epon Resins				X
RTV Silicones				X
Polyesters				X
5) <u>Ceramics</u>				
Rock Flux				X
Sauereisen P-1			X	
Temporell 1500				X
Sauereisen 47				X

Teflon. After 20 days, the FEP Teflon showed a volume increase of 1.6%, a weight gain of 0.4%, a 38% loss in hardness, an increase in elongation of 2.9%, and a loss in strength of 20.5%. For both Teflons, the changes in physical properties took place within the first 2 days of immersion; after that time all other changes were nearly zero (the hardness loss of the FEP Teflon was an exception which was linear with time). Other non-metals tested were completely incompatible. Kel-F 300 absorbed the  $N_2O_4$  and became plastic; after 70 days of immersion, it showed a 6% volume increase, a 72% loss in strength, and a hardness loss of 76%. Polyethylene was tested only for short times (hours), since it oxidized immediately and became brittle.

As part of the long term compatibility testing conducted by JPL (reported earlier), various ceramics, lubricants, and plastics were immersed in  $N_2O_4$  at  $110^\circ F$  (Ref 52). The test techniques and procedures for these non-metal tests were the same as those for the JPL testing of metals in  $N_2O_4$ . Specific non-metals tested were a sapphire ball ( $Al_2O_3$ ); Kel-F grease coated on 6061-T6 aluminum, on 6Al-4V titanium, and on a sapphire ball; and a polytetrafluoroethylene (PTFE) named Rulon coated on the 6061-T6, 6Al-4V, and  $Al_2O_3$  materials. After approximately four years of immersion, SRI analyzed the results. The only non-metal analyzed for compatibility with  $N_2O_4$  was the  $Al_2O_3$  ball; the Rulon and Kel-F grease were only evaluated as protective coatings.  $Al_2O_3$  was completely compatible with  $N_2O_4$ , while the Rulon and Kel-F grease were ineffective as protective coatings. The Kel-F grease was loosened and was found as heavy, flocculent particles in the  $N_2O_4$ . The Rulon coating was removed from the 6Al-4V titanium and  $Al_2O_3$  specimens. It remained intact on the 6061-T6 aluminum, but no benefit was obtained from the coating since corrosion of the specimens occurred.

Further data on the compatibility of fluorinated hydrocarbons with  $N_2O_4$  has recently been reported by SRI (Ref 59). Samples of Fluon GP-1 and Teflon TFE-30 films were creased and folded to failure in air and after 20 hours of soaking in  $N_2O_4$ . For the Fluon GP-1, an increase in the cycles to failure of 3.3% was found, while for the Teflon TFE-30, a decrease in the cycles to failure of 16% was reported. From these results, SRI concluded that the flex resistance of the Fluon and Teflon films are not affected substantially by exposure to  $N_2O_4$ .

From the data presented so far, Teflon seems to be about the best non-metal one can use with  $N_2O_4$ . However, problems can exist depending on the application. TRW states that if Teflon is used for bladder service with  $N_2O_4$ , the FEP Teflon is probably preferable since TFE has  $N_2O_4$  permeability rates 3 times those of FEP (Ref 4). This conclusion seems supported by tests run at JPL (Ref 19). In 24-hr tests run at  $70^\circ F$ , TFE had a  $N_2O_4$  permeability rate of  $2.4 \text{ mg/in}^2/\text{hr}$  compared to the FEP rate of  $0.66 \text{ mg/in}^2/\text{hr}$ .

Besides permeability problems, JPL has recently found stress-cracking problems with bladders made of a Teflon laminate (Ref 32). As discussed in Chapter III, specimens of the standard Teflon laminate bladder material planned for the Mariner Mars 1971 spacecraft were stretched to failure while immersed in various solvents including  $N_2O_4$ . Both biaxial and uniaxial tests were performed. It was found that the standard laminate was highly sensitive to  $N_2O_4$  stress cracking. Because of this, JPL also tested a codispersion laminate to determine sensitivity to  $N_2O_4$ . The standard laminate consisted of a layer of TFE 30 Teflon covered with a layer of FEP 120 Teflon. The codispersion laminate consisted of a layer of FEP 9511 Teflon sandwiched between layers of a Teflon codispersion of 80% TFE 30 and 20% FEP 9511.

JPL deduced the following results from their tests:

- "(1) All solvents including  $N_2O_4$  significantly reduced the ultimate properties of the standard laminate, which indicates that this material is highly sensitive to solvent-stress-cracking.
- (2) Codispersion laminate resists solvent-stress-cracking.
- (3) A study of the solvent sensitivity of construction materials, FEP 120, FEP 9511, and TFE 30, revealed that only FEP 120 is significantly solvent-sensitive. This material, not used in codispersion laminate, is a major component of standard laminate and must therefore be labeled as the dominant contributor to the solvent sensitivity of standard laminate. This is further substantiated by the experimental observation that surface crazing, which precedes the failure of the standard laminate in solvent, occurs in FEP 120.

- (4) The solvent sensitivity of standard laminate is revealed only during immersion testing. Removing the specimens from the test solvent and air-drying them results in a recovery of their initial properties.
- (5) Both codispersion and standard laminates experience an immediate reduction in ultimate properties upon exposure to solvents, although the effect is more critical with the standard laminate. With further exposure, both codispersion and standard laminates undergo a recovery in ultimate properties. The codispersion laminate achieves or surpasses its initial properties, while the standard laminate, even with some recovery, displays significantly lowered properties as compared to its initial properties.
- (6) Codispersion laminate has superior flex fatigue properties as compared to standard laminate.
- (7) Crystallinity variation in the Teflon material did not affect the mechanical performance of either standard or codispersion laminate. It was believed that large increases in crystallinity could lead to brittle failure."

Thiokol-RMD attempted to develop a positive expulsion bladder material resistant to  $N_2O_4$  (Ref 60). This material consisted of a lamination of electroformed gold and carboxy nitroso rubber (CNR). The gold was added to make the laminate as impermeable as possible. In a series of compatibility tests, Thiokol found the gold/CNR laminate to be fairly resistant to  $N_2O_4$ .

Further data on CNR with  $N_2O_4$  was obtained by TRW in compounding studies to develop polymeric bladder materials (Ref 26). As a result of these studies, TRW chose a HYSTL resin cured TFE Teflon reinforced CNR compound, designated Compound 288-3, as their prime candidate. This new compound exhibited resistance to  $N_2O_4$  attack comparable to similar CNR formulations but had superior permeability characteristics.

At high temperatures, all non-metals are apparently incompatible with  $N_2O_4$ . In pre-screening tests to select a bladder material for a sterilizable propulsion system, Martin Marietta immersed different non-metals in dry  $N_2O_4$  ( $H_2O = .03\%$ ) at temperatures of  $275^\circ F$  for periods up to 88 hours (Ref 28). All rubbers (butyl, EPR, and nitroso rubber) either blistered, ignited or completely dissolved. Both TFE and FEP Teflon showed losses in strength of about 7% and changes in elongation up to 50%. It was also noted that the  $N_2O_4$  washed out particles of Teflon which caused the  $N_2O_4$  to turn milky. Kynar was severely attacked. Although Teflon did fare better than the other non-metals tested, no non-metal was considered compatible with  $N_2O_4$  at the high temperature. Conversely, aluminum oxide and beryllium oxide ceramics were immersed in dry  $N_2O_4$  at  $275^\circ F$  for 600 hours with no sign of chemical attack and no increase in weight (Ref 58).

VII. FLUORINE

#### A. COMPATIBILITY SUMMARY

The compatibility of both metals and non-metals with  $F_2$  is summarized in Table 10, as determined by interpreting available compatibility information. Specific references used in this determination are listed in the table. Compatibility of a material with  $F_2$  was based on the criteria that the material be essentially unaffected by static and dynamic (impact, flow, etc.)  $F_2$  exposure (negligible corrosion for metals and negligible reaction and loss of physical properties for non-metals): listing of a material was based on the same criteria used for the other propellants. The compatibility ratings presented in Table 10 are based on the extent to which the propellant affects the material.

Table 10 F<sub>2</sub> Summary Compatibility Chart

Material	Rating					References	Remarks
	1	2	3	4	5		
<b>Metals</b>							Rated for both LF <sub>2</sub> and CF <sub>2</sub> (<400°F)
<b>1) Aluminums</b>							
a. Aluminum alloys in general	A, B					4, 54, 57, 63, 64, 65, 66 4, 65, 66 68	
b. 1100	A					57, 66	
c. 2014	A					54	
d. 2024	A					65	
e. 2219	A					65	
f. 5052	A					4, 65	
g. 6061	A						
h. 7079	A						
<b>2) Steels</b>							
a. Steels in general	A, B					4, 63, 65, 66, 69	
b. Stainless steels in general	A, B					4, 63, 65, 66, 68, 69 4, 63, 65, 68	
c. 301 cryoformed	A, B					4, 65, 68	
d. 304	B					4, 65, 68	
e. 316	A					63	
f. 321	A					4, 63, 65	
g. 347	A					4, 65	
h. 410	A					4, 65	
i. 420	A					4, 65	
j. PH 15-7 Mo	A					4, 65	
k. AM350	A					4, 65	
l. Carpenter 20Cb	A					4	
m. Maraging steels	B					4, 63, 65	

Table 10 (Continued)

Material	Rating					References	Remarks
	1	2	3	4	5		
3) Titaniums							
a. Titanium Alloys in General			A, B			54, 65, 67	Based on shock sensitivity data. Conflicting data on shock sensitivity.
b. 6Al-4V		A	A			54, 65, 67	
c. 5Al-2.5Sn			A			65	Conflicting data on shock sensitivity.
d. 8Al-1Mo-1V		A	B			65, 67	
4) Miscellaneous Metals							
a. Nickel Alloys in General	A					4, 62, 63, 65, 66	Rated for liquid only. Same as above
b. A-nickel	A					4, 63, 66	
c. Monel	A					4, 62, 65, 66	
d. Inconel	A					4, 62, 63, 65, 66	
e. Ni-200	A					63, 68	
f. Cu-Ni Alloys	A					65	
g. Copper	A					4, 63, 65, 68	
h. Brasses	A					4, 63, 65	
i. Silver	A	A				68	
j. Tantalum		C, D				76, 85, 86	
k. Columbium		C, D				76, 85, 86	
l. Mg Alloys in General		A, B				4, 65, 66	Rated for liquid only. Same as above
m. AZ-31 Mg		A				4, 65	
n. AZ-91 Mg		A				66	
o. AZ-81A Mg		A				66	
p. MIA Mg		A				66	
q. HM-31 Mg		A				4, 65	
r. HK-31 Mg		A				4	
s. Molybdenum		D				64, 85, 86	
t. Tungsten		D				64, 85, 86	

Table 10 (Concluded)

Material	Rating					References	Remarks
	1	2	3	4	5		
Non-Metals							
Teflon FEP		A				4,65,70,72	Rated for static service with CF <sub>2</sub> only. All non-metals incompatible for dynamic service.
Teflon TFE		A				4,65,70,72	
Halon TFE		A				4,65,70,72	
CTFE's in general			A			70	
Kel-F			A			65,70,71	
Chlorinated Polyethylene			A			70	
All other non-metals in general				A,B		4,57,65,70,71	
1 - Compatible	A - Rating based on data on the specific material with the						
2 - Probable Compatibility	specific propellant						
3 - Doubtful Compatibility	B - Rating based on data on a similar or sister material with						
4 - Incompatible	the specific propellant						
5 - Unable to Rate	C - Rating based on data on the specific material but with a						
	sister propellant						
	D - No specific data.						

## B. GENERAL DISCUSSION

Fluorine is one of the most powerful oxidizing agents known and will react with practically all organic and inorganic substances. The activation energy to initiate combustion of materials is much lower with fluorine than with any other nonfluorine-containing oxidizer, and many materials will react spontaneously on exposure to fluorine. Whether a substance will burn spontaneously on exposure depends on the conditions of the exposure. If the exposure conditions are such that the required activation energy is available and not dissipated quickly, ignition will occur. Activation energy can be supplied by chemical, thermodynamic or mechanical means, singly or in combination. Energy supplied by pressure, temperature, impact, friction, or a high flow velocity may cause the spontaneous combustion of materials when exposed to fluorine. The dissipation of activation energy is dependent upon a material's properties and/or shape. Materials with high thermal conductivity have a tendency to resist ignition with fluorine because the heat of reaction can be easily dissipated. The ratio of surface area to mass will also influence whether a material will ignite and be consumed when exposed to fluorine. If this ratio is very large, such as for powdered metal, the heat of the surface reaction may initiate combustion and the entire material may be consumed because of the reduced heat dissipation capability. Therefore, the compatibility of a material with fluorine depends to a large degree upon the application and operating conditions.

Irrespective of the application considerations discussed above, certain materials do show more compatibility with  $F_2$  than others. For instance, most metals show a high degree of compatibility with  $F_2$  while practically all non-metals are totally incompatible with  $F_2$ . This differentiation can be attributed to the type of surface reaction which occurs. For most metals, reaction with fluorine produces a tenaciously attached fluoride film on the surface which forms a protective barrier against further reaction. No such protective film is formed with non-metals, however, so that the non-metal is eventually reacted away. The higher thermal conductivity of metals compared to non-metals also contributes to the lower reactivity exhibited by metals. The energy created when the fluoride film is initially formed on the metal surface is easily dissipated; no such dissipation is available when the surface of the non-metal reacts.

Even though fluorine presents one of the worst materials/propellant reactivity problems, other compatibility problems do not exist, e.g., fluorine exhibits excellent thermal stability and resistance to catalytic breakdown. Therefore, when considering materials for use with  $F_2$ , the prime concern is reactivity.

#### 1. Compatibility with Metals

According to TRW (Ref 4), practically all metals show a high degree of corrosion resistance to  $F_2$ . TRW states that this corrosion resistance is due to the formation of a protective fluoride film which is initially formed on the metal surface. The effectiveness of the protective film is based, to an extent, on the solubility in fluorine of the various metal fluorides forming the film. TRW believes that an equilibrium between the reactive rate, forming the films, and the solubility rate, dissolving the films, is reached after a time, thereby creating a steady but minimal corrosion rate. TRW rated 1100, 7079 and 6061 aluminum, 304, 316, 347, AM 350, 410, 420, PH 15-7 Mo, and Carpenter 20 stainless steel, A-nickel, brass, copper, magnesium alloys HK-31, AZ-31, and HM-31, and Monel as acceptable for service with liquid fluorine. TRW considered a metal compatible if it had a corrosion rate  $<1$  mil per year and didn't cause decomposition. The TRW ratings were based on literature surveys conducted as of 1967.

Further data on the protective nature of fluoride films is presented by Fink and White (Ref 85). According to Fink, a fluoride film will offer protection to the parent metal as long as the film is not volatile at the temperature under consideration. Therefore, metal fluorides which are volatile at low temperatures probably do not give protection against liquid fluorine ( $LF_2$ ) and definitely do not give protection against higher temperature gaseous fluorine ( $GF_2$ ). The melting or sublimation points of selected fluorides are listed in Table 11. This information provides an indication of the compatibility of the parent materials.

Table 11 Melting or Sublimation Regions of Selected  
Fluorine Compounds (Ref 85 and 86)

PROBABLY INCOMPATIBLE			PROBABLY COMPATIBLE		
Below -70°F	-70°F to 70°F	70°F to 250°F	250°F to 850°F	850°F to 1700°F	Over 1700°F
CF <sub>4</sub>	AsF <sub>3</sub>	UF <sub>6</sub>	SbF <sub>3</sub>	SnF <sub>4</sub>	TlF <sub>3</sub>
BF <sub>3</sub>	WF <sub>6</sub>	NbF <sub>5</sub>	TlF <sub>4</sub>	BeF <sub>2</sub>	AlF <sub>3</sub>
SiF <sub>4</sub>	GeF <sub>4</sub>	TaF <sub>5</sub>	AgF	BiF <sub>3</sub>	CoF <sub>2</sub>
PF <sub>3</sub>	TeF <sub>6</sub>	VF <sub>5</sub>		BiF <sub>5</sub>	CrF <sub>2</sub>
PF <sub>5</sub>	SeF <sub>6</sub>	PtF <sub>6</sub>		CrF <sub>4</sub>	CrF <sub>3</sub>
SF <sub>6</sub>	MoF <sub>6</sub>			CuF	CaF <sub>2</sub>
AsF <sub>5</sub>	SbF <sub>5</sub>			PbF <sub>2</sub>	CdF <sub>2</sub>
				PbF <sub>4</sub>	CuF <sub>2</sub>
				LiF	FeF <sub>2</sub>
				MnF <sub>2</sub>	MgF <sub>2</sub>
				HgF <sub>2</sub>	NiF <sub>2</sub>
				KF	NaF
				AgF <sub>2</sub>	
				ThF <sub>4</sub>	
				ZnF <sub>2</sub>	
				ZrF <sub>4</sub>	

Additional information on metal fluoride films has been reported by Fester (Ref 62). According to Fester, film formation or corrosion can be expected to occur when clean metals are exposed to fluorine. With pure fluorine, a fluoride film is formed on the metal surface (about 75% of the limiting film thickness is formed after 15 minutes exposure at one atmosphere). This fluoride film essentially becomes a part of the metal surface rather than being attached, and very little additional reaction occurs with pure fluorine. However, if moisture is present, corrosion occurs. The moisture reacts with fluorine to form hydrogen fluoride, which attacks the metal film and the metal itself. Because the film immediately reforms, a cycle is set up in which the base metal is successfully attacked or reacted away. This process continues until either the hydrogen fluoride or the metal is exhausted; thus, the provision of a clean, dry system is stressed. It should be noted, however, that hydrogen fluoride is a solid (FP= - 117°F) existing as frozen particles in liquid fluorine. Because of this, no HF attack will occur until the temperature is sufficient to liquify the HF. Fester further states that nickel and monel have demonstrated the best performance over the widest ranges of temperature and pressure (-320 to 1200°F and 0 to 1200 psig); but, for many operating conditions, other metals are quite suitable. (Monel is generally used in systems employing hydrogen fluoride.)

Most of the reports published up through about 1967 present essentially the same material compatibility information. This includes the reports by TRW, DMIC, Douglas, and Schmidt (Ref 4,5,61 and 63). The common data referred to in these reports were obtained primarily by NASA-Lewis, Air Products, and Allied Chemical (Ref 63 thru 66).

The fluorine compatibility testing conducted by NASA-Lewis (Ref 63 ) consisted of static exposure tests conducted in 1954, metal ignition temperature tests conducted in 1958, and dynamic compatibility tests conducted in 1962. For the static tests, various metal test specimens were exposed alternately to  $LF_2$  and  $GF_2$  for periods up to 3½ months. The test specimens consisted of 35-0 and 525-0 aluminum, 321 and 347 stainless steel, A-nickel, and low-leaded brass tubes. Upon completion of exposure, only a small weight gain for each

specimen was reported. This was attributed to the formation of the fluoride films. Metallurgical examination showed no signs of intergranular corrosion except in the case of the nickel specimen. However, this corrosion was considered negligible for the time period involved. The physical appearances of the test specimens were reported by the researchers as follows:

- "(1) Both exposed and unexposed surfaces of nickel appeared identical.
- (2) Both aluminum samples appeared considerably lighter in color but appeared unchanged otherwise.
- (3) Iridescence that occurred in some areas of the stainless steels indicated the presence of fluoride films. This was most prevalent in 347-series steels; however, occurrence was not general in test specimens.
- (4) The low-leaded brass was lightly covered with a reddish film that was not continuous, but generally covered the entire surface."

There was no visual difference reported between those portions of the test specimens exposed only to the gaseous phase and those exposed to both liquid and gas, nor was the gas-liquid demarcation line detectable on the specimens.

The NASA-Lewis metal ignition tests were performed to determine the ignition temperatures of metals in  $F_2$  atmospheres (Ref 64). For these tests, wires of various metals were heated electrically while exposed to  $F_2$ . The approximate ignition temperatures found for the metals tested are presented in Table 12. Use of these metals should, therefore, be limited to temperatures considerably below those indicated.

For their dynamic compatibility tests, NASA Lewis ran flow tests with various metals to see if  $F_2$  flow greatly affected fluoride film formation and corrosion resistance (Ref 63). Specimens of several metals (nickel, stainless steel, aluminum, and brass) in various configurations were exposed to  $LF_2$  under controlled conditions of flow and pressure. Rigid control was maintained to ensure cleanliness of both the test system and the specimens. The test specimens were fabricated in three basic configurations; orifices for producing high velocities; flat-faced plugs for flow impact tests; and triangular wedges for turbulence effects and exposure of sharp edges

Table 12 Approximate Ignition Temperature of Various Metals in  $\text{GF}_2$  (Ref 64)

Metal	Ignition Temperature, °F
Aluminum	Above Melting Point
Copper	1275
Molybdenum	400
Monel	740
Nickel	2120
302 Stainless	1255
Tungsten	540

and corners. No measurable physical erosion or chemical attack occurred with any of the test specimens even at flow velocities up to 400 feet per second at a temperature of  $-320^{\circ}\text{F}$  and pressures up to 1500 psig.

In both 1960 and 1962, Air Products reported results of  $\text{F}_2$  compatibility tests conducted for the Air Force (Ref 65). The tests reported in 1960 consisted of static immersion tests, stress corrosion tests, tensile rupture tests, flexure tests, and impact sensitivity tests. For the immersion tests, specimens of various metals were statically exposed to  $\text{LF}_2$  at one atm for periods of time ranging from a few hours to two weeks. No  $\text{H}_2\text{O}$  (i.e., HF) content was reported for the test fluorine. The metals tested were 1100, 2017, 5052, 6061 and 7079 aluminum; 304, 316, 347, and 420 stainless steel; PH 15-7 and AM-350 high-strength steel; nickel, Monel, 30% and 10% Ni cupro-nickel, 6Al-4V and 5Al-2.5Sn titanium, HK-31 and AZ-31 magnesium, copper, and various brasses. Average corrosion rates less than one mil/yr were measured for the 2017 Al, 5052 Al, both titaniums and casted brass. Those metals with corrosion rates between 0.5 and 1 mil/yr were 1100 Al, 6061 Al, 7079 Al, AM-350 steel, Monel, 30% Ni cupro-nickel, both magnesiums and yellow brass with the rest of the specimens having rates less than 0.5 mils/yr but not under 0.1 mil/yr.

For the stress corrosion tests, curved bars of the metals used in the immersion tests were stressed to various levels up to their yield strength and then submerged in  $\text{LF}_2$  for up to 15 days. Dye-penetrant and power-optical inspection revealed no sign of either corrosion or stress cracking.

For the tensile rupture tests, titanium, brass, copper, Monel, and aluminum test specimens were ruptured while immersed in  $LF_2$ . No apparent reaction was reported except in the case of the titanium specimens. Of six tests performed with titanium, one specimen was observed to have ignited.

The flexure tests consisted of flexing thin metal strips in  $LF_2$  once per second for up to 6 hours; the test metals used were copper, brass, aluminum and Monel. No increase in corrosion resulted, indicating the flexibility and resistance of the fluoride film.

The 1960 impact tests conducted by Air Products consisted of impacting both aluminum and titanium samples with various striker geometries (flat, pointed, hollow, etc). Stainless steel and aluminum strikers were used for the aluminum tests while the titanium samples were impacted with Monel or titanium strikers. Impact levels ranging from 2.6 to 61 ft-lbs were employed. Out of 12 specimens, only one aluminum sample ignited. With titanium, however, reaction occurred with 31 of the 51 specimens tested, thus indicating that titanium might be shock sensitive in  $LF_2$ .

The  $F_2$  compatibility data presented by Air Products in 1962 (Ref 65) consisted of long term static immersion test results. For the evaluation, 4.2 square-inch test specimens of various metal alloys were immersed in  $LF_2$  for one year. Five specimens of each alloy were used. The alloys tested were 304 and 410 stainless steel, PH 15-7 steel, Monel, pure copper and nickel, 1100 and 6061 aluminum, 6Al-4V and 5Al-2.5Sn titanium, and AZ-31 and HM-31 magnesium. Upon test completion, average corrosion rates (based on weight change) of less than 0.0035 mils/yr were reported for the 304 stainless, PH 15-7 (recorded rate of .001), copper, nickel, and Monel specimens. The 410 stainless, 1100 and 6061 aluminum, both titaniums, AZ-31 magnesium, and HM-31 magnesium specimens had average corrosion rates just under 0.063, 0.21, 0.28, 0.35, and 0.68 mils/yr, respectively. From these data, it would seem that the earlier (1960) Air Products static immersion test data were not truly representative of actual corrosion rates of metals exposed to  $F_2$ . The higher

corrosion rates reported for the earlier tests were probably due to either having contaminants such as HF present in the fluorine, or more likely, the short test times employed. The weight changes measured in the earlier tests were due to fluoride film formation and were, therefore, not representative of steady state fluorine corrosion.

Allied Chemical reported results of exposing various metal alloys to high temperature fluorine gas (Ref 66). For these tests, 1100, 2024, and 5154 aluminum, MIA, AZ81A, and AZ91C magnesium, Monel, A-nickel, and 304L stainless steel specimens were exposed for 5 days to fluorine gas, ranging in temperature from 80 to 1000°F. At 80°F, corrosion rates ranging from zero to 0.3 mils/yr were measured for all of the alloys. However, at 1000°F all specimens gave rates greater than 1 mil/yr. The approximate temperature range at which a corrosion rate greater than 1 mil/yr first became evident was between 400 and 670°F for 1100 aluminum, 2024 aluminum, and Monel; between 650 and 1000°F for MIA, AZ81A, and AZ91C magnesium, 5154 aluminum, and A-nickel; and between 80 and 400°F for 304L stainless steel.

Martin Marietta conducted both torsion and tensile fracture tests on 6Al-4V and 8Al-1Mo-1V titanium specimens in 1966 (Ref 67). For the torsion tests, four tensile specimens of 6Al-4V titanium were twisted to fracture while immersed in  $LF_2$ . No detectable reaction occurred. For the tensile tests two 6Al-4V specimens and four 8Al-1Mo-1V specimens were pulled to fracture while immersed in  $LF_2$  pressurized with helium. For the 8Al-1Mo-1V specimens, pressures ranging from zero to 100 psig were employed. Again, no reaction was observed.

Since 1967, additional  $F_2$  compatibility data has been reported. During the first phase of a study for the Air Force, McDonnell Douglas conducted ABMA open cup impact tests on various alloy-oxidizer combinations (Ref 57). These tests were described previously in Chapter VI. Only 2014-T6 aluminum was tested with  $LF_2$ . Discs, 40 mils thick, were impacted at 70 ft-lb. Out of twenty tests conducted at -320°F, there were zero reactions.

McDonnell Douglas also reported the results of galvanic corrosion studies with  $LF_2$  (Ref 68). Various metal couples were exposed to  $LF_2$  having low concentrations of HF to see if galvanic corrosion could be detected. The metal couples tested were Ni-200 with 2014-T6 Al, 2014-T6 with 316 SS, Ni-200 with 316 SS, Ag with Invar 36 (nickel alloy), 304L with Invar 36, Ag with 304L SS, and 1100 Al with Cu. The containers for both specimen couples and  $F_2$  were made of 316 stainless steel. Test time and temperature were 21 days at  $-320^\circ F$ . All of the metal couples had corrosion rates greater than usually reported for these alloys when tested alone. For instance, the highest corrosion rate of 0.25 mils/yr was found for the 1100 Al specimen coupled with Cu. The lowest rate was 0.01 mils/yr for the 304L SS specimen coupled with Ag. Besides ordinary corrosion, fairly severe pitting occurred with both the 2014-T6 Al coupled with 316 SS and the Ag coupled with Invar 36 specimens. Also, the 2014-T6 showed signs of intergranular corrosion. Both the Invar 36 and 316 SS showed none of these effects. From these results, the authors felt that galvanic corrosion effects will definitely be present for metal couples exposed to  $LF_2$  if these couples are composed of metals differing in electrode potential by a fairly large amount. The following relative-galvanic corrosion series was presented by the authors for the metals tested:

304L stainless steel	
Copper	
316 stainless steel	Increasing
Invar 36	Anodic
Nickel-200	Behavior
Silver	
2014-T6 aluminum	
1100 aluminum	

Therefore, use of either 304L or Cu with either 2014 or 1100 Al should probably be avoided to minimize galvanic corrosion effects.

As part of Boeing's fracture toughness and flaw growth tests, discussed earlier in Chapter VI, 2219-T851 Al and 6Al-4V Ti as-welded weldment specimens

were tested with  $LF_2$  at  $-320^{\circ}F$  and 450 psig (Ref 54). Of the two alloys tested, the 2219 weldments showed the lowest threshold stress intensity values. For this alloy, a threshold stress intensity of  $15.5 \text{ Ksi}\sqrt{\text{in}}$  was obtained while for the 6Al-4V Ti weldments, an intensity of  $28 \text{ Ksi}\sqrt{\text{in}}$  was reported. Both of these values are high enough to conclude that no functional problems should exist for pressurized  $LF_2$  tanks manufactured from either alloy.

Some of the most recent information on  $F_2$  compatibility has been reported by Martin Marietta (Ref 69). Twelve screen specimen assemblies, representing candidate materials and fabrication techniques used for capillary screen devices, were manufactured for test with  $LF_2$ . The specimen assemblies consisted of a cylindrical, 325 x 2300 mesh, Dutch twill type stainless steel wire cloth supported by a coarse 80 mesh stainless steel inner screen. Both resistance and fusion welds were employed in the fabrication. The two layers of screen were fusion welded to a metal cap plate at one end and a metal washer plate at the other end. No weld rod was employed. Cleaning techniques for fine mesh screen systems to be used with fluorine were evaluated by exposing the cleaned screen specimens to  $GF_2$  passivation and then immersing the assemblies in  $LF_2$ . Normal chemical cleaning for fluorine systems, high-temperature vacuum annealing, and chemical cleaning followed—by annealing were evaluated. All three cleaning procedures were successful since the test assemblies were successfully passivated and stored in  $LF_2$  for up to 35 days. Based on the results obtained, a fluoride film buildup or corrosion rate between  $3.5 \times 10^{-6}$  and  $6.35 \times 10^{-6}$  in/year was calculated based on the assumption of a logarithmic rate mechanism. Using microscopic examination, no surface film was observed on a cross-section of the 325 x 2300 screen after test, nor was any evidence of attack or screen deterioration apparent. Based on these limited data, it appears that high surface area, low thermal capacity systems, such as capillary screen systems, can be successfully used with  $F_2$  if properly cleaned and passivated.

## 2. Compatibility with Non-Metals

According to TRW (Ref 4), non-metals are totally unacceptable for  $F_2$  service since all non-metals are severely attacked when exposed to  $F_2$ . Only

Teflon under static conditions has shown some compatibility. According to TRW, Teflon apparently reacts with  $F_2$  to break down its polymers and form unsaturated, low molecular weight fluorocarbons which do not adhere to the surface. Any flow of the propellant or movement of material over the Teflon surface will remove these fluorocarbons which are thus valueless as a protective film. Therefore, for any dynamic applications, Teflon would be unsuited.

Air Products, in summarizing test results prior to 1963, classified various non-metals for static use with both  $GF_2$  and  $LF_2$  (Ref 65). The Air Products listing for some of the more common non-metals is shown in Table 13. Teflon would seem to be compatible. Also, fluorinated hydrocarbons such as Kel-F may be usable but at low pressures. Rubbers would seem to be unusable.

In a series of tests conducted by NASA-Lewis (Ref 70), the compatibility of various non-metal materials with  $F_2$  and  $O_2$  mixtures (FLOX) were investigated. Both dynamic and static tests were run utilizing both gaseous and liquid FLOX. The concentration of the  $F_2$  in the FLOX propellant was varied up to 100%  $F_2$ . A summary of the type of reactions observed between the non-metals and fluorine is presented in Table 14. Basically, the dynamic tests consisted of flow tests at high pressure. Even the highly fluorinated and chlorinated hydrocarbons such as Teflon, Kel-F, and CPE, were incompatible with  $F_2$  under dynamic conditions. However, it took a flow velocity of 230 to 280 feet per second for both the Halon TFE and Teflon TFE samples to react.

Further dynamic tests with non-metals have been reported by McDonnell Douglas (Ref 71). Type 316 stainless steel discs, coated on one side with Kel-F 90, petroleum jelly, polyurethane, and acrylic lacquer, were impact tested in  $LF_2$ . After applying the organic coatings, the specimens were exposed to gaseous fluorine for one hour at one atmosphere at  $77^\circ F$ . Following passivation, specimens were impact tested in a modified ABMA tester in liquid fluorine at  $-320^\circ F$  at 72 ft-lb energy level. All impacts yielded reactions ranging from moderate to extreme, indicating that all organic residues were impact sensitive. One of the petroleum jelly coated specimens and one of the acrylic lacquer coated specimens reacted violently in the liquid fluorine before actual impact. Reactions occurred spontaneously after about five seconds contact with liquid fluorine. Neither the Kel-F 90 nor the polyurethane foam specimens reacted prior to impact. Under another program, McDonnell Douglas found that Viton

Table 13 Compatibility of Various Non-Metals for Static Fluorine Service (Ref 65)

Non-Metal	(-320°F)LF <sub>2</sub>		(Rm Temp)GF <sub>2</sub>	
	1 Atm	1500 psia	1 Atm	1500 psia
Ruby (Al <sub>2</sub> O <sub>3</sub> )	A	A	A	A
Alumina	N.D.	N.D.	A	N.D.
Asbestos	N.D.	N.D.	A	N.D.
Graphite	N.D.	N.D.	A	B
Charcoal	N.D.	N.D.	C	N.D.
Teflon	A	A	A	A
Kel-F	A	B	A	B
Neoprene	D	N.D.	A	B
Rubber	N.D.	N.D.	C	N.D.
Polyvinyl Chloride	N.D.	N.D.	A	B
Plexiglass	A	B	A	B
Tygon	A	B	A	B
Polystyrene	N.D.	N.D.	B	N.D.
Polyethylene	N.D.	N.D.	B	N.D.
Polyester Plastics	N.D.	N.D.	C	N.D.

NOTE:

A = No reaction  
 B = Reaction but no burning  
 C = Burning  
 D = Explosion  
 N.D. = No Data

Table 14 Reactions of Non-Metals with Fluorine (Ref 70)

Material	Type of Reaction			
	Smooth Burning		Explosive Burning	
	Gas	Liquid	Gas	Liquid
<u>(a) Static Tests</u>				
Viton A		X		
Trifluoropropyl Rubbers				
LS-53	X	X		
LS-63		X		
Tygon		X		
Neoprene		X		
Polyurethane Foam	X			
Graphite				X
Nylon				X
Polyethylene				X
Buna N				X
Bakelite				X
<u>(b) Dynamic Tests</u>				
Teflon TFE		X		
Halon TFE		X		
Kel-F 81		X		
Plaskon 2400 (CTFE)		X		
Halon TVS (CTFE)		X		
Nickel-filled Teflon		X		
Teflon FEP		X		
Kel-F 81 amorphous	X	X		
Kel-F 82	X	X		
Lucite		X		
Rulon A (MoS <sub>2</sub> filled TFE)				X
Kynar				X
Viton A			X	X
Chlorinated Polyethylene				
CPE 401		X		
CPE 402				X
CPE 403-XCL		X		

reacted violently upon exposure to  $GF_2$  at 500 psi and  $-240^\circ F$  (Ref 57).

From the data presented so far, it would seem that Teflon is probably compatible with fluorine under static conditions. However, if Teflon contains organic solvents such as trichloroethylene or Freon 113 used in cleaning operations, it may then be totally incompatible with  $F_2$ . On the basis of tests performed on Teflon gaskets soaked in either trichloroethylene or Freon 113 and then exposed statically to  $LF_2$ , Boeing found that the Teflon became incompatible (burned) if it absorbed (or contained) more than 0.35% trichloroethylene (Ref 72). However, after absorbing as much as 0.85% Freon 113, no reaction was observed between Teflon gaskets and  $LF_2$ , indicating that this solvent is more compatible with  $LF_2$  than trichloroethylene. Tests were also conducted to see if solvent concentrations could be reduced. Teflon gaskets containing as much as 0.43% trichloroethylene were vacuum-oven dried for up to four hours. After this period of drying, the trichloroethylene concentration was reduced to only 0.06%. Therefore, this technique seems applicable for removing certain types of trace impurities from Teflon prior to fluorine exposure.

VIII. OXYGEN DIFLUORIDE

VIII. OXYGEN DIFLUORIDE

## A. COMPATIBILITY SUMMARY

The compatibility of non-metals with  $\text{OF}_2$  is summarized in Table 15. Metals were not included since there is little difference between the compatibility of metals with  $\text{OF}_2$  and their compatibility with  $\text{F}_2$ . Therefore, the compatibility of metals with  $\text{F}_2$ , presented in Table 10 of Chapter VII, applies equally to the compatibility of metals with  $\text{OF}_2$ . This approach was not applicable to non-metals since differences existed in the compatibility of non-metals with  $\text{OF}_2$  and  $\text{F}_2$ , discussed in Section B of this chapter. A non-metal was included in Table 15 on the basis of direct data, data on a similar material, or data on the material with a similar propellant. The ratings reflect the extent to which the propellant affects the non-metal.

Table 15 CF<sub>2</sub> Summary Compatibility Chart for Non-Metals

Non-Metal	Rating					References	Remarks
	1	2	3	4	5		
Teflon FEP		A				74, 80	All non-metals listed rated for both dynamic and static liquid service.
Teflon TFE		A				74, 80	
Halon TFE		A				80	
CTFE's in general		B				80	
ALMAC CTFE		A				80	
Plaskon 2200 CTFE		A				80	
Genetron VK or HL			A			74	
Mylar			A, C			65, 74	
Kel-F		B		C		74, 80	
All rubbers in general				C		4, 65, 70	
Polyethylene				C		4, 65, 70	
TRW elastomer 202-1		A				40	
All other non-metals in general					D		Testing needed (no specific data).

- 1 - Compatible
  - 2 - Probable Compatibility
  - 3 - Doubtful Compatibility
  - 4 - Incompatible
  - 5 - Unable to Rate
- 
- A - Rating based on data on the specific material with the specific propellant
  - B - Rating based on data on a similar or sister material with the specific propellant
  - C - Rating based on data on the specific material but with a sister propellant
  - D - No specific data

## B. GENERAL DISCUSSION

Oxygen difluoride is a powerful oxidizing agent very similar to  $F_2$  and the halogen fluorides. It is generally a stable compound in that it neither detonates by sparking, nor thermally decomposes at ordinary storage temperatures ( $OF_2$  will begin to decompose thermally at approximately  $470^\circ F$  (Ref 4)). Therefore, the only problems connected with its storage are ones caused by its high reactivity (corrosion, etc.) and not its decomposition.

When considering the high reactivity of  $OF_2$  and its effects on storage materials, information on  $F_2$  is of importance. Both  $OF_2$  and  $F_2$  behave almost identically in regard to their capability for reacting with practically any inorganic or organic compound. Although  $OF_2$  is generally considered less reactive than  $F_2$  (Ref 4), most authors (Ref 62 and 73) usually recommend that the same storage materials and techniques used for  $F_2$  should also be used for  $OF_2$  since differentiation between the reactivity of the two oxidizers is difficult. In general, it can at least be said that materials considered compatible with  $F_2$  will be as compatible or more compatible with  $OF_2$  (Ref 5). Therefore, the materials compatible with fluorine, as presented in Chapter VII, would be considered suitable for use with  $OF_2$ . These data are not reiterated here; instead, only data showing differences in compatibility between  $OF_2$  and  $F_2$  are presented.

### 1. Compatibility with Metals

The information presented in Reference 39 and References 73 through 80 was reviewed in evaluating the compatibility of metals with  $OF_2$ . These references summarize static immersion, dynamic flow, tensile, and impact testing of metals with  $OF_2$ . Only References 76 and 77 contain data differing from those found with  $F_2$ . Unexpectedly, the differences tend to show better compatibility with  $F_2$  than with  $OF_2$ .

Douglas conducted impact sensitivity and corrosion tests in investigating the compatibility of various storage metals with  $OF_2$  (Ref 76). The results of the impact tests do not disagree with similar results obtained with  $F_2$ . However, some of the corrosion results do disagree with results reported for  $F_2$ . Lox-clean metal discs were tested in an open cup ABMA type impact tester

at  $-320^{\circ}\text{F}$ . Up to 20 tests per metal type were conducted to determine if any of the test metals would ignite and burn upon impact when in contact with  $\text{OF}_2$ . The corrosion tests consisted of two types. In the first case, Lox-clean metal specimens were placed in 316 stainless steel containers filled with liquid  $\text{OF}_2$  at  $-110^{\circ}\text{F}$ . The tests lasted one year; corrosion rates were determined by change in weight. The second test series was similar to the first, except that test duration was only one day and the  $\text{OF}_2$  used was doped with 1%  $\text{H}_2\text{O}$  to determine the effect moisture would have on  $\text{OF}_2$  corrosion. In both corrosion tests, none of the samples were first passivated with  $\text{OF}_2$  or  $\text{F}_2$ .

Aluminum alloys (1100, 2014, 2024, 2219, 7075, etc), stainless steels (301, 316, 347, AM350, AM355 and PH 15-7), nickel and copper alloys, and different miscellaneous metals (5Al-2.5Sn Ti, Mg, Ta, and columbium-A) were selected for the impact tests. All the aluminums, stainless steels and nickel and copper alloys showed no signs of ignition when impacted at 72 ft-lbs. However, both the Ti and Mg alloys flashed upon impact and appeared melted. The Ta and Nb samples showed no impact sensitivity.

These metals were also tested for corrosion. All materials appeared compatible except for 5Al-2.5Sn titanium. Based on testing, titanium alloys seem to have excellent corrosion resistance to  $\text{F}_2$ . Why this particular alloy exhibited incompatibility with  $\text{OF}_2$  cannot be readily explained unless contamination was present.

TRW presents the results of tests conducted at Douglas which investigated corrosion of metal orifices when subjected to liquid  $\text{OF}_2$  flow (Ref 77). The results showed that 1100 aluminum is not very resistant to this condition, but Monel 400A, 316 and 347 stainless steel, nickel-200, 2014 and 6061 aluminum, columbium, and Cufenloy-40 show good to fair resistance. TRW further states that aluminum alloys 2014, 2219, and 6061 are subject to intergranular corrosion adjacent to welds, but that none of the metals are prone to stress-corrosion cracking in  $\text{OF}_2$ . It would appear that some aluminum and copper alloys are unsuitable for dynamic  $\text{OF}_2$  service. This is in direct opposition to the dynamic flow tests conducted at NASA-Lewis, as discussed previously in Chapter VII. In the NASA-Lewis tests, both aluminum and copper orifices were essentially

unaffected by  $LF_2$  flow (Ref 63). Therefore, either aluminum or copper alloys do react differently with  $OF_2$  than with  $F_2$  or some other factor, such as contamination, may have been present in the Douglas tests.

## 2. Compatibility with Non-Metals

The information in Ref 73 through 81 plus Ref 40 was used in evaluating compatibility of non-metals with  $OF_2$ . As with the metal data, any compatibility information which differs from that for  $F_2$  is presented. In general, the non-metals are more compatible with  $OF_2$  than with  $F_2$ .

In flow tests run at  $-320^\circ F$  and 7 psia for up to 5 hours in duration, Allied Chemical exposed small orifices (exposure area approximately 3 to 2 in<sup>2</sup>) of Teflon, Mylar, and Genetron VK and HL polymers to liquid  $OF_2$  flowing at 0.85 ft/sec (Ref 74). No reaction was observed. The only effects noted were minor weight gains of less than 0.9 mg in the Teflon and Mylar samples and weight losses of approximately 3 mg in the Genetron samples.

In more recent dynamic flow tests, Allied Chemical exposed orifices made out of various fluorinated plastics to liquid  $OF_2$  flow at much higher pressures and flow velocities than in the earlier tests (Ref 79). FEP and TFE Teflon, TFE Halon, and Almac and Plaskon 2200 chlorotrifluoroethylene orifices, 0.0135-in. diameter, were tested at flow velocities up to 300 ft/sec and pressures as high as 500 psig. Upon test completion, none of the orifices showed any sign of reaction or erosion and weight changes were minimal. On the basis of these tests, Allied considered the test materials to be chemically compatible with liquid  $OF_2$ , even under the high pressure and flow velocity conditions.

TRW conducted compounding studies to develop and characterize elastomeric materials suitable for use as positive expulsion bladders with  $OF_2$  (Ref 40). As a result, TRW developed an alumina reinforced, peroxide cured CIS-4 polybutadiene as their optimum compound. This formulation was designated compound 202-1.

To verify applicability of the material for use as an expulsion bladder for  $OF_2$ , TRW conducted tensile rupture, expulsion, long-term static immersion and permeability tests on compound 202-1. Specimens strained to breaking while immersed in  $OF_2$  at  $-109^\circ F$  ignited. However, only 13% by weight was consumed and the remaining material still retained its mechanical properties.

In small scale expulsion tests conducted at  $-109^{\circ}\text{F}$ , a 202-1 diaphragm went through 40 expulsions without any apparent degradation. Specimens of 202-1 stored in both relaxed and bent conditions for 42 days at  $-109^{\circ}\text{F}$  showed only minor mechanical property changes. Based on the test data, TRW calculated a loss in strength of only 0.3% per year and a propellant loss rate due to permeability of less than 0.1% per year for a 10-in. diameter bladder containing  $\text{OF}_2$  at  $-139^{\circ}\text{F}$ . This would seem to indicate that compound 202-1 could be used as a bladder material for  $\text{OF}_2$  service. However, any rupture or tearing of such a bladder would have to be avoided to prevent triggering ignition of the compound with  $\text{OF}_2$ .

IX. FLOX

IX. FLOX

## A. COMPATIBILITY SUMMARY

According to the information available to date, no differences exist between the compatibility of materials with fluorine and Flox mixtures containing 70% or more, fluorine. Therefore, the compatibility summary for metals and non-metals with fluorine, presented in Table 10 of Chapter VII, is also applicable for Flox mixtures ( $>70\% F_2$ ). One possible difference may exist with titanium. Titanium alloys have shown a tendency toward shock sensitivity with  $F_2$  and were rated as having doubtful compatibility. The same rating is also applicable with Flox; however, compatibility with Flox is probably more doubtful since titanium alloys are definitely shock sensitive with oxygen. This is especially true for Flox as the concentration of oxygen is increased. As with fluorine and oxygen difluoride, the primary concern with Flox is the extent that the propellant affects the material.

C3

## B. GENERAL DISCUSSION

Flox is a mixture of liquid fluorine and liquid oxygen. Typical mixtures are 80%  $F_2$ /20%  $O_2$  and 70%  $F_2$ /30%  $O_2$ , although JPL has recently become interested in a Flox mixture of 88%  $F_2$ /12%  $O_2$ . Flox, like  $F_2$ , is capable of reacting with practically any inorganic or organic compound. Therefore, most authors usually recommend only those materials which have shown compatibility with  $LF_2$  for service with Flox. TRW, for instance, specifically states that any material which performs well in  $LF_2$  will also work in Flox (Ref 4 ).

### 1. Compatibility with Metals

Essentially no information is available on the compatibility of metals with Flox mixtures. As stated above, most authors just recommend metals which are compatible with  $F_2$ , e.g., Schmidt presents only compatibility data on  $F_2$  but applies the results to Flox mixtures (Ref 63). Therefore, those metals recommended as being compatible for  $F_2$  service (Chapter VII) would also be compatible with Flox mixtures. Since titanium has exhibited a tendency toward shock sensitivity with fluorine (Chapter VII) and is definitely shock sensitive with oxygen (Ref 5 and 82) titanium and its alloys are probably shock sensitive in Flox (especially those mixtures having fairly high oxygen concentrations). Until further information becomes available, the use of titanium in Flox systems should probably be avoided.

### 2. Compatibility with Non-Metals

As with metals, very little specific information exists on the compatibility of Flox mixtures with non-metals. About the only information available is contained in a NASA-Lewis report describing compatibility tests performed on a number of polymeric materials using various mixtures of fluorine and oxygen in both the gaseous and liquid states (Ref 70 ). Both dynamic flow and static immersion tests were conducted.  $F_2$  concentration varied up to 100%. All test samples were first washed with soap and water, rewashed with an appropriate cleaning solvent, and finally dried with He. The results showed:

- 1) Reactions between Flox and polymeric materials under static conditions are a function of the concentration of fluorine in the mixture.

Several materials which did not react with Flox under static conditions were reactive under dynamic conditions. In general, the higher the flow velocity, the lower the fluorine concentration each material withstood;

- 2) Generally, the unimpregnated, highly fluorinated and highly chlorinated materials were more compatible than materials containing atoms such as hydrogen in their molecular structure or materials impregnated with some noncompatible additive. The fully fluorinated straight-chain polymers, such as Halon TFE and Teflon TFE, were the most compatible with Flox;
- 3) Materials with higher crystallinity (orderly molecular alignment) were more resistant to attack by Flox than the more amorphous materials;
- 4) A comparison between liquid ( $-320^{\circ}\text{F}$ ) and gaseous ( $30^{\circ}$  to  $70^{\circ}\text{F}$ ) test results indicated that the liquid was more reactive at pressures up to 400 psig.

X. REFERENCES

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