NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Memorandum 33-561

Survey of Materials for Hydrazine Propulsion Systems in Multicycle Extended Life Applications

C. D. Coulbert
G. Yankura

(NASA-CR-128491) SURVEY OF MATERIALS FOR HYDRAZINE PROPULSION SYSTEMS IN MULTICYCLE EXTENDED LIFE APPLICATIONS C.D. Coulbert, et al (Jet Propulsion Lab.) 15 Sep. 1972 144 p
CSCL 20I G3/27
N73-11788
Unclas
46206

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA
September 15, 1972

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Memorandum 33-561

Survey of Materials for Hydrazine Propulsion Systems in Multicycle Extended Life Applications

C. D. Coulbert
G. Yankura

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

September 15, 1972

PRECEDING PAGE BLANK NOT FILMED

PREFACE

This survey was performed by the Propulsion Division of the Jet Propulsion Laboratory for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Materials Division of the MSFC Astronautics Laboratory with Mr. John T. Schell acting as technical representative.

PRECEDING PAGE BLANK NOT FILMED

CONTENTS

CONTENTS (contd)

FIGURES

ABSTRACT

This report presents an assessment of materials compatibility data for hydrazine monopropellant propulsion systems applicable to the Space Shuttle vehicle missions. Materials were evaluated for application over a 10-yr/100-mission operational lifetime with minimum refurbishment.

A general materials compatibility rating for a broad range of materials and several propellants based primarily on static liquid propellant immersion testing and an in-depth evaluation of hydrazine decomposition as a function of purity, temperature, material, surface conditions, etc., are presented.

The most promising polymeric material candidates for propellant diaphragms and seals appear to have little effect on increasing hydrazine decomposition rates, but the materials themselves do undergo changes in physical properties which can affect their 10-yr performance in multicycle applications. The available data on these physical properties of elastomeric materials such as EPT-10 and AF-E-332 as affected by exposure to hydrazine or related environments is presented.

The data in this report provides a basis for the preliminary selection of propulsion system materials. The results of system and component long-term compatibility studies currently being conducted by the Air Force, Martin-Marietta, JPL, and others plus the completion of studies recommended in this report will enable the prediction of the 10-yr multicycle performance of the selected materials.

I. INTRODUCTION

The objective of this report is to summarize and assess the existing information and data on materials compatibility with hydrazine monopropellant as applied to the requirements of Space Shuttle vehicle auxiliary propulsion systems. It is expected that these systems will be capable of 10-yr/100-mission operational lifetimes with minimum refurbishment. Allowing for qualification and checkout procedures, a 10-yr/1000 total cycle lifetime was fixed as the performance requirement for this study. It was assumed that the temperatures of interest would span the normal liquid range of hydrazine (+2 to +110°C).

The sources of information for this study included recently published reports (Refs. 1-5), parts of which are included here as appendices, plus contacts with agencies currently engaged in hydrazine compatibility studies (Refs. 6-8) and a review of the work in progress at JPL (Refs. 8-13). In much of the research on hydrazine compatibility the times of testing were two years or less and the tests were noncyclic or were limited to a few cycles (except in the case of valve seals and seats).

It appears that cyclic performance of metals does not pose a special design problem, but the long-term life and properties of polymeric materials used for bladders or diaphragms subject to 1000 operating cycles over a 10-yr period are largely unknown. Therefore, recommendations for an experimental program in this technical area have been formulated.

II. MATERIAL SELECTION AND RATING CRITERIA

Compatibility of metallic and nonmetallic materials with hydrazine is concerned with two principal phenomena: degradation of the material and decomposition of the hydrazine. Other effects such as catalyst bed poisoning, filter plugging, and propulsion performance degradation have not been experienced as pacing or critical problems.

A. Metallic Materials

In the case of metals considered as candidate structural materials, the controlling degradation phenomenon has been hydrazine decomposition (Ref. 1). This is normally manifested as gas evolution with a consequent system pressure rise. In cases where metallic corrosion, pitting, or sludge formation were excessive, the system pressure rise usually exceeded acceptable limits first (Ref. 14). Furthermore, in most cases where hydrazine decomposition was significant, the decomposition rates appeared to be controlled by impurity catalyzed reactions traceable to insufficient propellant purity or to cleaning and passivation techniques (Ref. 5).

For structural applications in tanks, lines, and valves, the three major types of metallic materials selected have been the alloys of aluminum, titanium and stainless steels. All three have been or are currently specified in flight-rated hydrazine systems including those for the Viking Lander and Mariner series spacecraft (Refs. 8, 10, 11, and 15). The particular alloys selected and those for which there is the most complete compatibility data include the aluminum alloys 6061, 2014 and 2219, the titanium alloy 6Al-4V, and the stainless steels 301, 304, and 321 (Appendix A). All of these alloys when tested by immersion in propellant grade hydrazine have exhibited much less than 1 mil/yr surface erosion. Data on some of these materials (6061-T6Al, 2014-Al) is available for periods of 4 or more years; other tests are in progress (Refs. 6, 16) which will provide immersion data for periods of up to 5 years and longer. Cryoform 301 stainless steel, which is a controlled-chemistry, specially hardened form of SS 301, has proved very compatible with hydrazine in tank storage tests (Ref. 6) and in fracture mechanics tests at NASA-MSC.

The long-term rates of decomposition of hydrazine in contact with metals is difficult to predict for many reasons, but the curves in Fig. 1, which presents data from three sources, indicate that storage in certain materials is feasible for a 10-yr period at temperatures below 50 °C. It may be noted that Rocketdyne (Ref. 5 and Appendix B) and SRI (Ref. 17) conducted decomposition tests at elevated temperatures for times of less than 1 month and extrapolated the reaction rates to lower temperatures, whereas the JPL data point (Ref. 3) took 4 years to generate. This data demonstrates the high sensitivity of decomposition to storage temperatures (factor of 10 in 20 °C). Sensitivity to impurities and other controlling parameters are discussed in Appendix B and will also be considered herein subsequently.

There is no data available indicating that those materials in contact with hydrazine are subject to stress corrosion cracking, intergranular corrosion, or shock sensitivity. Fracture mechanics data is currently being obtained on three alloys: titanium 6Al-4V (by Martin-Marietta), aluminum 6061-T6 (Boeing for JPL), and Stainless Cryoform 301 (NASA-MSC). Initial results indicate that no special problems exists for long-term stress or fatigue application of these metals.

A detailed discussion of the compatibility rating of a broad range of metals under different conditions of propellant exposure is presented in Ref. 1. The "Hydrazine" section of that report is included herein as Appendix A. A further discussion of some of the conflicting compatibility results reported in Appendix A is presented in Section IV.

B. Nonmetallic Materials

The primary applications for nonmetallic materials in hydrazine propellant systems are in expulsion systems as diaphragms or bladders and as valve seats or seals. Although Teflon seems to be one of the more compatible materials for N_2H_4, it is very permeable to N_2H_4 and therefore is not used as a diaphragm material but is used satisfactorily in O rings. The types of elastomeric materials currently considered most suitable for hydrazine storage are the EPR (ethylene propylene rubbers) and EPT (ethylene propylene terpolymer) compounds (Refs. 11, 13, and 15). The summary of hydrazine compatibility data on these and other nonmetallics is presented in Appendix A, which includes a discussion of the effects of various fillers used. The available physical property data on EPT-10 and similar materials currently being evaluated at JPL as a diaphragm material is presented in Appendixes C and D.

With regard to the use of elastomeric materials as a diaphragm material in contact with hydrazine over a period of 10 yr and subject to 1000 cycles, it is clear that available data has not established this capability for any of the above candidate materials. Storage and system tests which are currently being conducted are concerned with 1- or 2-yr missions and a limited number of cycles.

Section II-B-2 of Appendix A reports a N_2H_4 decomposition rate of 0.0038%/day (or 4% in 3 yr) in contact with EPR samples at 37.8°C (110°F). Lower values have been achieved by a passivation treatment consisting of a fairly long presoak in hydrazine. Quantitative data on real-time decomposition rates applicable to 10-yr operation is not available.

In the Shuttle mission, however, pressure rise in a closed system over a 10-yr period or change in the hydrazine composition over a several year period may not be problems because the system will be used, drained, and refilled many times over the 10-yr period. Of greater concern will be the fatigue life or cycling performance of the tank diaphragm and possibly the effects of the permeability of hydrazine into the pressurant gas system and components. Limited data is available on the effect of hydrazine contact and immersion on physical properties of elastomers such as elongation, permeability, tensile strength, modulus, compression set, stress relaxation, fatigue, creep, swelling, etc. More is needed, and recommendations in this area are discussed in Section VI.

Elastomeric valve seat materials evaluated by TRW (Ref. 18) and JPL in multimillion cycle tests have included several Teflon and Kel-F composites and EPT compounds. Results have indicated that the TRW-developed EPT compound designated AF-E-102 is one of the most satisfactory for long-life valve seat application.

III. PROPELLANT CHEMISTRY

A. Research on Hydrazine Decomposition

A major comprehensive investigation of the liquid phase thermal decomposition of hydrazine is reported in Ref. 5. A major portion of this report has been reproduced as Appendix B herein for convenience. This report answers many questions concerning the relative effects on hydrazine decomposition of a large number of parameters. Testing was conducted in sealed Pyrex ampoules with an internal volume of 1.0 ml filled with 0.3 ml of liquid hydrazine. The amount of propellant decomposition was calculated by breaking the ampoules in a vacuum system and determining the amount of nitrogen and hydrogen present.

The parameters investigated during this program as reported in Ref. 3 (Appendix B) included the following:

(1) Fluids: propellant grade hydrazine, three batches; purified hydrazine, two sources.

(2) Temperatures: 95 to 246°C.

(3) Times: 0.3 to 600 h.

(4) Pressure: vapor pressure to 4137 kN/m^2 (600 psi).

(5) Ampoule cleaning and passivation.

(6) Ullage volume.

(7) Amount of glass surface.

(8) Quartz vs Pyrex ampoules.

(9) Metal surfaces: 321 SS, 304 SS, 316 SS, 347 SS, Ni, Fe, Al, Be, Hg, Chromel A, and copper.

(10) Cleaning and passivation of metals.

(11) Propellant impurities: H_2O, NH_3 aniline, toluene, NH_4Cl, NaCl, Fe, carbazic acid, etc.

(12) Propellant pretreatment and additives: acids, bases, resins, oxides, etc.

Because of the many combinations of parameters involved and the constraints of the experimental techniques used, caution must be used in the direct application of this Rocketdyne data to the design of a propulsion system and to the prediction of its long-term performance. However, several important conclusions applicable to system design may be drawn with regard to important parameters, and these are discussed below under appropriate headings.

1. Time and temperature. Some 1000 separate experiments were conducted and several significant quantitative decomposition rate relationships were established with respect to time and temperature. However, the longest test time was 600 h and the lowest temperature employed was 95°C, with most data taken at 128 or 171°C at times less than 200 h. The extrapolation of decomposition rate data to lower temperatures and longer times is shown as an Arrhenius plot in Fig. 6 of Appendix B. In terms of 10-yr decomposition and for temperatures between 2 and 110°C, the Rocketdyne data for SS 321 is plotted in Fig. 1 together with SRI (Ref. 17) and JPL (Ref. 3) data for hydrazine in Pyrex ampoules. Although the Rocketdyne data demonstrates the sensitivity of decomposition rates to such parameters as impurities, surface-to-volume ratios, and ullage volumes, consistent quantitive relationships could not be defined. It is encouraging, therefore, that the comparison in Fig. 1 between 4-yr data in 40 cc of hydrazine compares favorably with 100-h data on 0.3 cc of hydrazine.

2. Propellant purity. The composition of propellant grade hydrazine is descibed by MIL-P-26536 C (Ref. 19) in terms of hydrazine, water, and particulate as follows:

N_2H_4 – 98% minimum by weight.

H_2O – 1.5% maximum by weight.

Particulate – 10 mg/l (maximum).

This specification does not define limits on specific impurities which have been identified in propellant grade hydrazine (Ref. 5) such as ammonia, aniline, toluene, iron, and carbazic acid (reaction product of N_2H_4 a CO_2), even though the impurities in the hydrazine (at the ppm level) or in the propellant system hardware cause the compatibility problems. This specification is currently under review by the Air Force and is subject to modification in accordance with user requirements.

Rocketdyne conducted tests with both propellant-grade hydrazine and hydrazine purified by two techniques. In Pyrex, the high-temperature stability of hydrazine was improved by purification approximately an order of magnitude. However, it is not clear from the chemical analysis of the purified hydrazine (Appendix B, Table 3) which critical impurities were removed. Purified hydrazine still contained >0.2% H_2O plus NH_3, aniline, and toluene. Furthermore, the rate of purified hydrazine decomposition in contact with 321 stainless steel (Appendix B, Fig. 8) after 100 h approached that for propellant grade hydrazine. This may possibly be related to the leaching of iron, chromium, and nickel into the purified hydrazine as demonstrated by immersion tests with radioactive 304 stainless steel (Fig. 2). In these foil immersion tests, the concentrations of radioactive Fe and Cr in the hydrazine approached 40 ppm in 100 days.

The Rocketdyne studies indicate the sensitivity of decomposition to Fe, but no quantitive relationship could be established. In view of the fact that Fe can be leached into N_2H_4 from both stainless steel and titanium alloys, the long-term advantage of using purified hydrazine to decrease decomposition may be negligible.

The effects of specifically adding various amounts of ammonia, water, aniline, and toluene to purified hydrazine were investigated and the change in decomposition rate was recorded, but a consistent quantitative relationship could not be established.

From the standpoint of long-term system operations, the possible contamination of the hydrazine or the propulsion system by salt (NaCl) or salt water is of interest, and it was investigated by Rocketdyne. They concluded that NaCl contamination in the amounts investigated would not be detrimental.

The effect of acidic contamination, however, was critical, as shown by the addition of carbazic acid, HCl, and ammonium chloride. Because CO_2 reacts rapidly with hydrazine to form carbazic acid, the carbazic acid could come from the contact of hydrazine with air. It can be calculated, however, that hydrazine must contact considerable amounts of air to accumulate appreciable quantities of carbazic acid because sea level air contains approximately only 315 ppm CO_2.

The decomposition rate of purified hydrazine at 128°C in Pyrex ampoules did not increase with 0.12% carbazic acid added, but in the presence of 321 stainless steel the rate increased 1000 times. Similar effects were recorded for HCl and NH_4Cl additions.

Although the range of conditions affecting hydrazine stability covered by Rocketdyne was large, many anomalous data points suggest that all critical parameters were not defined but only touched upon. This is suggested by several quotes from the report (Appendix B):

(1) Page 67: "It is possible, of course, that the increase in rate which does occur results from impurities in the distilled water rather than from the water itself."

(2) Page 19: "The results of this investigation indicate that the thermal stability of propellant-grade hydrazine is determined by trace impurities which are present at concentrations near or below their detection limit."

(3) Page 33: "The average decomposition rate (for purified N_2H_4) in prepassivated ampoules was about 60 percent higher than in unpassivated ampoules --- propellant-grade hydrazine was employed in the passivation process, and is an indication that certain trace impurities may be rate controlling."

Until further specific data is available, it should be concluded that material compatibility ratings are not improved by using purified hydrazine.

B. Residue Formation

Hydrazine in contact with various metals and nonmetals leaches out contaminants which potentially could cause the formation of filter or valve clogging material. An investigation of this problem is reported by TRW in Ref. 20. The propellant-grade hydrazine was analyzed for dissolved metal content, selected anions and nonvolatile residue. Metal content analysis indicated traces of Fe, Al, Ni, Mn, Co, Cr, Cu, and Zn present at levels below 20 ppm.

It was established that various forms of residue could be formed by the addition of sufficient metal salts, but such high levels would only be experienced when other forms of degradation would be excessive, i.e., decomposition or corrosion.

Two cases of filter and line clogging in Intelsat and Mariner hardware were investigated (Ref. 20), and the sources of contamination were traced to grease, oil, or elastomeric contamination in one case and, in the second case, to trapped metal and metal oxides resulting from the valve fabrication process.

It has been observed (at JPL) that when EPT-10 elastomer is immersed in hydrazine, some of the Silene D (precipitate silica) is leached out of the rubber and is visible as a white particulate matter floating on the liquid. As a result, a hydrazine presoak passivation treatment is now used on EPT-10 in actual applications by Pressure Systems, Inc., Los Angeles, Calif.

A potential source of catalyst bed poisoning appears to be the depositing out of Fe on the catalytic surfaces during long periods of hydrazine flow. This effect was noted (reported verbally) by Boeing during studies with radioactive Fe ions in hydrazine. Apparently a monolayer of radioactive Fe was detected as a deposit on filter elements. A quantitative assessment of the seriousness of this phenomenon has yet to be determined.

C. Galvanic Corrosion

Metallic corrosion due to dissimilar metals in contact with hydrazine would appear to be a potential problem. JPL has bimetallic test coupon samples currently in long-term immersion tests in hydrazine at 43.3°C (110°F). These specimens include such combinations as 347 SS/6061-T6 Al, 347 SS/304 SS, 6Al-4V-Ti/303 SS, and 6061-T6/6Al-4V-Ti. In system hardware tests in which an aluminum or titanium tank is in contact with stainless steel lines, no problem has been demonstrated. However, corrosion was found (by JPL) on an aluminum seal used in a stainless steel line fitting.

D. Adiabatic Compression

The thermal stability of hydrazine vapor compressed adiabatically such as might be experienced in suddenly pressurizing propellant lines of different materials was reported by Aerojet (Ref. 21). The experimental results indicated that hydrazine is sensitive to adiabatic compression to 13.79 MN/m^2 (2000 psi) at initial temperatures between 93.3 to 103.3°C (200 to 218°F) in 304L, 316, 321 and 347 stainless steels, Hastelloy-x, and Haynes-25, at 54.4°C (130°F) in Inconel-x and 17-7PH, and below 37.8°C (100°F) in aluminum alloys. The interpretation of these results with eference to a specific application must be done cautiously since other system factors would influence the compression effects such as surface-to-volume ratios, flow rates, heat transfer, etc.

IV. CLEANING AND PASSIVATION

Cleaning and passivation of materials and components for hydrazine use involves the removal of dirt, grease, scale and foreign matter from surfaces as well as the development of a passive surface which is least reactive with the liquid propellant. There are a variety of cleaning agents, solvents, and descaling processes which are called out in available JPL cleaning specifications such as GPM-20068-GEN-A (1963), GMZ-50521-GEN-A (1966), and FS-504574-A as well as various processes specified in documents prepared by each of several agencies and companies for their own use plus those prepared as ASTM standards (Ref. 22).

A review of the literature and conversations with people in various companies indicate that most cleaning processes are satisfactory when the cleaning is done as specified and the cleaning agents are completely removed and the parts dried adequately. However, there are several areas of special concern where problems have been encountered and may affect the preparation of future specifications for cleaning, passivation, assembly, flushing, handling, storage and inspection. A potential problem has been noted in that buffed surfaces tend to trap surface impurities by the flow of the ductile metal (smearing).

A. Methanol Corrosion of Titanium

A large body of data exists (Ref. 23, 24) on the attack of titanium by methanol under various conditions. Since methanol is such a common solvent, care must be exercised to prevent its inadvertent contact with titanium during the life of the system.

B. Freon as a System Contaminant

Freon TF was used to rinse Pyrex capsules in which hydrazine immersion tests of titanium 6Al-4V specimens were conducted (Ref. 2). Residual

Freon reacted with the hydrazine, yielding N_2H_4HCl, which resulted in excessive N_2H_4 decomposition and severe corrosion of the titanium. Separate previous tests of titanium in Freon TF alone and with added Cl indicated no reaction or stress corrosion cracking of the titanium specimens (Ref. 25).

C. Effective Stainless Steel Passivation

The effect of surface treatment of 347 SS on the decomposition rate of hydrazine at 128°C is reported in Table 10 of Appendix B. Reduced decomposition rates were achieved by a 24-h hydrazine passivation treatment. However, a further decrease in decomposition rate by a factor of 4 was achieved when the 347 SS specimens which had been tested by immersion at 128°C in hydrazine for 64 h were cleaned and retested in hydrazine.

In tests by the Air Force (Refs. 6, 26) with hydrazine storage tanks of various metals, the tanks of 17-7 PH and AM 350 stainless steels experienced some pressure rise during the initial portion of the test. However, the test program was interrupted after 10 months for facility modification, and when the same tanks were refilled with hydrazine and returned to test, the pressure rises were remarkably lower and all tanks appeared more compatible.

Stainless steel is particularly susceptible to attack by the carbazic acid formed by the reaction of CO_2 with N_2H_4. Apparently if air contact can be avoided and adequate passivation achieved, then long-term storage of N_2H_4 in contact with a number of stainless-steel alloys is feasible. Specifications for "adequate passivation" have not yet been defined.

D. Flushing and Empty System Storage

This is also an area where adequate standards have not been established. Closed systems which have contained hydrazine (test tanks, etc.) and have been subsequently drained and flushed with water and stored for some time have shown signs of corrosion and release of ammonia (Refs. 9, 10).

It is possible that small amounts of residual hydrazine remaining after draining a system may decompose more readily in excess amounts of water or moist air, yielding corrosive compounds including moist ammonia gas which attacks aluminum.

Elastomers such as EPT-10 used as tank bladders or diaphragms absorb hydrazine, which then remains in the EPT-10 after the system is drained and dried. Subsequent exposure of the EPT-10 to air has been found to cause the formation of carbazic acid on the rubber surface.

E. Pretreatment of EPT-10 Elastomer

A presoak treatment of EPT-10 has been developed and is now used by Pressure Systems Inc., the EPT-10 vendor, to reduce the leaching of Silene D and sulphur from the EPT-10 into the hydrazine during use. The pretreatment includes a 168-h continuous soak in hydrazine followed by water and Basic H rinses and soaking in water and vacuum drying.

V. CONCLUSIONS

As a result of this study the following conclusions have been reached:

(1) A number of commercial metal alloys of aluminum, titanium and stainless steels can be used in hydrazine systems for long-term storage and cyclic flow applications.

(2) There is no indication from available published data that metals in contact with propellant-grade hydrazine are subject to stress corrosion cracking, intergranular corrosion, embrittlement, shock sensitivity, or similar modes of degradation unless the hydrazine decomposition rate itself is excessive.

(3) The optimum cleaning and surface passivation techniques for long-life multiple-use systems have not been developed yet. Experience and isolated data indicate that hydrazine in contact with well-cleaned stainless steels develops increasingly passive surfaces. Even data on hydrazine in contact with copper indicates a passive surface can be developed on this nominally incompatible metal.

(4) Cleaning and passivation criteria should be extended to include control of the hydrazine system environment all through its anticipated lifetime. Inadvertent exposure of hydrazine system

internal surfaces to halogenated solvents, excessive air and moisture, etc., should be provided for in appropriate specifications.

(5) Very limited data is available on the problem of valve performance degradation, filter plugging, or catalyst bed poisoning over long lifetimes. Nearly all documented problems have been traced to gross contamination anomalies rather than the accumulation of trace contaminants in nominally compatible systems.

(6) The most promising elastomers for use in contact with hydrazine as a propellant tank diaphragm material or in sealing applications are the EPR or EPT compounds. These have been judged satisfactory for 1- or 2-yr mission applications with limited cycling requirements. Their long-life cyclic performance and properties in contact with a hydrazine system environment have not been established.

VI. RECOMMENDATIONS

The following recommendations are made:

(1) Continue the development of temperature-time decomposition rate data for candidate metals and elastomers over significant lengths of time. Such data is currently being generated at JPL for some 400 metallic and nonmetallic specimens in hydrazine at temperatures of 43.3 and 71°C (110 and 160°F) including testing with purified hydrazine.

(2) Establish the long-term physical property characteristics of candidate elastomeric materials such as EPT-10 and AF-E-332 as applicable to multicycle use over a 10-yr period exposed to hydrazine, pressurants, cleaning fluids, and storage environments. The development of the elastomer "property surface" which relates stress, strain, time, and temperature provides a useful tool for predicting the creep, fatigue and stress relaxation

behavior of polymers. Using appropriate test techniques, a time compression factor can be established which for typical elastomers can provide a basis for predicting 10-yr fatigue performance from data gathered over a period of a few weeks. Additional properties required for elastomers in contact with hydrazine include strength, modulus, elongation, biaxial stress response, permeability, swelling, and compression set. The variation in these properties with time, temperature, presoak treatments, environment, and dimensions needs evaluation.

(3) Develop and standardize suitable cleaning, passivation, inspection, and storage process specifications. Some of these criteria are being evolved in the Mariner, Viking, and P-95 (Air Force) programs but do not take into account the cyclic and multimission requirements of the Shuttle vehicle.

(4) Perform and analyze storage and cycling tests of prototype systems at elevated temperatures (50 to 100°C) over significant time periods (2 yr or more) to evaluate engine performance, catalyst bed poisoning, valve leakage, filter plugging, diaphragm flex life, diaphragm permeability, etc.

REFERENCES

1. Uney, P. E., and Fester, D. A., Material Compatibility with Space Storable Propellants, Design Guidebook, MCR-72-26, Martin Marietta Corp., Denver Div., Denver, Colo., Mar. 1972.

2. Salvinski, R. J., Advanced Valve Technology, Volume II, Materials Compatibility and Liquid Propellant Study, Interim Report 06641-6014-R000, TRW Systems Group, Redondo Beach, Calif., Nov. 1967.

3. Muraca, R. F., and Whittick, J. S., The Results of Long-Term Storage Tests for Compatibilities of Spacecraft Materials with Hydrazine and Hydrazine Mixtures, 915581-6 (JPL Contract 951581), Stanford Research Institute, Menlo Park, Calif., Oct. 1967.

REFERENCES (contd)

4. *Compatibility of Materials with Rocket Propellants and Oxidizers*, DMIC Memorandum 201, Battelle Memorial Institute, Columbus, Ohio, Jan. 1965.

5. Axworthy, A. E., et al., *Research on Hydrazine Decomposition*, Final Report, AFRPL-TR-69-146, Rocketdyne, North American-Rockwell, Canoga Park, Calif., July 1969.

6. White, H. M., *Long-Term Storability of Propellant Tankage*, Technical Report AFRPL-TR-71-20, Edwards, Calif., Mar. 1971.

7. Green, R. L., and O'Brien, J. R., *Advanced Techniques for Determining Long-Term Compatibility of Materials with Propellants*, Interim Report D180-14839-1, The Boeing Co., R&E Div., Seattle, Wash., June 1972.

8. Hagler, R., "JPL Internal Report of Visit to Hughes Tool El Segundo on Intelsat IV Propulsion System," Internal Report 384FS-70-194, Jet Propulsion Laboratory, Pasadena, Calif., Apr. 9, 1970.

9. Porter, R. N., et al., *Storage Tests of Nitrogen Tetroxide and Hydrazine in Aluminum Containers*, Technical Report 32-1039, Jet Propulsion Laboratory, Pasadena, Calif., Jan. 15, 1967.

10. Phillips, D. U., "Aluminum Component Corrosion," Interoffice Memorandum 384-MVM-71-456, Jet Propulsion Laboratory, Pasadena, Calif., May 25, 1971.

11. Stanford, H. B., and Porter, R. N., *Propellant Expulsion in Unmanned Spacecraft*, Technical Report 32-899, Jet Propulsion Laboratory, Pasadena, Calif., July 1, 1966.

12. Cuddihy, E. F., *Solvent-Stress-Cracking and Fatigue Properties of Liquid-Propellant Expulsion Teflon Bladders*, Technical Report 32-1535, Jet Propulsion Laboratory, Pasadena, Calif., Aug. 1, 1971.

13. Keller, O. F., and Toth, L. R., *ALPS Generant Tank and Cell Assembly*, Technical Report 32-865, Jet Propulsion Laboratory, Pasadena, Calif., Feb. 28, 1966.

14. Tolberg, W. E., Rewick, R. T., and Dolder, M. P., *Chemical and Metallurgical Analysis of 6Al-4V Titanium Test Specimens Exposed to Hydrazine (N_2H_4) Liquid Propellant*, SRI Report 951581-11, Stanford Research Institute, Menlo Park, Calif., Apr. 15, 1971.

15. Repar, J., *Flight and Experimental Expulsion Bladders for Mariner 69*, APCO 6935-2010 (SE), APCO Accessory Products Company, Whittier, Calif., July 1969.

REFERENCES (contd)

16. Toth, L. R., and Keller, O. F., "Material Compatibility," in Supporting Research and Advanced Development, Space Programs Summary 37-60, Vol. III, Jet Propulsion Laboratory, Pasadena, Calif., Dec. 31, 1969, p. 211.

17. Ross, D. S., Hendry, D. G., and Kirshen, N. A., Study of the Basic Kinetics of Decomposition of MMH and MHF and the Effects of Impurities on Their Stability, AFRPL-TR-71-114, Stanford Research Institute, Menlo Park, Calif., Sep. 15, 1971.

18. Martin, J. W., and Jones, J. F., Elastomeric Valve Seat Materials for Hydrazine Propulsion Systems, AFML-TR-70-200, TRW Systems Group, Redondo Beach, Calif., Dec., 1970.

19. Military Specification Propellant, Hydrazine, MIL-P-26536C, USGPO, Washington, D. C., May 23, 1969.

20. Salvinski, R. J., Investigation of the Formation and Behavior of Clogging Material in Earth and Space Storable Propellants, Interim Report 08113-6016-R000, TRW Systems, Redondo Beach, Calif., Oct. 1968.

21. Vander Wall, E. M., Suder, J. K., Beegle, R. L., and Gabeal, J. A., Propellant/Material Compatibility Study, Technical Report AFRPL-TR-71-741, Aerojet Liquid Rocket Co., Aerojet-General Corp., Sacramento, Calif., December, 1971.

22. Heinz, M. H., and Orton, G. F., "Effects of Heat Sterilization and Chemical Decontamination on Hydrazine Propulsion Systems for Planetary Landers (U)," Proceedings of the 10th Liquid Propulsion Symposium (U), Las Vegas, Nevada, Nov. 19-21, 1968 (Confidential).

23. Corrosion of Titanium, DMIC Memorandum 218, Battelle Memorial Institute, Columbus, Ohio, Sep. 1966.

24. Accelerated Crack Propagation of Titanium by Methanol, Hologenated Hydrocarbons, and Other Solutions, DMIC Memorandum 228, Battelle Memorial Institute, Columbus, Ohio, Mar. 1967.

25. Kamber, K. T., Kendal, E. G., and Schieler, L., Stress and Chemical Corrosion of Titanium Alloy in Freon Environment, TR-0158 (3250-10)-5, Air Force Report SAMSO-TR-67-62, Aerospace Corp., El Segundo, Calif., 1967.

26. Mears, R. B., Long-Term Storability of Propellant Tankage and Components, Interim Report 1, AFRPL-TR-70-43, Edwards, Calif., May 1970.

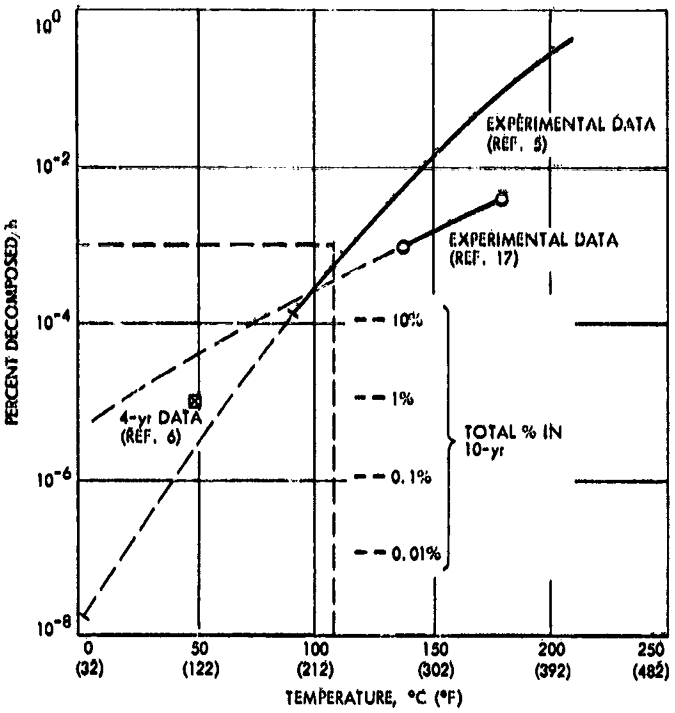


Fig. 1. Decomposition of propellant-grade hydrazine in Pyrex or compatible container vs temperature

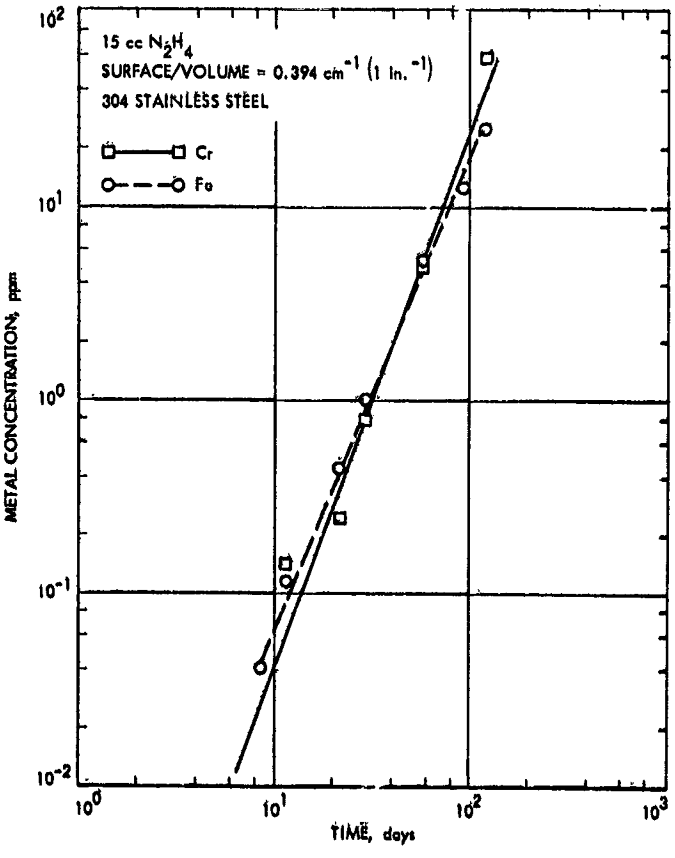


Fig. 2. Concentration of metal leached into hydrazine from immersed radioactive specimen

APPENDIX A

SUMMARY OF MATERIAL COMPATIBILITY WITH HYDRAZINE

The material presented in this appendix is a partial reprinting of Martin-Marietta Report MCR-72-26, Martin-Marietta Corp., Denver, Colo., Mar. 1972.

II. HYDRAZINE (N_2H_4)

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.

Table 1 N_2H_4 Summary Compatibility Chart

Material	Rating					References	Remarks
	1	2	3	4	5		
Metals							Ratings based on non-contaminated N_2H_4, i.e., no Cl_2 or CO_2 contaminants.
1) Aluminums							
a. Aluminum alloys in general		A,B				1,2,3,4,5,6,7,10, 13,14	
b. Pure	A					2	
c. 1100	A					4,5,7	
d. 2014	A					4,5,6,7	
e. 2021		A				6	
f. 2024	A					4,5	
g. 2219		B				1,2,4,5,6,7	
h. 3003	A					4,5	
i. 5052	A					4,5	
j. 6061	A		A			4,5,13,10,14	Conflicting data
k. 356		A				4,5,13	
2) Steels							
a. Stainless Steels in General			A,B			1,2,3,4,5,6,7,8,14	
b. 301 Cryoformed		A^1	B^2			1,2,6	1. for short term use (<6 mo.) 2. long term use (>6 mo.)
c. 304		A^1	A^2			2,3,8	
d. 316				A		2	
e. 321		A^1	A^2			2,3,4,5,14	
f. 347			A_2			2,6,7	
g. 410		A^1	B^2			1,2,4,5	
h. 430		A^1	B^2			1,2,4,5	
i. 440C		A^1	B^2			1,2,4,5	
j. 17-4 PH or 17-7 PH		A^1	A^2			1,2,4,5,6	
k. AM350 or AM355			A_2			1,6,8	
l. A-286		A^1	B^2			1,2,6	
m. Maraging steels			C			29	
n. Non-stainless steels				A		1,4,5	

Table 1 (Continued)

Material	Rating 1	2	3	4	5	References	Remarks
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		1,2,4,5	
b. Pure nickel				A		1,2,9	
c. Zinc			A			4,5	
d. Brass				A		1,4,5	
e. Bronze				A		1,4,5	
f. Copper				A		1,4,5	
g. Magnesium					A		Not enough data
h. Lead		B,C	A			1,4,5,28	Conflicting data
i. Cobalt				A		1,4,5	
j. Molybdenum				A		1,4,5	
k. Tantalum	A					1,4,5	
l. Silver					A		Not enough data
m. Gold				A		9	
n. Platinum		A				4,5,13	
o. Tin		A				1,4,5	
p. Zirconium	A					1,4,5	
q. Chromium		A^1	B^2			1,4,5	1. for short term use (<6 mo.) 2. long term use (>6 mo.)
r. 82/18 Au/Ni braze				A		9	
s. Monel			B			1,2	
t. Inconel			B			1,2	
u. Hastelloy Alloys			B			1,2	
Non-Metals							
1) Polymerics							
a. TFE Teflon		A				4,5,17	Rated for general use (no specific application, except as noted). Teflon is highly permeable.
b. FEP Teflon		A				4,5,17	

Table I (Concluded)

Material	Rating 1	2	3	4	5	References	Remarks
1) Polymerics (Cont'd)							
c. Kel-F		A				4,5,17	
d. Saran				A		4,5	
e. Natural rubbers			A			4,5	
f. Polyethylene		A				4,5,17	
g. Butyl rubbers			A			4,5,20,23	
h. Mylar				A		4,5	
i. Nylon				A		4,5	
j. Rulon (PTFE)		A	A			13,27	Conflicting data
k. EPR's in general		A				4,13,19,20,21,23, 27	Rated for no carbon black filler.
l. EPR 132		A				20,21	Same as above.
m. EPR's w/carbon black filler				A		20,21,23	
n. EPR SR722-70			A			20,22	
o. EPR E515-8			A			20,21	
p. EPT's in general		A				23	Same as above.
q. EPT-10		A				23,24,26	Same as above.
r. AF-E-102	A					25	
s. AF-E-332	A					26	
2) Lubricants							
a. Lubricants in general					D		
b. Graphite		A				5	
3) Miscellaneous non-metals							
a. Asbestos		A				5	
b. Metal oxides in general				A		4,5,16	

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

3. 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 (≈70°F) and in the absence of a catalyst, the average decomposition rate of N_2H_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 N_2H_4. However, N_2H_4 has become corrosive to metals when certain contaminants, such as CO_2 and Cl_2 have been added. Therefore, for long term storage of uncontaminated N_2H_4, the major concern is the degree that the metal being considered accelerates the N_2H_4 decomposition rate. For long term storage with non-metals, both catalytic and material attack must be considered.

1. Compatibility with Metals

According to Eberstein and Glassman the decomposition rate of N_2H_4 tends to increase when the N_2H_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 N_2H_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 N_2H_4 storage, while 6061 aluminum, 2219 aluminum, and 6Al-4V titanium would seem acceptable.

Tests conducted by Rocketdyne confirm the compatibility of N_2H_4 with high-purity aluminum but also indicate that some stainless steels might be compatible (Ref 2). The testing was conducted at 338°F with liquid propellant-grade N_2H_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 ($\approx 70^\circ$F)*. It would seem, therefore, that 304 and 321 stainless steels might be candidates for long term storage of N_2H_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 N_2H_4 at temperatures below 120°F. However, both also state that aluminum or titanium alloys are better storage materials since they exhibited compatibility even at 275°F.

TRW and DMIC issued survey reports on material compatibility which included recommendations for N_2H_4 (Ref 4 and 5). For these reports, a metal was considered applicable for long term service with N_2H_4 if it had a corrosion rate less than one mil/yr, would not promote N_2H_4 decomposition, and was not considered shock sensitive when in contact with N_2H_4. Compatibility recommendations for long term storage with N_2H_4, at temperatures below 75°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 N_2H_4. This is in direct opposition to the Eberstein and Glassman theory of N_2H_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, i.e., 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)

These rankings are not completely consistent with Table 1, Appendix A

Aluminum Alloys	Stainless Steels	Miscellaneous Metals
1100	410	Chromel-A
2014	416	Chromium Plating
2017	430	Gold
2024	440C	Hastelley-C
3003	302	Inconel
4043	304	Inconel-X
5052	316	K-Monel
5456	317	Monel
6061	321	Nichrome Braze
6066	347	Platinum
716	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°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°F and then for 48 weeks at 165°F. 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°F and 120°F, except for the 304 stainless steel which was run at 160°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°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 1½ times that of the control sample. For the 160°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 N_2H_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 N_2H_4 in tests conducted at AFRPL (Ref 9). Samples of the materials were immersed for up to 24 hr in test capsules filled with N_2H_4 maintained at 140°F. Decomposition of the N_2H_4 was determined by measuring the number of moles of NH_3 formed. The capsules containing the samples showed excessive NH_3 production. Thus, these results are also in agreement with the theory of Eberstein and Glassman.

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°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°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°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±5°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 carbazic 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°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:

(1) $CFCl_2CClF_2 + 2N_2H_4 \longrightarrow N_2H_4HCl + CFHClCClF_2 + N_2 + 2NH_3$

(2) $CFCl_2CClF_2 + 6N_2H_4 \longrightarrow 2N_2H_4HCl + CFH_2CClF_2 + 2N_2 + 4NH_3$

(3) $CFCl_2CClF_2 + 6N_2H_4 \longrightarrow 3N_2H_4HCl + CFH_2CHF_2 + 2N_2 + 2NH_3$

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 $CFHClCCLF_2$, CFH_2CClF_2, and CFH_2CHF_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°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 μin/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 mateial 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°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°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 specimens. The capsules were used to hold both the N_2H_4 and the test specimens so that no dissimilar materials would be in contact with the N_2H_4 during testing. Both capsule temperature and pressure were monitored during the tests. In addition to the above metals, an A-70 titanium bellows was also tested in a 6Al-4V Ti capsule.

Each test article was subjected to 6 cycles of exposure at 275°F. This consisted of 64 hours at 275°F followed by 8 hours for cooldown to ambient temperature and reheat to 275°F. Prior to testing, all specimens, capsules, and other hardware exposed to hydrazine were passivated for 18 hours at 175°F in an aqueous hydrazine solution (1 part N_2H_4 and 3 parts H_2O by volume). The test capsules were then filled with hydrazine. The titanium bellows and the 6061-T6 aluminum specimens were not introduced until the second cycle. The hydrazine decomposition rates were lowest for the titanium specimens. The decomposition rates with the 321 stainless steel specimens were about three times greater than those with titanium, while the aluminum samples produced decomposition rates about one order of magnitude higher than those with titanium, while the aluminum samples produced decomposition rates about one order of magnitude higher than those with titanium. In addition, the aluminum samples showed evidence of corrosion. A white, powdery film was deposited on both aluminum specimens and the 6061-T6 aluminum specimens were slightly pitted. Hydrazine samples taken from both the aluminum capsules following the test contained small quantities of a white, gelatinous precipitate. The A-70 titanium bellows sample and the 6Al-4V titanium specimens were unaffected.

Much of the results reported by both SRI and McDonnell (Ref 13 and 14) conflicts with the other reported data on the compatibility of titanium and aluminum alloys with hydrazine. In fact, the two sets of results tend to conflict with each other. SRI found 6061 aluminum to be compatible but 356 aluminum to be incompatible while 356 aluminum contains less alloying agents than 6061 aluminum. On the other hand, McDonnell found 6061 aluminum to be incompatible. McDonnell also found corrosion of the aluminum samples, while SRI did not. The McDonnell tests were run at 275°F while the SRI analyzed tests were run at 110°F. However, the Rocketdyne tests (Ref 2) run at 338°F showed no corrosion or excessive decomposition for the aluminum samples.

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 5×10^{-9}, 6×10^{-9}, 6×10^{-9}, and 4×10^{-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 6.6×10^{-7}, 8.1×10^{-7}, 6.6×10^{-7}, and 8.0×10^{-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 compliment 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, chromium, 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 Cl_2, 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 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 N_2H_4 applications. Von Doehren states that Teflon, Kel-F, and polyethylene are suitable for general use with N_2H_4 (Ref 17). DMIC rated Teflon, butyl rubber compound 805-70, Graphitar 2 and 50, and Denlanian as suitable storage materials with N_2H_4 below 140°F, while rating polyethylene, graphite, SBR rubber, asbestos, and Kel-F suitable below 75°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 ±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°F (Ref 4). Polyethylene was rated suitable only for service below 80°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 those 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. This reliance on butyl rubber and EPR as a storage material seems justified, for at least 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°F. The butyl rubber showed permeability rates between 0 and 0.001 mg/in.^{2}/hr and a fuel decomposition rate of 0.1%/day, while the EPR samples showed permeability rates between 0.001 and 0.4 mg/in.^{2}/hr and a maximum fuel decomposition rate of 0.0038%/day.

Compatibility test data seemingly disagreeing with the ratings given by DMIC, TRW, and AFRPL 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 formuations.

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 test polymer containers had pressure increases below 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 ($\Delta P \approx 50$ 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.^{2}/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_2H_4. Testing is still in progress. Preliminary results indicate that sterilization does not significantly effect the compatibility of EPT-10 with N_2H_4. 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_2H_4. 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_2H_4 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_2H_4 thruster valves. This study centered around the use of peroxide-cured ethylene-propylene rubbers reinforced with TRW polyurethane resin, Hystl. 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, Hystl, 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 Hystl) 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/Hyatl 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.

X. REFERENCES

1. Eberstein, I. J., and Glassman, I.: Consideration of Hydrazine Decomposition. Laboratory Report 490, Princeton University, Princeton, New Jersey, December 1959.

2. Axworthy, A. E., et al.: Research on Hydrazine Decomposition. AFRPL-TR-69-146, Rocketdyne, Canoga Park, California, July 1969.

3. Caudill, C. L., and O'Brien, A. W.: Design and Fabrication of Hydrazine Storability Test Tanks. AFRPL-TR-69-112, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California, June 1969.

4. Salvinski, R. J., et al.: Advanced Valve Technology, Volume II - Materials Compatibility and Liquid Propellant Study. 06641-6014-R000, TRW Systems Group, Redondo Beach, California, November 1967.

5. White, E. L., Boyd, W. K., and Berry, W. E.: Compatibility of Materials with Rocket Propellants and Oxidizers. Memorandum 201, Defense Metals Information Center, Columbus, Ohio, January 1965.

6. Branigan, J. E.: "Long-Term Storage of Liquid Rocket Propellant Tankage and Components." SAE paper No. 700800, presented at National Aeronautic and Space Engineering and Manufacturing Meeting, Los Angeles, California, October 5-9, 1970.

7. Carter, J. L.: A Preliminary Evaluation of the Compatibility of Hydrazine - Blend Fuels in Metal Containers at Elevated Temperatures (U). NWC TP 4157, Naval Weapons Center, China Lake, California, June 1968 (Confidential).

8. Rockenfeller, J. D.: "Materials Compatibility with Hydrazine-Based Monopropellants (U)." Proceedings of the 10th Liquid Propulsion Symposium (U), Las Vegas, Nevada, November 19-21, 1968 (Confidential).

9. Dee, L. A., et al.: The Catalytic Decomposition of Hydrazine on Gold, Nickel, and a Gold/Nickel Brazing Alloy. AFRPL-TR-69-77, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California, April 1969.

10. Salvinski, R. J., et al.: Investigation of the Formation and Behavior of Clogging Material in Earth and Space Storable Propellants. 08113-6016-R000, TRW Systems, Redondo Beach, California, October 1968.

11. Mars, J.: Compatibility Testing of C Series and J Series Stainless Steel Fittings. Memorandum, Rocket Research Corp., Redmond, Washington, July 16, 1969.

12. Tolberg, W. E., et al.: Chemical and Metallurgical Analyses of 6Al-4V Titanium Test Specimens Exposed to Hydrazine (N_2H_4) Liquid Propellant. 951581-11, Stanford Research Institute, Menlo Park, California, April, 1971.

13. Crutchfield, C. A., Muraca, R. F., and Whittick, J. S.: *The Results of Long-Term Storage Tests for Compatibilities of Spacecraft Materials with Hydrazine and Hydrazine Mixtures*. 951581-6, Stanford Research Institute, Menlo Park, California, October 1967.

14. Heinz, M. H. and Orton, G. F.: "Effects of Heat Sterilization and Chemical Decontamination on Hydrazine Propulsion Systems for Planetary Landers (U)." *Proceedings of the 10th Liquid Propulsion Symposium (U)*, Las Vegas, Nevada, November 19-21, 1968 (Confidential).

15. Kircher, J. F. and Vaughan, D. A.: *Radiation Effects on Liquid Propellants*. CR109767 Part 2, Battelle, Columbus Laboratories, Columbus, Ohio, January 1971.

16. Personal Communication with S. P. Vango, Jet Propulsion Laboratory, Pasadena, California, June 1970 and July 1971.

17. VonDoehren, P. J.: *Propellant Handbook*. AFRPL-TR-66-4, Air Force Rocket Propulsion Laboratory, Edwards, California, January 1966. (Confidential)

18. Personal Communication with A. O'Brien and M. Bolt, Martin Marietta Corporation, Denver, Colorado, October 1969.

19. Stanford, H. B. and Porter, R. N.: *Propellant Expulsion in Unmanned Spacecraft*. Technical Report 32-899, Jet Propulsion Laboratory, Pasadena, California, July 1966.

20. Howell, G. W.: "Use of Elastomers for Higher Performance, Lower Cost Liquid Rocket Propulsion Systems (U)." *Proceedings of the 10th Liquid Propulsion Symposium (U)*, Las Vegas, Nevada, November 19-21, 1968 (Confidential).

21. Takimoto, H. H. and Denault, G. C.: *Hydrazine Compatibility with Ethylene-Propylene Elastomers*. SAMSO-TR-69-153, The Aerospace Corporation, El Segundo, California, February 1969.

22. Muraca, R. F. et al.: *Post-Test Analysis of Generant Tank, Part No. 9116270-11*. 951581-7, Stanford Research Institute, Menlo Park, California, April 1968.

23. Repar, J.: *Flight and Experimental Expulsion Bladders for Mariner 69*. APCO No. 6935-2010 (SE), APCO Accessory Products Company, Whittier, California, July, 1969.

24. Personal Communication with M. Polzin and N. McKenna, Martin Marietta Corporation, Denver, Colorado, November 1971.

25. Martin, J. W. and Jones, J. F.: Elastomeric Valve Seat Materials for Hydrazine Propulsion Systems. AFML-TR-70-200, TRW Systems Group, Redondo Beach, California, December 1970.

26. Martin, J. W., et al.: Elastomers for Liquid Rocket Propellant Containment. AFML-TR-71-59 PT1, TRW Systems Group, Redondo Beach, California, June 1971.

27. Berry, W., et al.: A Study of Materials Compatibility with Hydrazine. ESRO CR-34, British Aircraft Corporation, Bristol, England, March 1971.

28. Brady, H. F., and DiStefano, D.: Sterilizable Liquid Propulsion System, Part I. MCR-68-119, Martin Marietta Corporation, Denver, Colorado, August 1968.

29. Rosenberg, S. D., et al.: "Materials Compatibility of the Hydrazine Family of Fuels." Paper presented at the 23rd Meeting of the ICRPG Liquid Propellant Test Methods Working Group, Naval Postgraduate School, Monterey, California, March 28-29, 1968.

30. Piccirillo, F.: "Compatibility of Stainless Steels with Monomethylhydrazine and Inhibited Nitrogen Tetroxide." Paper presented at the 23rd Meeting of the ICRPG Liquid Propellant Test Methods Working Group, Naval Postgraduate School, Monterey, California, March 28-29, 1968.

31. Liquid Propellant Manual. Chemical Propulsion Information Agency, Johns Hopkins University, Silver Springs, Maryland, December, 1966. (Confidential)

32. Cuddihy, E. F.: Solvent-Stress-Cracking and Fatigue Properties of Liquid-Propellant Expulsion Teflon Bladders. Technical Report 32-1535, Jet Propulsion Laboratory, Pasadena, California, August 1971.

33. Krumland, L. R.: Propellant Properties Manual for Hydrazine, Hydrazine Nitrate, and Water Mixtures. Report No. 66-0750, AiResearch Manufacturing Division, The Garrett Corporation, Los Angeles, California, March 1967.

34. Personal Communication with L. Toth, Jet Propulsion Laboratory, Pasadena, California, June 1970.

35. Lee, D. H.: A Survey of the Compatibility of Various Materials with Hydrazine and Mixtures of Hydrazine, Hydrazine Nitrate, and Water. Memorandum No. 20-152, Jet Propulsion Laboratory, Pasadena, California, December 1957.

APPENDIX B

RESEARCH ON HYDRAZINE DECOMPOSITION

The material presented in this appendix is a partial reprinting of Rocketdyne Report AFRPL-TR-69-146, North American Rockwell Corp., Rocketdyne Div., Canoga Park, Calif., July 1969

INTRODUCTION

The utility of hydrazine as a storable propellant is well established. Its limitations result principally from a high melting point and a moderate thermal stability. Hydrazine is sufficiently stable that gas evolution is apparently not a problem during normal storage in packaged systems; reliable long-term storage data are lacking. The use of hydrazine as a vehicle in gelled heterogeneous propellants is limited by gas evolution in some cases, but this results from interaction of the hydrazine with the gelling agent or the added solid. It is usually assumed that the thermal stability of hydrazine is borderline for use in tactical systems that may undergo aerodynamic heating, e.g., 400 F for 1 hour; again, sufficient experimental data were lacking prior to this program. Hydrazine can be used as a thrust chamber coolant only in systems that have been carefully designed with consideration for its limited thermal stability. However, the tendency of hydrazine to decompose thermally is advantageous in at least one application, i.e., thrusters in which hydrazine is catalytically decomposed as a monopropellant.

Extremely limited information is available relating to the kinetics or the mechanism of the decomposition of liquid hydrazine. Attempts have been made to discover additives that will increase the thermal stability of hydrazine, but these investigations were conducted without benefit of a knowledge of the type of reaction mechanism involved in the decomposition (free-radical or ionic), or of the site of the decomposition (on the wall or in the bulk of the liquid). Hydrazine is sufficiently stable that liquid-phase decomposition studies must be conducted either at very slow rates of reaction or at elevated temperatures where a high pressure is required to maintain the liquid phase. It is for these reasons, apparently, that most hydrazine decomposition studies have been conducted in the vapor phase even though the liquid-phase decomposition may be of the most practical interest.

In the case of the decomposition of hydrazine vapor, the rates have been determined under a variety of conditions, but the detailed reaction mechanisms have not been established. The decomposition of the vapor has been found to be a heterogeneous reaction (on the wall of reactor) below approximately 700 C, and a homogeneous reaction above this temperature (Ref. 1). A number of free-radical mechanisms have been proposed for the homogeneous decomposition of hydrazine vapor (Ref. 2 through 4), but these have been selected primarily to yield the correct stoichiometry and have not been based on well-established kinetic parameters such as reaction order (the uncertainty in the reaction order is exemplified by the data in Ref. 2).

A limited number of investigations of the liquid-phase decomposition of hydrazine have been reported. Most of these are described in Ref. 5 through 13. Some of these investigations are discussed by Eberstein (Ref. 14). Perhaps the most interesting of the previous investigations is that of Lucien (Ref. 5) which is discussed later in this report. Unfortunately, Lucien did not establish that most of his measured reaction was occurring in the liquid phase.

It was the objective of this program to establish the stability of liquid hydrazine under various conditions and to elucidate the reaction mechanisms involved. The role of impurities in the decomposition was to be determined. It was assumed that liquid hydrazine can decompose either homogeneously or heterogeneously (on the surface of the reactor) depending on the temperature and the area and type of surface in contact with the liquid. It was anticipated, also, that ionic mechanisms will be important in the liquid-phase decomposition of hydrazine which is a highly polar liquid with a dielectric constant of 52 at room temperature.

This investigation can be generally divided into three areas: (1) homogeneous decomposition, (2) heterogeneous decomposition on metal surfaces, and (3) role of impurities.

The approach under area 1 was to investigate the decomposition kinetics under conditions where the homogeneous mechanism would be expected to predominate (glass reactors, elevated temperatures, purified hydrazine). Investigations in solvents and with added salts were used to distinguish between possible ionic and free-radical mechanisms.

The heterogeneous decomposition kinetics, area 2, were investigated at lower temperatures with the liquid in contact with various metal surfaces. The effect of the pretreatment given the metal surface was also studied.

Under area 3 (role of impurities), the impurities normally present in hydrazine were determined. The possible detrimental effect on stability of these impurities was investigated by adding them to samples of purified hydrazine and, also, by attempting to effect their removal by pretreating the hydrazine. The susceptibility of hydrazine to potential impurities also was investigated (e.g., carbazic acid, which can form from reaction with CO_2 in air).

The results of this investigation are presented in approximately the above order in this report. However, some series of experiments relate to more than one of these general areas. Data relating mainly to the establishment of the kinetic parameters (homogeneous and heterogeneous) are presented first. This is followed by the results relating to the role of impurities. Finally, the work aimed specifically at determining the reaction mechanisms involved is presented.

SUMMARY

The objective of this program was to establish the thermal stability of hydrazine under various conditions and to elucidate the reaction mechanisms involved. The effect of impurities on the thermal stability was emphasized because it was determined rather early in the program that purified hydrazine is considerably more stable than propellant-grade hydrazine.

KINETIC PARAMETERS IN PYREX AMPOULES

The liquid-phase decomposition rates were measured at small extents of reaction in sealed pyrex ampoules at temperatures from 90 to 246 C, and reaction times from 0.3 to 600 hours. It was established that the decomposition rate is a function of the purity of the sample, and that the decomposition rate decreases with time. At 171 C, the average decomposition rates in percent per hour are, respectively, 0.04, 0.004, and 0.0003 for propellant-grade, distilled, and BaO-pretreated samples of hydrazine. The product ammonia was found not to inhibit the reaction, and the rate is not pressure dependent.

The stoichiometry observed throughout the program for liquid-phase decomposition was that which gave very little hydrogen (approximately 5 percent or less "percent ammonia decomposed"). The activation energy for decomposition in the glass ampoules is about 20 kcal/mole.

HETEROGENEOUS DECOMPOSITION ON METAL SURFACE

The rate was found to be strongly dependent on the type of metal in contact with the liquid and on the type of pretreatment the surface had been given. However, the rate on well-passivated stainless steel was only slightly higher than the rate obtained in the pyrex ampoules. The heterogeneous decomposition rate is not as dependent on the purity of the hydrazine sample as is the rate in the absence of a metal surface. It may be that impurities from the metal surface dissolve in the liquid.

ROLE OF IMPURITIES

It was established that the thermal stability of both propellant-grade and distilled hydrazine is determined by the occurrence of an impurity-catalyzed reaction. Of the known impurities in hydrazine, water, iron, and carbazic acid were found to be detrimental to thermal stability. Trace acidic and metallic impurities appear to be critical.

EFFECT OF ACIDIC ADDITIVES

The decomposition of hydrazine was found to be very susceptible to acid catalysis, particularly in the presence of a metal surface. One percent of an acidic impurity can increase the decomposition rate by a factor of 1000.

EFFECT OF HYDRAZINE PRETREATMENT

It was found that contacting propellant-grade hydrazine with technical-grade BaO reduces its decomposition rate (in glass) by two orders of magnitude. A similar effect could be obtained by adding a few hundred ppm of Na_2S. It is concluded that this latter treatment removed both trace metal impurities and acid contaminants by precipitating them as sulfides and by neutralization ($S^{=} + N_2H_5^{+} \rightarrow HS^{-} + N_2H_4$) respectively. The BaO pretreatment was shown to remove acidic materials from the liquid. Pretreatment with other insoluble bases and other samples of BaO also increased the thermal stability but not to as great an extent as one specific sample of BaO (probably because it contains a soluble sulfide impurity).

INVESTIGATION OF DECOMPOSITION MECHANISM

By the addition of various salts to change the ionic strength of the liquid hydrazine, it was established that the rate-determining step involves the reaction of a singly charged and a doubly charged ion of the opposite sign. The following mechanism is proposed for the impurity-catalyzed homogeneous reaction:

$$N_2H_5^+ + M(X)_4^{--} \longrightarrow M(X)_4^- + NH_3 + NH_2 \qquad (1)$$

$$M(X)_4^- + 2N_2H_4 \longrightarrow M(X)_4^{--} + N_2H_5^+ + N_2H_3 \qquad (2)$$

$$NH_2 + N_2H_4 \longrightarrow N_2H_3 + NH_3 \qquad (3)$$

$$2N_2H_3 \longrightarrow N_2 + 2NH_3 \qquad (4)$$

where M is a transition metal ion and X is a negative ion (e.g., Cl^- or $N_2H_3^-$).

Other techniques used to determine the mechanisms included solvent studies and measurement of electrical conductance and dielectric constant.

ANALYSIS OF HYDRAZINE

Gas chromatography techniques were developed to investigate the trace impurities in hydrazine. Toluene was found to be a trace impurity in commercial hydrazines at the 100- to 300-ppm level.

RATE AND KINETIC PARAMETERS IN PYREX

The rate of decomposition of liquid hydrazine was measured in sealed pyrex ampoules to determine its inherent stability in the absence of a metal surface and the effect of impurities on its thermal stability.

METHOD OF MEASUREMENT OF DECOMPOSITION RATE

In the absence of any side reactions involving impurities, the decomposition of hydrazine must follow the stoichiometry:

$$N_2H_4 \longrightarrow \frac{4}{3}(1 - f)\ NH_3 + \frac{1}{3}(1 + 2f)\ N_2 + 2f\ H_2 \qquad (5)$$

where f is commonly referred to as the "fraction of ammonia decomposed," and can vary from 0 to 1 but usually does not exceed 0.25.

At the small amounts of hydrazine decomposition of interest in this program, it is difficult to measure directly the amount of hydrazine decomposed or the amount of NH_3 formed. However, the separation and measurement of the noncondensable products, N_2 and H_2, can be done rapidly and accurately. In the method used in this program, the measured quantities are the ratio, R, of H_2 to N_2 and the total moles of noncondensable products ($N_2 + H_2$). The value of f can be calculated as follows:

$$f = R/(6 - 2R) \qquad (6)$$

The amount of hydrazine decomposed is calculated from the measured amount of noncondensable gas as follows:

$$\text{moles } N_2H_4 = [3/(1 + 8f)]\ (\text{moles } N_2 + \text{moles } H_2) \qquad (7)$$

The details of the experimental procedure are presented in a later section of this report. In summary, the hydrazine is placed in a thick-walled glass ampoule, the sample is frozen and the ampoule evacuated and sealed, the ampoule is then heated for the desired time and broken open in a vacuum system. The hydrazine and ammonia are condensed in a LN_2-cooled trap, the total pressure of the noncondensable products (N_2 + H_2) is measured with a multirange McLeod gage, and the noncondensable gases are analyzed in a mass spectrometer. From the initial amount of hydrazine introduced into the ampoule and the known volume of the gas-measuring system, the percent hydrazine decomposed is calculated using Eq. 7 .

The relationship between the moles of N_2H_4 decomposed and the total moles of N_2 and H_2 formed (Eq. 7) is plotted in Fig. 1 as a function of the percent hydrogen present in the noncondensable product. It will be seen later that considerably less than 30-percent hydrogen is found in the noncondensable products from the decomposition of liquid hydrazine under most of the conditions investigated. Thus, between 0.33 and 0.55 moles of noncondensable products usually form per mole of hydrazine decomposed.

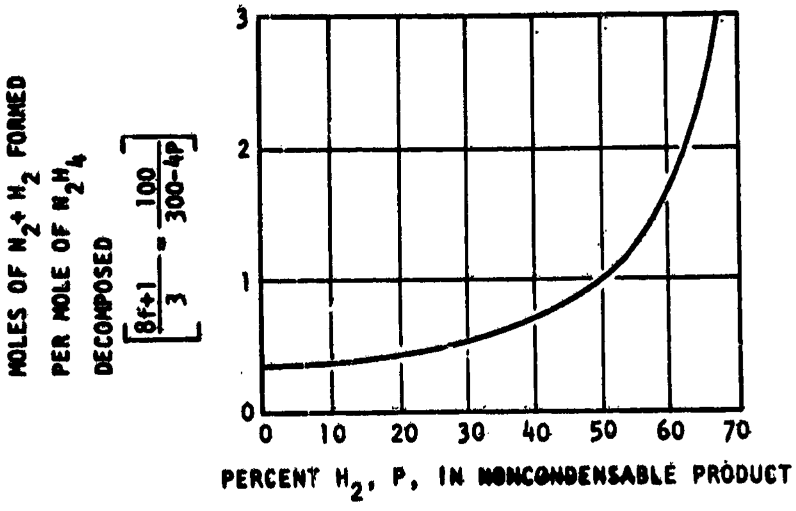


Figure 1. Moles of Noncondensable Gas Formed per Mole of Hydrazine Decomposed as a Function of Percent H_2 in Noncondensable Products (Eq. 7)

In a typical experiment, the ampoule had a total internal volume of 1.0 milliliters and 0.3 milliliters of liquid hydrazine was employed. It can be calculated that at temperatures around 170 C, where the vapor pressure of hydrazine is about 7 atmospheres, more than 1 percent of the hydrazine is initially in the vapor phase.

The initial pressure in the ampoule is equal to the vapor pressure of hydrazine. As the reaction proceeds, the pressure increases by the pressure of noncondensable products (about an additional 3 atmospheres for 1 percent hydrazine decomposed at 170 C) and the pressure of the NH_3 which is not soluble in the hydrazine (about an additional 8 atmospheres for 1 percent hydrazine decomposed--assuming that most of the NH_3 is in the vapor phase at this temperature). Thus, the total pressure in the ampoule would be about 60 atmospheres (900 psi) at 170 C after 5-percent of the hydrazine has decomposed in a typical experiment.

The decomposition of more than a few percent of the hydrazine would usually result in breakage of the ampoule by the excessive pressure of the products. This was not a serious limitation because the interest in this program was in the kinetics of decomposition at low extents of decomposition. For most applications, the decomposition of more than a few percent of the propellant (prior to use or while being employed as a coolant) could not be tolerated.

Prior to use, the ampoules were cleaned with aqua regia, rinsed, dried, and, for the later experiments, passivated with propellant-grade hydrazine for 24 hours, rinsed with distilled water and dried. The hydrazine passivation did not affect the rates obtained at higher temperatures except that it reduced the incidence of occasional spurious high results. At lower temperatures (<130 C), however, the rate in the absence of a metal surface was markedly reduced by prepassivation of the ampoules.

RESULTS: PROPELLANT-GRADE HYDRAZINE IN PYREX

The decomposition of propellant-grade hydrazine was found to be a relatively slow process even at moderate temperatures. Most of the studies in pyrex ampoules were conducted at 171 C (340 F) because this gave conveniently measurable decomposition rates on the order of 1 percent in 24 hours.

All of the data obtained on the decomposition rate of "as-received" propellant-grade hydrazines are listed in Table 1, and the results at 171 and 128 C are plotted as a function of time in Fig. 2 and 4 (Fig. 3 shows the initial decomposition rate of propellant-grade hydrazine on an expanded scale). When a phenomenon was under investigation (such as the effect of additives or of metal surfaces), blank runs were usually made to ensure that any effects observed were real. Many of the experiments listed in Table 1 were such blank experiments.

Reproducibility

It may be seen from Fig. 2, 3, and 4 that completely reproducible results could not be obtained. It was found, however, that the effects of interest to the program were of sufficient magnitude that this lack of reproducibility did not prevent conclusions from being drawn with respect to the reaction mechanisms and the roles of impurities and additives. It did require, however, that more experiments be conducted to establish the kinetic parameters associated with the phenomena of interest.

The possible causes of the scatter of the data were investigated in some detail early in the program. It was determined that the magnitude of the scatter was considerably greater than could arise from the combined possible errors in the measurement of (1) the initial sample size, (2) the moles of noncondensable products, (3) the H_2 to N_2 ratio, and (4) the reaction temperature.

The effect of prepassivating the ampoules with hydrazine before the final filling was next investigated. It may be seen from Fig. 2 and 3 that passivation has little, if any, effect on the results obtained at 171 C. However, three of the 171 C experiments gave apparently spurious results (Experiments 39, 116, and 117) and were not plotted in Fig. 2. Because these were three of the experiments in unpassivated ampoules it is possible that prepassivation would have prevented the spurious results. It may be seen from Fig. 4

TABLE 1

RESULTS WITH PROPELLANT-GRADE HYDRAZINE IN PYREX AMPOULES

Experiment No.	Sample	Temperature, C	Time, hours	Percent Hydrogen in Noncondensable Product[a]	Percent Hydrazine Decomposed		Remarks
					Total	Per Hour	
8	L-104A	171	17	(7)[b]	0.52	0.031	21-percent ullage
15				7	0.57	0.033	16-percent ullage
16				7	0.88	0.052	31-percent ullage
17				(7)	0.67	0.039	23-percent ullage
18				(7)	0.68	0.040	26-percent ullage
19				(7)	0.53	0.031	69-percent ullage
20				(7)	1.0	0.059	73-percent ullage
21				(7)	0.57	0.033	69-percent ullage
22			↓	(7)	0.62	0.036	71-percent ullage
30			1	(10)	0.086	0.086	
31			2.1	(10)	0.12	0.060	
32			4	(10)	0.21	0.054	
34			8	(10)	0.40	0.050	
35			16	(10)	0.54	0.034	
36			32	(10)	1.2	0.038	
37			64	(10)	1.5	0.023	
38			80	(10)	1.6	0.019	
39			96	(10)	5.9	0.062	High result
40			112	(10)	2.1	0.018	
42			128	6.6	2.5	0.020	
43			0.25	6.8	0.014	0.056	
44			0.50	11.9	0.033	0.066	
45			0.75	12.4	0.061	0.082	
67			21	(10)	0.87	0.041	
68	↓		120	13.9	1.75	0.015	
84	H-1726		18	12.9	0.58	0.032	
85			42	6.6	1.28	0.030	
87	↓		114	(10)	2.78	0.024	
88	L-104A		282	(10)	3.4	0.012	
116			285	(10)	6.9	0.024	High result
117			282	(10)	5.1	0.018	High result
156			0.6	(10)	0.026	0.043	
159			0.6	(10)	0.026	0.043	
166			0.6	(10)	0.030	0.050	
268			20	(10)	0.77	0.039	Blanks for NH_3
269			20	9.9	0.74	0.037	Experiments
270			20	12.1	0.72	0.036	↓
437			66	11.9	1.36	0.021	
439	↓	↓	66	(10)	1.15	0.017	

TABLE 1
(Continued)

Experiment No.	Sample	Temperature, C	Time, hours	Percent Hydrogen in Noncondensable Products[a]	Percent Hydrazine Decomposed		Remarks
					Total	Per Hour	
440	L-104A	171	66	(10)	1.23	0.019	
441			66	(10)	1.32	0.021	
603[c]			24	5.3	0.96	0.040	
605[c]			48	10.7	1.65	0.034	
606[c]			8	(5)	0.44	0.055	
607[c]			153	6.3	4.2	0.028	
608[c]			4	7.9	0.20	0.050	
609[c]			2	1.4	0.11	0.055	
610[c]			72	15.3	1.75	0.024	
757[c]			24	(7)	1.13	0.047	
758[c]			24	(7)	1.17	0.049	
813[c]			72	6.0	1.7	0.023	
814[c]			72	6.8	1.6	0.022	
914[c]	L-104B		24	(10)	0.95	0.039	
915[c]				(10)	0.82	0.034	
924[c]				6.1	0.95	0.039	
931[c]				2.3	1.09	0.045	
938[c]				(10)	0.71	0.030	
939[c]				(10)	0.72	0.030	
318	L-104A	128	13	(5)	0.35	0.027	Unpassivated
319			23	(5)	0.76	0.032	
320			33	(5)	0.75	0.018	
258			40	(5)	0.49	0.012	
259			40	(5)	0.48	0.012	
321			49	(5)	1.25	0.025	
322			76	(5)	2.10	0.027	
323			98	(5)	2.27	0.023	
237			144	2.6	0.76	0.0053	
238				(5)	0.73	0.0051	
239				1.7	0.61	0.0042	
359[c]			9	(5)	0.092	0.010	
360[c]			21	(5)	0.24	0.011	
361[c]			33	(5)	0.22	0.0067	
362[c]			57	2.4	0.35	0.0061	
363[c]			4	(5)	0.038	0.0095	
365[c]			21	6.4	0.082	0.0039	
366[c]			33	(5)	0.14	0.0042	
367[c]			55	(5)	0.19	0.0035	
368[c]			116	(5)	0.34	0.0029	
369[c]			283	(5)	0.70	0.0025	
370[c]			434	(5)	0.95	0.0022	
372[c]			73	(5)	0.31	0.0042	82-percent ullage

TABLE 1

(Concluded)

Experiment No.	Sample	Temperature, C	Time, hours	Percent Hydrogen in Noncondensable Products[a]	Percent Hydrazine Decomposed		Remarks
					Total	Per Hour	
373^{c}	L-104A	128	73	3.8	0.36	0.0049	73-percent ullage
374^{c}	↓	↓	↓	(5)	0.28	0.0038	62-percent ullage
376^{c}	↓	↓	↓	(5)	0.28	0.0038	44-percent ullage
377^{c}	↓	↓	↓	(5)	0.33	0.0048	30-percent ullage
378^{c}	↓	↓	↓	(5)	0.25	0.0034	28-percent ullage
402^{c}	↓	↓	64	(5)	0.28	0.0044	
403^{c}	↓	↓	↓	(5)	0.26	0.0041	
404^{e}	↓	↓	↓	(5)	0.25	0.0039	
406^{c}	↓	↓	↓	(5)	0.36	0.0056	
448^{c}	↓	↓	↓	(5)	0.17	0.027	
449^{e}	↓	↓	↓	(5)	0.17	0.027	
502^{c}	↓	↓	76	4.6	0.25	0.0033	
503^{c}	↓	↓	↓	(5)	0.36	0.0047	
504^{c}	↓	↓	↓	(5)	0.32	0.0042	
773^{c}	↓	↓	24	(5)	0.11	0.0046	
774^{e}	↓	↓	↓	(5)	0.10	0.0042	
775^{c}	↓	↓	↓	(5)	0.10	0.0042	
199	↓	90	264	(5)	0.16	0.00060	Unpassivated
200	↓	↓	264	(5)	0.16	0.00060	Unpassivated
721^{e}	↓	↓	576	(5)	0.13	0.00022	
722^{c}	↓	↓	576	(5)	0.12	0.00021	
7	↓	149	20	(10)	0.15	0.0075	Unpassivated
677^{c}	↓	186	16	(10)	0.76	0.047	
680^{e}	↓	186	7	(10)	0.48	0.069	
11	↓	204	17	7	3.5	0.20	Unpassivated
697^{c}	↓	204	2	(10)	0.45	0.22	
698^{e}	↓	204	2	(10)	0.48	0.25	
686^{c}	↓	227	0.5	10.1	0.29	0.58	
690^{e}	↓	227	1	(10)	0.53	0.53	

[a] This value is the percent hydrogen, P, in noncondensable products ($N_2 + H_2$). The value of R for use in Eq. 6 is given by P/(100 - P).

[b] Values in parentheses were estimated from results of similar experiments. The effect of error in this value on percent hydrazine decomposed can be calculated from Fig. 1 or Eq. 6.

[c] In these experiments, ampoules were passivated overnight with hydrazine before filling. In the other experiments, the ampoules were cleaned but not passivated.

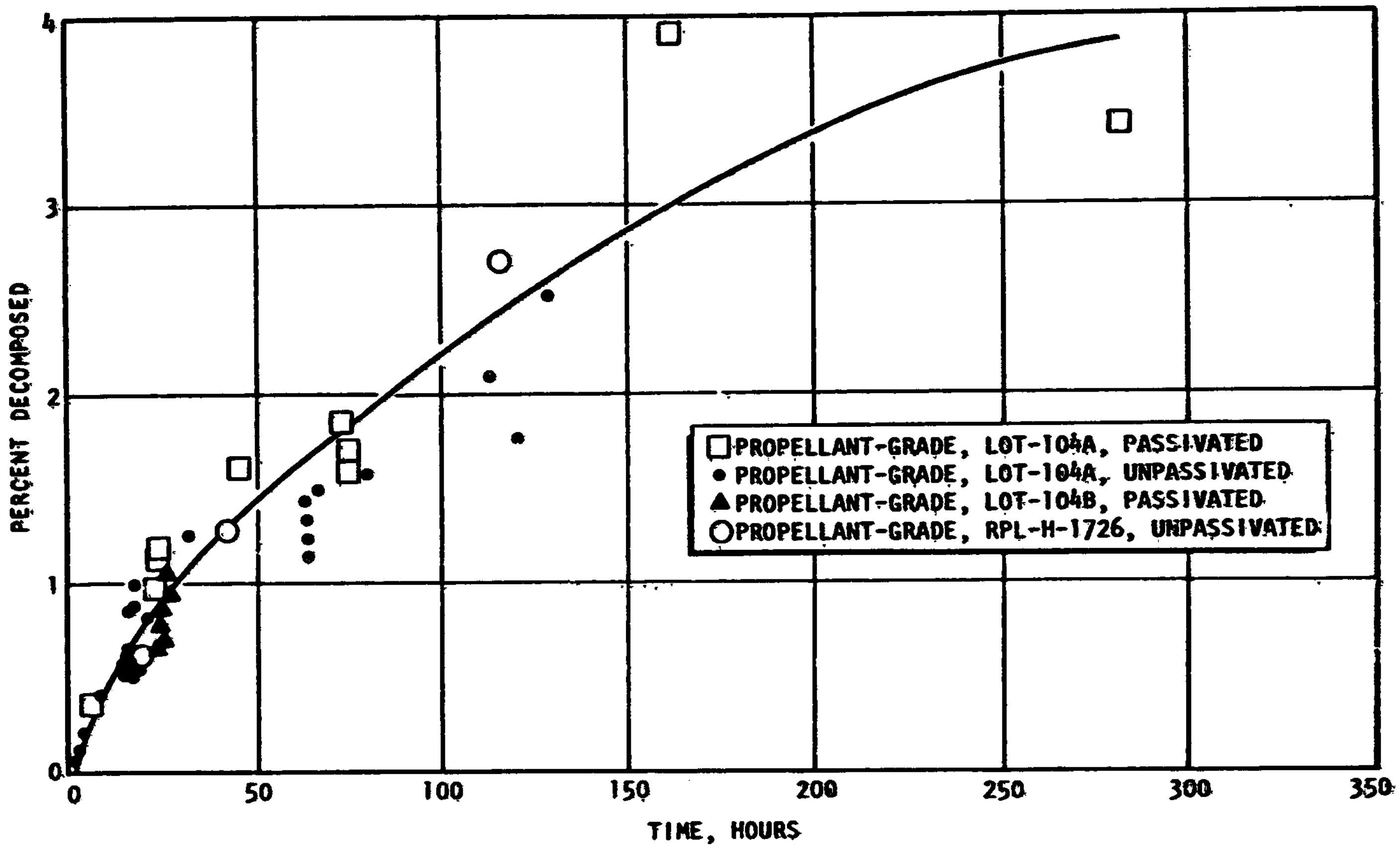


Figure 2. Decomposition of Hydrazine in Pyrex Ampoules at 171 C

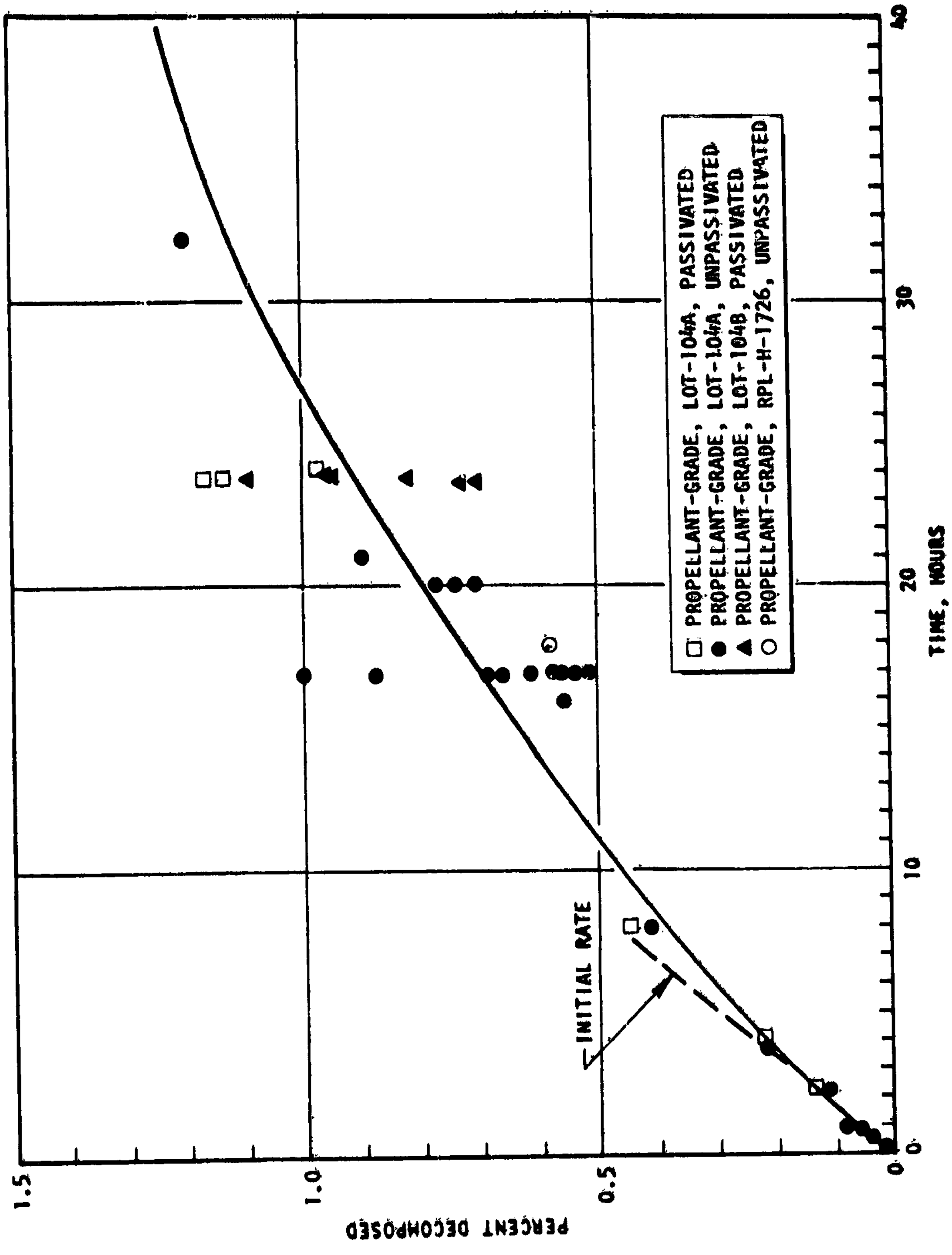


Figure 3. Initial Decomposition of Propellant-Grade Hydrazine at 171 C

17

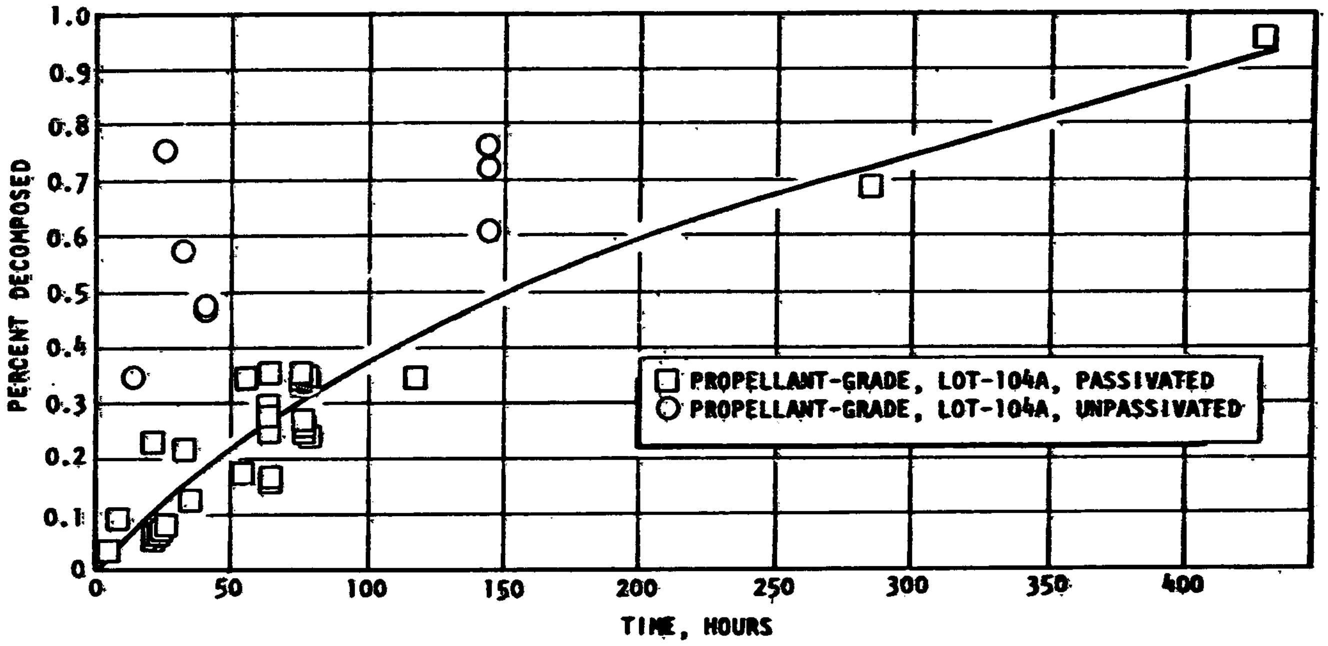


Figure 4. Decomposition of Hydrazine in Pyrex Ampoules at 128 C

and Table 1 that prepassivation of the ampoules in the 128 C experiments definitely decreases the decomposition rate and increases the reproducibility. Three of the 128 C experiments in unpassivated ampoules (Table 1--321, 322, and 323) gave more than 1-percent decomposition and could not be plotted in Fig. 4. A similar effect of ampoule prepassivation was observed at 90 C (Table 1) but not at the higher temperature of 204 C.

The reason for the scatter even when passivated ampoules are employed has not been completely established. It appeared early in the program that the decomposition rate is a function of the purity of the hydrazine sample. It was anticipated that the investigation of the role of impurities would permit the reproducibility to be improved later in the program. It turned out, however, that no simple relationship was established between the impurity content of the hydrazine and its decomposition rate. It will be seen later that the results of this investigation do indicate that the thermal stability of propellant-grade hydrazine is determined by trace impurities which are present at concentrations near or below their detection limit. Thus, the scatter could result from small changes in the concentrations of these impurities even though considerable care was taken in filling the ampoules (dry box, etc.). If this is the case, larger sample sizes would lead to more reproducible results--provided that the quantity of impurity added or removed during the filling of the ampoule was not proportional to the sample size. There is no indication from Fig. 5 (presented later) or from experiments 373 thru 378 in Table 1 that a larger sample would improve reproducibility, but further experiments would be required to establish this. The low order of reproducibility which was obtained is an additional indication that trace impurities are involved in the decomposition process.

The main reason that small samples of only 0.3 milliliters were used was that very thick-walled capillary tubing was required to contain the vapor pressure of hydrazine at the higher temperatures and to contain the pressure developed by the decomposition products. The use of appreciably larger sample sizes would have limited the investigation to considerably lower temperatures, or considerably more complex techniques would have to be employed. At lower temperatures, the experiments would have been inconveniently long with the most stable samples of hydrazine prepared later in the program. Additional advantages of the small sample size are safety and that small quantities of a specially prepared or purified sample of hydrazine can be studied under a number of conditions.

Although some exceptions were found, the reproducibility of a given series of experiments was better than the reproducibility from series to series. It was for this reason that blanks were employed as each phenomenon of interest was investigated.

Effect of Sample Source

Data are presented in Table 1 and Fig. 2, 3, and 4 for three different samples of propellant-grade hydrazine: L-104A, L-104B, and RPL-H-1726. The first sample was obtained from a propellant tank at Rocketdyne, the second was obtained from the same tank approximately 18 months later, and the third sample was typical propellant-grade hydrazine supplied from that in use at the Edwards Rocket Propulsion Laboratory. The analyses of these samples of hydrazine will be presented later in this report. It may be seen that the three samples of propellant-grade hydrazine had similar thermal stabilities.

Effect of Ullage Volume

A series of 17-hour experiments was conducted in ampoules of 2.5-millimeter ID Pyrex capillary tubing at 171 C with propellant-grade hydrazine. The amount of liquid loaded into the ampoule was varied to determine the effect on the decomposition rate of changing the ratio of the volume of the vapor-containing ullage to the volume of liquid. Because the liquid volume essentially determines the total amount of hydrazine in the ampoule, the percent decomposed will be proportional to $U/(1-U)$, where U is the fraction of ullage, if all of the observed reaction occurs in the vapor phase. If, however, only liquid-phase decomposition occurs, the percent decomposed will be independent of the amount of ullage, and of $U/(1-U)$.

The results obtained in this series of experiments are presented at the top of Table 1. The percent ullage listed was calculated at reaction temperature taking into account the thermal expansion of the liquid sample. These results are plotted in Fig. 7 as a function of U/(1-U). The results are independent of the percent ullage indicating that the observed decomposition occurs in the liquid phase. The average percent decomposition during these nine experiments was 0.67 with an average deviation of ± 18 percent.

The results of experiments at 128 C, in which the ullage volume was varied from 28 to 82 percent of the reactor volume, were similarly found to be independent of the ullage volume. These are Experiments 372 to 378 in Table 1.

The above results are of importance to the present program because they establish that the liquid-phase reaction can be measured without interference from decomposition of the vapor present in the ampoule. Coincidentally, they also yield information regarding the stability of hydrazine vapor in the presence of a glass surface at a high hydrazine pressure of about 7 atmospheres. It can be estimated from Fig. 5 that the maximum amount of hydrazine which could have decomposed in the vapor phase during any of these experiments was approximately 0.1 percent of the total hydrazine. Because 2 percent of the hydrazine is initially present in the vapor phase in the high-ullage experiments, this indicates that the half-life of hydrazine vapor under these conditions is at least 170 hours. The implications of this upper limit on the rate of decomposition of hydrazine vapor will be discussed in a later section.

Decomposition Rate as a Function of Time

It might be anticipated that the decomposition rateof liquid hydrazine would be constant with time for small extents of decomposition. This was found not to be the case, however, with propellant-grade hydrazine in pyrex ampoules. At 171 C (Fig. 2 and 3), the decomposition rate decreases with time from an initial value of 0.060 percent per hour to approximately 0.008 percent per hour. At 128 C (Fig. 4), the rate in passivated ampoules decreases with time from 0.0054 to 0.0014 percent per hour.

Because the concentration of hydrazine remains nearly constant in the liquid phase at these small extents of reaction, the observed change in the

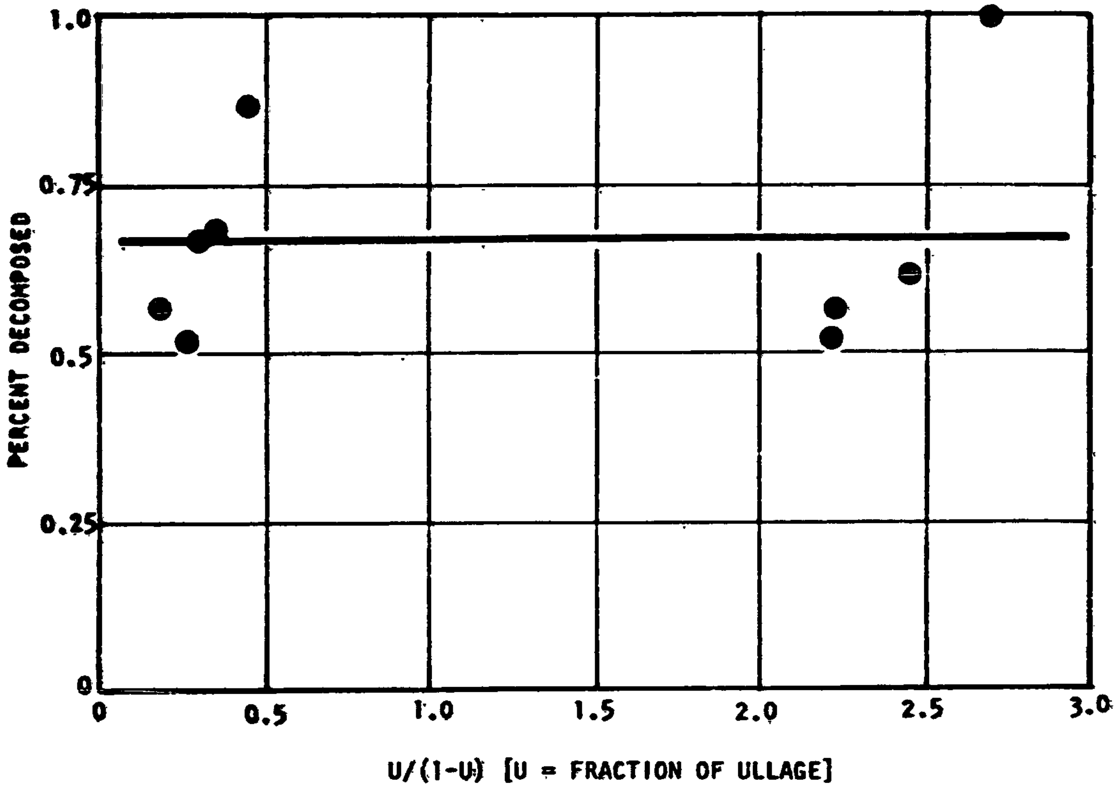


Figure 5. Effect of Ullage Volume on Decomposition of Propellant-Grade Hydrazine at 171 C in Pyrex Ampoules (17-Hour Experiments)

decomposition rate with time indicates that the decomposition of propellant-grade hydrazine in pyrex ampoules is not a simple homogeneous pyrolysis reaction. A number of possible causes of the decrease in rate with time were considered and investigated:

1. The reaction occurs heterogeneously on the wall of the reactor and the wall slowly becomes passivated.
2. The reaction is inhibited by the reaction product ammonia.
3. The observed reaction involves an impurity (either impurity-catalyzed or a direct reaction) and the impurity is either depleted or slowly converted to a nonreactive form.
4. The rate is an inverse function of the total pressure.

It will be shown on the following pages that (1) the reaction does not occur predominantly on the reactor wall, (2) added ammonia does not decrease the initial decomposition rate, and (3) the impurity aniline does not react directly with hydrazine under these conditions. It will be shown later that the rate of the liquid-phase decomposition of purified hydrazine is not a function of pressure.

On the basis of the results to be presented in this section and those to be presented later in the report regarding the role of impurities and the effects of additives and ionic strength, it has been concluded that the rate of decomposition of propellant-grade hydrazine is determined by the concentrations of trace impurities (probably involving an acidic impurity reacting with a trace metal ion). In terms of this proposed mechanism, the most likely explanation for the decrease in rate with time is that a trace impurity is slowly being removed at the glass surface or is being converted to an inactive form by slow reaction with the hydrazine (e.g., the conversion of metal ions to a chelate or a complex ion) or with other impurities (e.g., water). This explanation requires that the removal of the trace impurities only occurs at elevated temperatures, otherwise it should occur during the storage of the samples in glass bottles.

Effect of Added Glass Surface. It was established previously that the reaction occurs in the liquid phase in glass ampoules at elevated temperatures. A series of experiments was conducted at 171 C to determine whether this liquid-phase reaction occurs heterogeneously on the glass surface or homogeneously in the bulk of the liquid. Four ampoules were loaded with 1.3 milliliters of propellant-grade hydrazine (L-104A) and heated for 1 hour. Two of the ampoules had melting point capillary tubing present in the liquid phase increasing the surface in contact with the liquid by a factor of 2.7. The results obtained were somewhat unexpected: the hydrazine in each of the unpacked ampoules had undergone 0.062 percent decomposition while in each of the ampoules with added glass, only 0.037 percent had decomposed. This result suggests that impurities are being removed on the glass surface at 171 C, causing a marked decrease in the rate even during the first hour. However, later experiments presented in the next paragraph gave an increase in rate when the surface was increased.

The site of the reaction of propellant-grade hydrazine (L-104A) in the glass reactors was investigated further by adding fine glass beads to the ampoules. The beads increased the surface area by a factor of 12 but only increased the decomposition rate by a factor of approximately 3.5 (2.45 percent decomposed in 20 hours at 171 C). This indicates that the major portion (80 percent) of the decomposition of propellant-grade hydrazine occurs homogeneously in the liquid phase. It will be shown later, however, that this homogeneous reaction is mainly impurity-catalyzed. No explanation is apparent for the discrepancy between the two sets of experiments with added glass but it may be related to the difference in heating times: the added glass was aqua regia-cleaned in each case (see Experimental Procedures).

Effect of Added NH_3. A series of experiments was conducted to determine the influence of added NH_3 upon the decomposition rate of propellant-grade hydrazine at 171 C. Twelve ampoules of propellant-grade hydrazine (L-104A) were heated for 20 hours at 171 C. Four contained 1.33 percent added NH_3 (equivalent to that normally present after 1-percent hydrazine decomposition); four contained 2.67-percent NH_3, and four were blanks with no added NH_3. All four ampoules containing 2.67-percent NH_3 broke, presumably from the pressure of the ammonia, as did two containing the lower concentration of NH_3 (weaker ampoules of 3 mm ID Pyrex were employed in these experiments). The surviving ampoules gave the following results:

Experiment No.	Initial NH_3, mole percent	Percent Decomposed
261	1.33	0.51
267	1.33	0.55
268	0	0.77
269	0	0.74
270	0	0.72
271	0	0.48

The results with added NH_3 suggest an inhibiting effect, but they are almost within the usual scatter of the blank experiments. If the added NH_3 had no effect, about 0.7 percent hydrazine should decompose in 20 hours (Fig. 2), whereas if NH_3 inhibition is responsible for the observed decrease in rate in Fig. 2, only 0.4 percent should decompose (after decomposing 1 percent in 30 hours, Fig. 2, propellant-grade hydrazine will decompose 0.4 percent during the next 20 hours).

Since the results with added NH_3 were inconclusive because the runs at 2.7-percent ammonia were lost by ampoule breakage, additional experiments were conducted at higher NH_3 concentrations in stronger ampoules. Quartz reactors of 1 millimeter ID were used to prevent breakage. The heating time was 22 hours in all experiments at a temperature of 171 C.

Only a few experiments were conducted in quartz with propellant-grade hydrazine during the program. The blank runs (no added NH_3) gave percent decompositions of 1.6, 1.9, 1.5, and 1.1. These are higher than the value of 0.9 percent usually obtained in 3-millimeter ID pyrex ampoules. Because the decomposition of propellant-grade hydrazine is partly heterogeneous at 171 C (see above), much of this difference can be accounted for by the higher surface-to-volume ratio of the 1-millimeter ID capillary.

Three runs were made under the same conditions as above with 7.8-percent NH_3 added to the propellant-grade hydrazine. One ampoule broke and the other two samples of hydrazine underwent decompositions of 1.3 and 1.6 percent, respectively. It appears, therefore, that NH_3 had no effect on the decomposition rate, and its buildup as a product does not cause the observed decrease in decomposition rate with time (Fig. 2). Eight percent of added NH_3 is the equivalent to that which would be present after about 6 percent of the hydrazine decomposed in the absence of added NH_3. Thus, less than 0.2 percent decomposition should occur in 22 hours with added NH_3 if NH_3 inhibition accounted for the effect in Fig. 2 .

It is not surprising that NH_3 does not inhibit the reaction because at 171 C most of the NH_3 would be in the vapor phase. Lucien (Ref. 5) has reported that NH_3 does inhibit the liquid-phase decomposition of hydrazine; his results will be discussed later.

Direct Reaction of Aniline. A direct reaction with an impurity would be a possible cause of the observed decrease in the decomposition rate with time; the rate would decrease as the impurity is consumed. A possibility is the direct hydrogenation of the impurity aniline or toluene*. One possible stoichiometry for such a reaction is the following:

$$C_6H_5NH_2 + 3/2\ N_2H_4 \longrightarrow C_6H_{11}NH_2 + 3/2\ N_2 \qquad (8)$$

in which each mole of aniline reacted leads to the formation of 1.5 moles of noncondensable gas. Because the percent hydrazine decomposed is calculated from Eq. 7 , the complete reaction of the 0.23 mole percent aniline initially present in this hydrazine (L-104) would give a calculated percent decomposition of 0.99 percent (0.23 x 1.5 x 3).

Thus, one mechanism which is compatible with the observed results is that the aniline reacts directly with the hydrazine during the first 30 to 100 hours, and after that the observed decomposition rate is that of aniline-free hydrazine. This explanation is not tenable, however, since the results

---

*Toluene was found to be an impurity. This will be discussed further in a later section.

presented in the following paragraph show that neither the aniline nor the toluene present in propellant-grade hydrazine is consumed during 39 hours of heating.

A series of experiments was conducted at 171 C to determine if a direct reaction occurred in propellant-grade hydrazine between the impurity aniline and the hydrazine. Propellant-grade hydrazine was introduced into five 2.5-millimeter-ID glass capillaries, One was sealed for a blank; the other four were outgassed as usual and then sealed. Two of the outgassed ampoules were heated at 171 C for 39 hours. The other three ampoules were stored at room temperature. After breaking the ampoules in a dry box, analysis by gas chromatography revealed that all five samples contained approximately 0.8 weight percent aniline (previous aniline values for this material were 0.67 and 0.69 weight percent--a standardization error is believed to account for the difference) and approximately 300 ppm toluene. It is apparent from these results that aniline does not react with hydrazine at 171 C.

Stoichiometry

The percent hydrogen in the noncondensable gases is listed in Table 1 for those experiments in which it was measured. These values ranged from 1 to 15 percent for propellant-grade hydrazines in pyrex ampoules. This gives values of "f" according to Eq. 6 from 0.002 to 0.03 or 0.2 to 3 "percent ammonia decomposed." It is apparent, therefore, that under these conditions the reaction almost follows the possible stoichiometry (Eq. 5) in which no hydrogen is formed. The implications of this with respect to the reaction mechanism involved will be discussed in a later section.

Effect of Temperature

For a simple reaction, the activation energy is usually measured to gain additional insight into the reaction mechanism. Since it was shown that the rate of decomposition of propellant-grade hydrazine decreases with time at 171 C and 128 C, it is not possible to calculate a single activation energy.

An attempt was made, however, to put these data into an Arrhenius plot in Fig. 6 because this permits direct comparisons to be made of the various experiments presented throughout this report. The data obtained at temperatures other than 171 C and 128 C are also listed in Table 1 and are plotted as single points in Fig. 6 . At 90 C and 128 C, only the results obtained in passivated ampoules are included in the plot.

The line drawn through the "pyrex" data in Fig. 6 has a slope equivalent to an activation energy of 20.5 kcal/mole.

RESULTS: PURIFIED HYDRAZINE IN PYREX

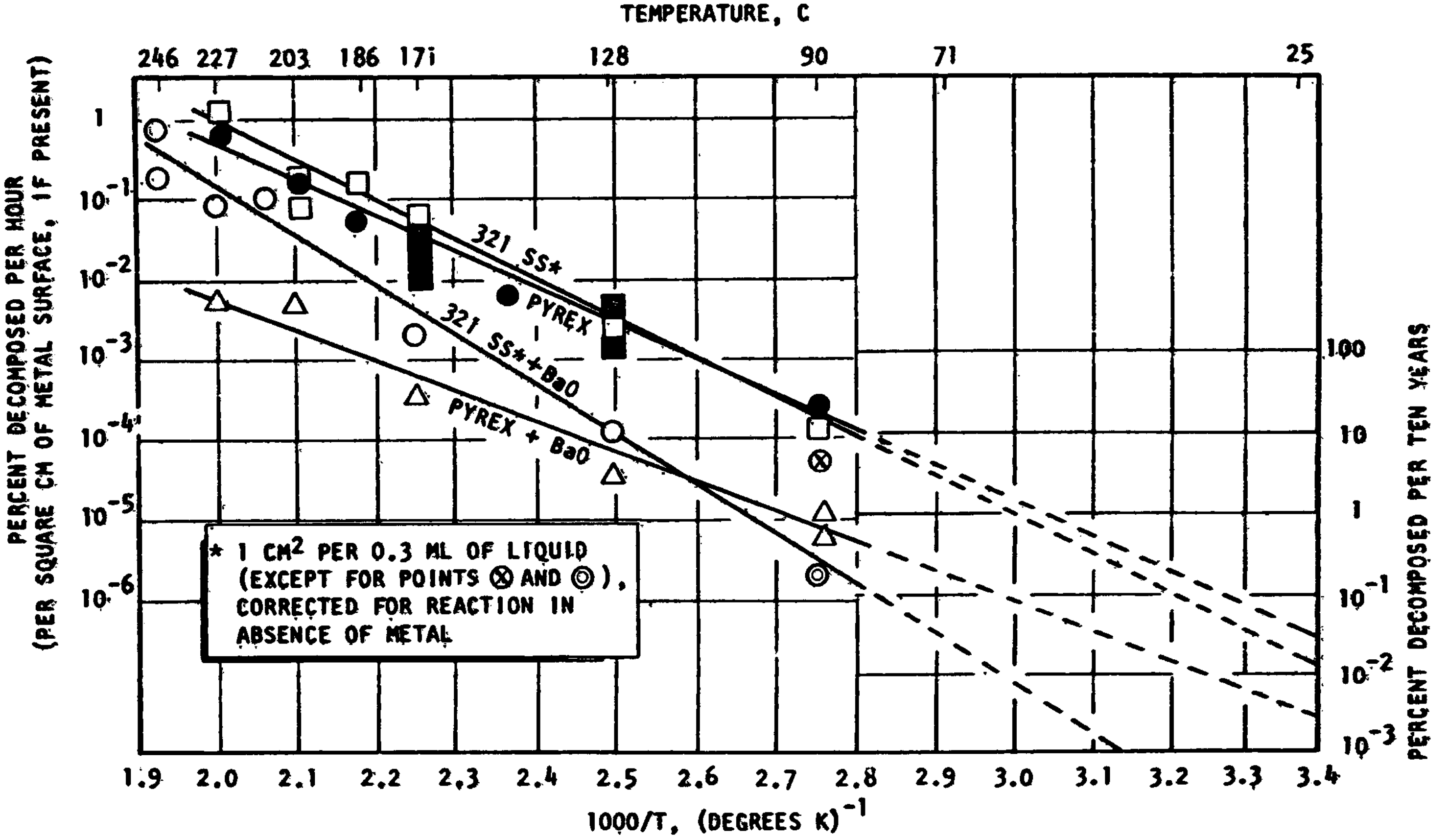
As a first step in establishing the role of impurities in the decomposition of hydrazine, the rate parameters for the decomposition of specially purified hydrazines were measured in pyrex ampoules for comparison with the results obtained with propellant-grade hydrazine. The experimental results obtained are listed in Table 2 .

Analysis of Hydrazine Samples

Two specially purified hydrazines were made available to this program through the cooperation of the U.S. Air Force Rocket Propulsion Laboratory and the Olin Mathieson Chemical Corporation. The Air Force material was prepared by reduced pressure distillation, and the Olin material was purified by a fractional crystallization technique. These samples of purified hydrazine and other hydrazine samples available to the program were carefully analyzed giving the results shown in Table 3 . The details of the analytical methods employed are given in a later section of this report.

Decomposition Rate as a Function of Time and Temperature

The data listed in Table 2 for Olin purified hydrazine in pyrex at 171 C are plotted in Fig. 7 (except for experiment 76 which gave a very high rate). Based on the curve drawn in Fig. 7 , the decomposition rate at



* 1 CM^2 PER 0.3 ML OF LIQUID (EXCEPT FOR POINTS ⊗ AND ◎), CORRECTED FOR REACTION IN ABSENCE OF METAL

Figure 6. Effect of Standard Surface, Temperature, and BaO Treatment on Decomposition Rate of Propellant-Grade Hydrazine (Arrhenius Plot)

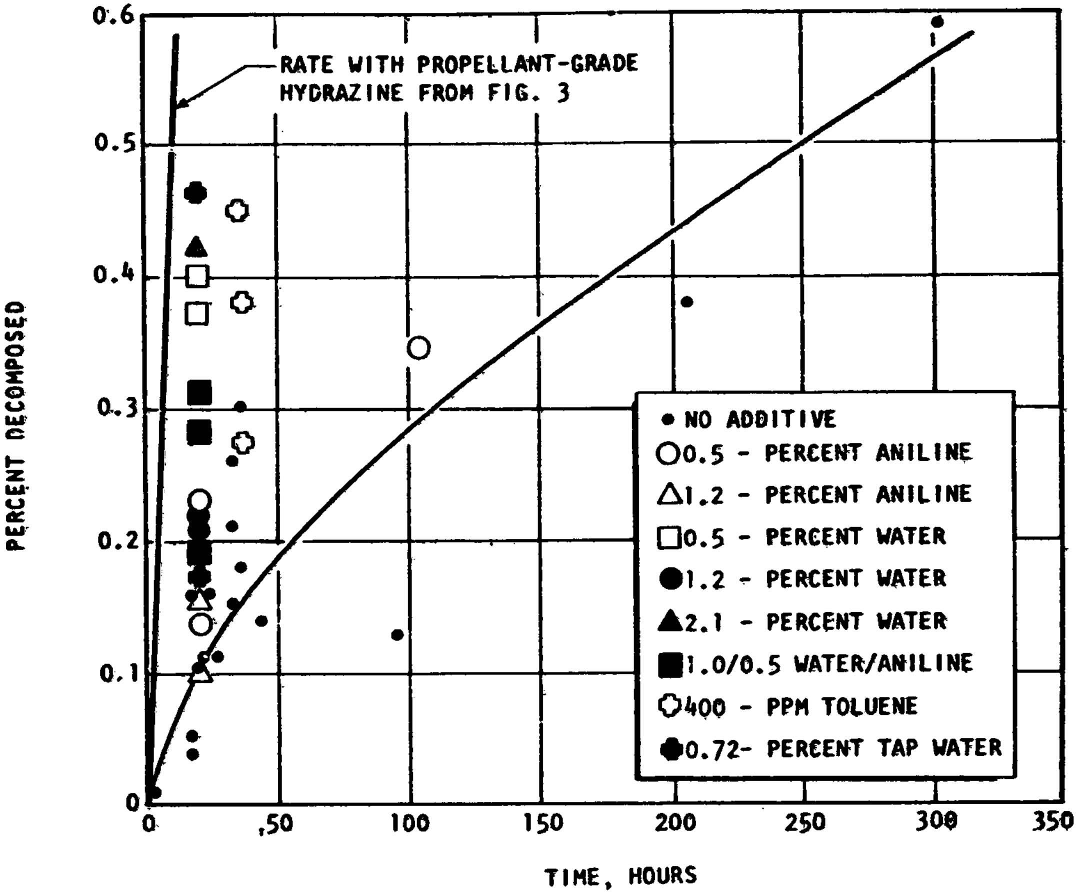


Figure 7. Decomposition Rate of Olin Purified Hydrazine in Unpassivated Pyrex Ampoules at 171 C and Effect of Added Impurities

TABLE 2

RESULTS WITH PURIFIED HYDRAZINE IN GLASS AMPOULES

Experiment No.	Sample	Temperature, C	Time, hours	Percent Hydrogen in Noncondensable Products[a]	Percent Hydrazine Decomposed		Remarks
					Total	Per Hour	
49	Olin	171	16	25.1	0.040	0.0025	
50			16	22.4	0.053	0.0033	
75			2	21.6	0.012	0.006	
76			8	3.6	0.60	0.075	High result
77			16	31.1	0.16	0.010	
78			44	(20)[b]	0.14	0.0033	
79			96	24.4	0.13	0.0014	
81			208	(20)	0.38	0.0019	
83			305	(20)	0.59	0.0020	
93			20	(20)	0.16	0.0082	
94			20	(20)	0.11	0.0055	
110			20	(20)	0.11	0.0055	
111			20	(20)	0.11	0.0055	
114			32	(20)	0.15	0.0048	
120			32	(20)	0.26	0.0082	
121			32	(20)	0.21	0.0065	
512[c]			2.8	(20)	0.020	0.0071	
517[e]			2.4	14.3	0.023	0.0103	
255		128	40	(20)	0.117	0.0029	
256		128	40	(20)	0.143	0.0035	
183		210	1.1	(20)	0.063	0.057	3-mm ID pyrex
272			48	16.4	3.22	0.067	1.5-mm ID pyrex
273			48	7.7	2.5	0.052	
274			24	(20)	2.4	0.100	
275			24	7.3	2.6	0.100	
276			48	18.1	2.1	0.044	
325[d]			16	(20)	1.52	0.095	2-mm ID quartz
327[d]			23	(20)	1.45	0.063	
328[d]			41	19.6	2.62	0.064	
329[d]			53	(20)	3.70	0.070	
330[d]			4	29.4	0.57	0.14	
331[d]			69	26.4	3.46	0.050	
295	RPL-PUR	171	20	(15)	0.045	0.0022	
296			20	13.0	0.044	0.0022	
297			20	(15)	0.031	0.0015	
298			40	13.1	0.077	0.0019	
299			40	(15)	0.068	0.0017	
300			40	(15)	0.058	0.0014	
382			66	(15)	0.22	0.0033	
383			66	13.5	0.29	0.0044	
384			66	(15)	0.37	0.0056	
454[c]			66	(20)	0.38	0.0058	

31

TABLE 2
(Concluded)

Experiment No.	Sample	Temperature, C	Time, hours	Percent Hydrogen in Noncondensable Products[a]	Percent Hydrazine Decomposed	
					Total	Per Hour	Remarks
455[c]	RPL-PUR	171	66	(20)	0.46	0.0070	
456[c]			66	22.3	0.34	0.0052	
457[c]			66	(20)	0.36	0.0055	
810[c]			72	15.9	0.14	0.0019	
811[c]			72	11.6	0.16	0.0022	
847[c]			24	23.1	0.13	0.0054	
848[c]			24	(15)	0.15	0.0062	
950[c]			24	14.0	0.14	0.0058	
951[c]			24	(15)	0.11	0.0046	
537[c]		128	24	1.2	0.019	0.00079	
538[c]			109	2.3	0.087	0.00080	
539[c]			12	(2)	0.0093	0.00077	
540[c]			1	(2)	0.0050	0.0050	High Result
541[c]			292	11.2	0.182	0.00062	
542[c]			8	(2)	0.0085	0.0011	
543[c]			3	(2)	0.0047	0.0016	
544[c]			5	(2)	0.0064	0.0013	
349		205	3	(23)	0.14	0.047	
350			7	20.6	0.79	0.11	
351			12	23.5	0.53	0.043	
353			13	(23)	0.33	0.025	
354			13	(23)	0.57	0.044	
355			13	24.7	0.43	0.033	
356			13	(23)	0.54	0.042	
357			13	(23)	0.43	0.033	
358			13	(23)	0.35	0.027	
725[c]		242	5.3	(12)	0.80	0.15	
726[c]		242	5.3	(12)	0.87	0.16	
733[c]		246	1	(12)	0.25	0.25	
734[c]			1	(12)	0.26	0.26	
735[c]			1	(12)	0.20	0.20	
736[c]			5	(37)	1.18	0.24	
737[c]			5	(23)	1.54	0.31	

[a] This value is the percent hydrogen, P, in noncondensable products ($N_2 + H_2$). The value of R for use in Eq. 6 is given by P/(100 - P).

[b] Values in parentheses were estimated from results of similar experiments. The effect of error in this value on percent hydrazine decomposed can be calculated from Fig. 1 or Eq. 7.

[c] In these experiments, ampoules were passivated overnight with hydrazine before filling. In other experiments, the ampoules were cleaned but not passivated.

[d] These experiments were in quartz ampoules--others in pyrex

TABLE 3

HYDRAZINE ANALYSIS

Sample	Composition, weight percent						
	N_2H_4	H_2O	NH_3	Aniline	Toluene	Fe	Carbazic Acid[c]
Eastman (95 Percent)	98.9	0.64	0.03	0.42	0.03		
MCB (97 Percent)	99.1	0.45	0.07	0.37	0.03		
RPL-H-3083[a]	98.8	0.70	0.05	0.49	0.01	$<10^{-5}$	
RPL-H-1726[a]	98.8	0.74	0.05	0.49	0.01	$<10^{-5}$	
RPL-H-690[a]	98.8	0.77	0.05	0.46	0.01	$<10^{-5}$	
Lot-104A[b]	98.3	0.85	0.20	0.67	0.03	0.00010	0.025
Lot-104D[b]	98.4	0.70	0.18	0.66	0.020		
Olin Purified	99.7	0.2-0.3	<0.1	0.0049	$<10^{-4}$	$<10^{-5}$	
Olin Mother Liquor	94.5	4.7	0.03	0.74	0.0026		
RPL Purified No. 1	99.3	0.38	<0.01	0.26	0.00027		0.015
RPL Purified No. 2	99.6	0.24	<0.01	0.15	$<10^{-4}$		

[a] Typical propellant-grade hydrazine from RPL.
[b] Propellant-grade from Rocketdyne tank.
[c] Carbazic acid assuming that all CO_2 liberated when sample is placed in sulfuric acid comes from carbazic acid.

171 C decreases from an initial rate of 0.008 to 0.0013 percent per hour. Thus, the rates obtained with the Olin purified hydrazine are about a factor of 7 lower than these obtained with propellant-grade hydrazine. This indicates that the thermal stability of propellant-grade hydrazine is controlled by impurities which are removed by the Olin purification process.

The rates obtained in pyrex at 171 C with the RPL purified hydrazine (Table 2) show considerably more scatter than do the results with the Olin purified hydrazine, but the average decomposition rate is about the same (0.0039 percent per hour for the RPL purified). This indicates that distillation is also an effective method of increasing thermal stability. It is of interest that the average rate in the prepassivated ampoules was about

60-percent higher than that obtained in unpassivated ampoules. This may result from the fact that propellant-grade hydrazine was employed in the passivation process, and is an indication that certain trace impurities may be rate-determining.

Much of the remainder of the data in Table 2 will be discussed later in connection with various experiments for which these data represent the baseline. However, it may be seen by comparing the rates listed in Table 2 with the propellant-grade/pyrex curve in Fig. 6 that both purified hydrazines give rates at all temperatures which are nearly an order-of-magnitude lower than those obtained with propellant-grade hydrazine.

Effect of Glass Surface

A series of experiments was conducted to determine whether the slow decomposition of purified hydrazine occurred on the reactor wall or homogeneously in the bulk liquid. Three 22-hour experiments were carried out at 172 C with glass beads added to the Olin purified hydrazine. The beads increased the glass surface in contact with the hydrazine by factors of 7.3, 9.0, and 12.4 in the three reactors and the amount decomposed increased by factors of 22, 19, and 30, respectively, over that in the unpacked reactor (2.90, 2.42, and 3.96 percent versus 0.13 percent).

These results apparently establish that the decomposition of purified hydrazine is predominantly heterogeneous at 172 C. The fact that the rate of decomposition increases more rapidly than the increase in surface area would indicate that the beads have a surface which is more active towards the decomposition of hydrazine than is the wall of the Pyrex capillary tubing. Another possible explanation is that the glass surface introduces trace impurities into the hydrazine.

These results with added glass surface indicate that the kinetics and mechanism of the inherent homogeneous decomposition of liquid hydrazine cannot be studied unless a method can be found to inhibit the rate of decomposition on the glass surface. It will be seen later that methods were discovered under this program which do decrease the heterogeneous decomposition by another order-of-magnitude.

Quartz ampoules were employed in some experiments at higher temperatures because it is less likely that strains will develop during the sealing process. It was expected that this would reduce ampoule breakage at the higher vapor pressures. The Olin purified hydrazine was tested at 210 C in 2-mm ID quartz ampoules. The results obtained at 4, 15, 23, 41, 53, and 59 hours gave an approximately linear decomposition rate of 0.060 percent per hour (Table 2). It is shown in Table 4 that the same average rate is obtained with the Olin purified hydrazine at 210 C in pyrex and quartz ampoules if a correction is made for the difference in the surface-to-volume ratio of the ampoule (Table 2); it was shown above that most of the reaction apparently occurs on the wall of the reactor. It thus appears that quartz and pyrex surfaces are comparable in activity as sites for the heterogeneous decomposition of hydrazine. The RPL purified hydrazine also gives about the same rate in pyrex at 205 C (Tables 2 and 4).

TABLE 4

COMPARISON OF RESULTS OBTAINED IN QUARTZ AND PYREX AMPOULES

Sample	Ampoule	Temperature, C	Average Rate, percent decomposed per hour		
			1.5 mm	2.0 mm	3.0 mm
Olin Mathieson Purified	Pyrex	210	0.087	(0.065)*	(0.043)
Olin Mathieson Purified	Quartz	210	(0.080)	0.060	(0.040)
RPL Purified	Quartz	205	(0.070)	(0.052)	0.035

*Values in parenthesis are corrected for internal diameter of ampoule, assuming the rate is inversely proportional to the diameter.

Effect of Pressure

Lucien (Ref. 5) has published data which indicate that the rate of thermal decomposition of liquid hydrazine is strongly pressure dependent at temperatures around 250 C. Experiments were conducted with the RPL purified hydrazine to determine if this reported pressure effect is real (liquid-phase reactions are not expected to show a marked pressure dependence). The initial pressure was varied by the addition of the inert gas argon to each ampoule. The results of these 5-hour experiments at 246 C are presented in Table 5 (hydrazine volume of 0.126 milliliter and ullage volume of 0.75 milliliter):

TABLE 5

EFFECT OF PRESSURE ON DECOMPOSITION
RATE OF PURIFIED HYDRAZINE

Experiment	Initial Argon Pressure, psi	Initial Total Pressure, psi*	Decomposition, percent
736	0	340	1.18
737	0	340	1.54
739	131	471	1.36
740	170	510	1.76
741	166	506	1.31
744	264	604	1.16

*Initial argon pressure plus hydrazine vapor pressure

These results clearly demonstrate that the rate of hydrazine decomposition is not pressure dependent. According to Lucien's results (Ref. 5), the rate should increase dramatically when the total pressure minus the vapor pressure of hydrazine drops below about 100 psia, and an explosion should occur below 10 psia. Because all of our experiments start with only the vapor pressure of hydrazine, they should therefore immediately explode--which they do not. The rates reported by Lucien at 250 C are higher by factors of 7 to 15 than those reported here under similar conditions.

Effect of Mercury

Experiments were conducted to determine whether mercury (the confining medium in Lucien's apparatus) catalyzes the decomposition of hydrazine. At 246 C, the addition of 0.4, 0.8, and 1.1 milliliter of mercury was found to have no influence upon the rate of decomposition of RPL purified hydrazine. Rates of 0.25 percent per hour were obtained with mercury added and in glass ampoules alone.

Effect of Ullage

A set of 5.3-hour experiments was conducted to determine the effect of the ratio of gas ullage to liquid hydrazine volume upon the decomposition rate of RPL purified hydrazine at 242 C. An appreciable contribution of vapor-phase reaction under these conditions would partially explain Lucien's pressure effect because the ullage volume in his system was inversely proportional to the pressure (under his constant pressure conditions). The results obtained are presented in Table 6 .

TABLE 6

EFFECT OF ULLAGE VOLUME ON DECOMPOSITION
RATE OF PURIFIED HYDRAZINE

Experiment	Volume Hydrazine, milliliters	Volume Ullage, milliliters	Final Total Pressure, psi*	Final Product Gas Pressure, psi	Decomposition, percent
724	0.126	0.744	383	51	1.18
725	0.376	0.549	478	146	0.80
726	0.376	0.556	488	156	0.87
727	0.753	0.130	1197	865	0.58
728	0.753	0.088	1672	1340	0.61

*Product gas pressure plus hydrazine vapor pressure. Ammonia is assumed to have a low solubility in hydrazine at this temperature.

These results could be construed as indicating a slight pressure effect. However, the previous set of experiments shows that this is not the case. The results of these experiments indicate that vapor decomposition in the reactor ullage is not negligible with purified hydrazine at this temperature, but the majority of the reaction does occur in the liquid phase.

Discussion of Lucien's Results

Lucien (Ref. 5) studied the isothermal, constant pressure decomposition of hydrazine and of hydrazine-ammonia mixtures. His apparatus consisted of a glass J-tube immersed in a constant temperature bath. The bottom of the J was filled with mercury. The upper part of the short leg was the reaction chamber and in the long leg a constant nitrogen pressure was maintained above the mercury column.

No explanation is evident which will explain all of Luciens results; he found a marked pressure effect, an inhibiting effect of ammonia, and a very high activation energy of about 72 kcal/mole. It is possible, however, that he may have been measuring mainly a vapor-phase reaction in the reactor ullage because his ullage volume was not fixed (as in this study), but rather, varied inversely with the total pressure on the system. This would not explain, however, why he obtained higher rates than reported here in the earlier part of some of his experiments where the ullage volume to liquid volume was the same as in the sealed ampoules.

It is <u>possible</u> that ammonia inhibits the decomposition of hydrazine vapor but not the liquid-phase decomposition. If Lucien were measuring a vapor-phase reaction, he would then observe an inhibiting effect of ammonia whereas ammonia would not affect the decomposition of propellant-grade hydrazine because the ullage reaction is negligible under these conditions. Ammonia would have a better chance of inhibiting the vapor-phase reaction because at these high temperatures, most of the ammonia present in the system will be in the gas phase rather than dissolved in the hydrazine liquid phase.

Eberstein (Ref. 14) concludes that Lucien was probably measuring a vapor-phase reaction. He proposes the following mechanism:

$$N_2H_4 \text{ (liquid)} \longrightarrow N_2H_4^* \text{ (gas)} \qquad (9)$$

$$N_2H_4^* \longrightarrow 2NH_2 \longrightarrow \text{products} \qquad (10)$$

$$N_2H_4^* + X \longrightarrow N_2H_4 + X^* \qquad (11)$$

He attributes the decrease in reaction rate with increasing pressure to reaction (11).

Eberstein accounts for the high activation energy observed by Lucien by adding the heat of vaporization to the bond dissociation energy of hydrazine. A simpler mechanism, in which the hydrazine vapor decomposes by a first-order process with an activation energy of 60 kcal/mole, would give the same apparent activation energy (70 kcal/mole) because the concentration of hydrazine would be maintained at its vapor pressure. There is a problem with this mechanism, however. Shock tube data have shown that the homogeneous vapor-phase decomposition of hydrazine would be slow at these temperatures, and a heterogeneous vapor decomposition reaction would be expected to have a considerably lower activation energy.

Stoichiometry

It may be seen from Table 2 that the amounts of hydrogen formed from the decomposition of the purified hydrazines are, on the average, higher than from propellant-grade hydrazine in pyrex ampoules. The percent hydrogen ranged from 14 to 31 with the Olin purified hydrazine (3- to 9-percent ammonia decomposed) and from 1 to 37 percent with the RPL purified hydrazine (0.2- to 12-percent ammonia decomposed).

RATE AND KINETIC PARAMETERS OF HETEROGENEOUS DECOMPOSITION

The kinetics of the heterogeneous decomposition of liquid hydrazine on metal surfaces was investigated in some detail because this is the mode of decomposition most likely to be of practical interest. Pyrex ampoules were again employed but in this case each ampoule contained a metal specimen in contact with the liquid hydrazine. In most experiments, the metal was in the form of a tube open on both ends and having a geometrical surface area of 1.0 cm^2 (compared with the approximately 4 cm^2 of glass in contact with the liquid), and the ampoule contained 0.3 ml of hydrazine.

It was found, as anticipated, that the heterogeneous decomposition rate is markedly affected by the type of metal employed and by the procedure used to clean and treat the metal specimens. Data illustrating this effect will be presented later in this section.

A "standard" metal surface was employed for many of the experiments relating to heterogeneous decomposition so that the effects of parameters other than the type and condition of the surface could be compared. The metal chosen for this was type-321 stainless steel which had been cleaned in boiling trichloroethylene, passivated at room temperature in propellant-grade hydrazine for 24 hours, rinsed in distilled water, and dried. It was beyond the scope of this program to determine the optimum alloys and cleaning procedure with respect to compatibility with hydrazine. It should not be construed, therefore, that this standard metal surface necessarily represents the optimum condition for storage of hydrazine. For these standard condition tests, the ampoules (but not the metal specimens) were cleaned in aqua-regia as usual, and both the ampoules and the specimens were passivated with hydrazine.

The use of the standard 321 stainless-steel surface turned out to be inconvenient in one respect. With propellant-grade hydrazine, the increase in the decomposition rate resulting from the addition of this surface was about the same as the rate obtained in the empty, passivated pyrex ampoules resulting in rather sizeable blank corrections under these conditions. It will be seen, however, that under most of the other conditions investigated, the rate in the absence of the metal surface was considerably slower than with the standard metal surface present. A metal less compatible with hydrazine than 321 stainless steel could have been used but this would have given conditions much different from those of practical interest.

RESULTS: PROPELLANT-GRADE HYDRAZINE ON STANDARD 321 STAINLESS STEEL

The kinetic parameters were measured in the presence of the standard 321 stainless-steel surface over a range of temperatures, and 128 C was selected as the most convenient temperature for studying the effects of parameters other than temperature on the heterogeneous decomposition rate.

The results obtained with propellant-grade hydrazine under these conditions are presented at the top of Table 7. All of these data were obtained under the standard conditions described above. The total percent hydrazine decomposed (before correcting for the amount which would have decomposed in the absence of the metal specimen) are plotted as a function of heating time in Fig. 8 (upper curve) for the experiments at 128 C. It may be seen that the heterogeneous decomposition rate on metal appears to be approximately linear with time (with a slight indication of an induction period). The dotted curve in Fig. 8 represents the reaction rate with propellant-grade hydrazine in the absence of metal surface (this curve is taken from Fig. 4). The average heterogeneous decomposition rate for propellant-grade hydrazine at 128 C was obtained from Fig. 8 by taking the difference between the slope of the upper line and the average slope of the dotted curve (blank conditions). This value of 0.0024 percent decomposed per hour is plotted (□) at 128 C in the Arrhenius plot of Fig. 6. It happens to fall in the center of the range of values which represent the decomposition rate in the ampoule alone at various heating times.

TABLE 7

RESULTS WITH STANDARD 321 STAINLESS STEEL SURFACE (1 cm^2 OF SURFACE AND 0.3 cc OF LIQUID, UNLESS SPECIFIED)

Experiment No.	Sample	Temperature, C	Time, hours	Percent Hydrogen[a]	Percent Hydrazine Decomposed[b]	Blank Correction, percent	Corrected Percent Hydrazine Decomposed		Remarks
							Total	Per hour	
490	L-104A	128	76	(5)	0.47	0.30[c]	0.17		
491				(5)	0.45	0.30[c]	0.15		
492				(5)	0.57	0.30[c]	0.27		
493				3.8	0.51	0.30[c]	0.21		
587			72	4.1	0.33	0.29[c]	0.04		
588			24	3.0	0.25	0.11[c]	0.14		
589			49	5.4	0.25	0.21[c]	0.04		
590			168	(5)	1.01	0.56[c]	0.45		
591			8	11.7	0.034	0.03[c]	--		
592			96	5.6	0.47	0.36[c]	0.11		
593			3	29.1	0.0079	0.01[c]	--		
594			1	(30)	0.0032	0.005[c]	--		
889	L-104B		24	(10)	0.54	0.11[c]	0.43	0.018	High result
666	L-104A	171	1	(5)	0.14	0.06[d]	0.08	0.080	
667			2	(0.3)	0.24	0.12[d]	0.12	0.060	
668			4	(5)	0.50	0.20[d]	0.30	0.075	
669			8	6.0	0.82	0.40[d]	0.42	0.052	
675		187	0.5	(5)	0.071	0.03[e]	0.04	0.080	
676			16	3.2	4.32	1.01[e]	3.31	0.21	
678			4	8.2	0.71	0.25[e]	0.46	0.12	
679			7	(5)	1.31	0.44[e]	0.87	0.12	
696		203	2	(5)	0.82	0.44[f]	0.38	0.19	
685		227	0.5	7.0	0.72	0.28[g]	0.44	0.88	
689		227	1	(5)	1.50	0.55[g]	0.95	0.95	

TABLE 7

(Concluded)

Experiment No.	Sample	Temperature, C	Time, hours	Percent Hydrogen[a]	Percent Hydrazine Decomposed[b]	Blank Correction, percent	Corrected Percent Hydrazine Decomposed		Remarks
							Total	Per Hour	
720	L-104A	90	576	(5)	0.213	0.127[h]	0.086	0.00015	1 cm^2
717	↓	↓	↓	8.8	0.199	0.127[h]	0.072	0.00012	3 cm^2
718				(5)	0.244	0.127[h]	0.117	0.00020	3 cm^2
719				(5)	0.232	0.127[h]	0.105	0.00018	3 cm^2
521	RPL-PUR	128	2.1	19.9	0.0042	0.0021[i]	0.0021	0.0010	
522	↓	↓	51	5.5	0.25	0.05[i]	0.20	0.0039	
523			199	4.5	1.06	0.20[i]	0.86	0.0043	
524			24	16.4	0.049	0.024[i]	0.025	0.0010	
525			32	7.9	0.127	0.032[i]	0.095	0.0030	
526			8	(15)	0.021	0.008[i]	0.013	0.0016	
527			6	25.3	0.011	0.006[i]	0.005	0.00083	
528			292	4.3	1.83	0.29[i]	1.54	0.0053	
529			144	4.8	0.97	0.14[i]	0.83	0.0058	
530			74	7.5	0.31	0.07[i]	0.24	0.0032	
531			1	(15)	0.0026	0.0010[i]	0.0016	0.0016	
532			3	28.7	0.0070	0.0030[i]	0.0040	0.0013	
533			168	5.2	0.87	0.17[i]	0.70	0.0042	
534			109	5.5	0.49	0.11[i]	0.38	0.0035	
535			12	3.5	0.038	0.012[i]	0.026	0.0022	
536			5	(15)	0.016	0.005[i]	0.011	0.0022	

[a] This value is the percent hydrogen, P, in noncondensable products ($N_2 + H_2$). The value of R for use in Eq. 2 is given by P/(100-P).

[b] Measured value uncorrected for reaction in absence of metal

[c] From Fig. 4

[d] From Fig. 3

[e] From line in Fig. 6, blank = 0.063 percent per hour

[f] From line in Fig. 6, blank = 0.22 percent per hour

[g] From line in Fig. 6, blank = 0.55 percent per hour

[h] From line in Fig. 6, blank = 0.00022 percent per hour

[i] Average rate from Table 2, blank = 0.0010 percent per hour

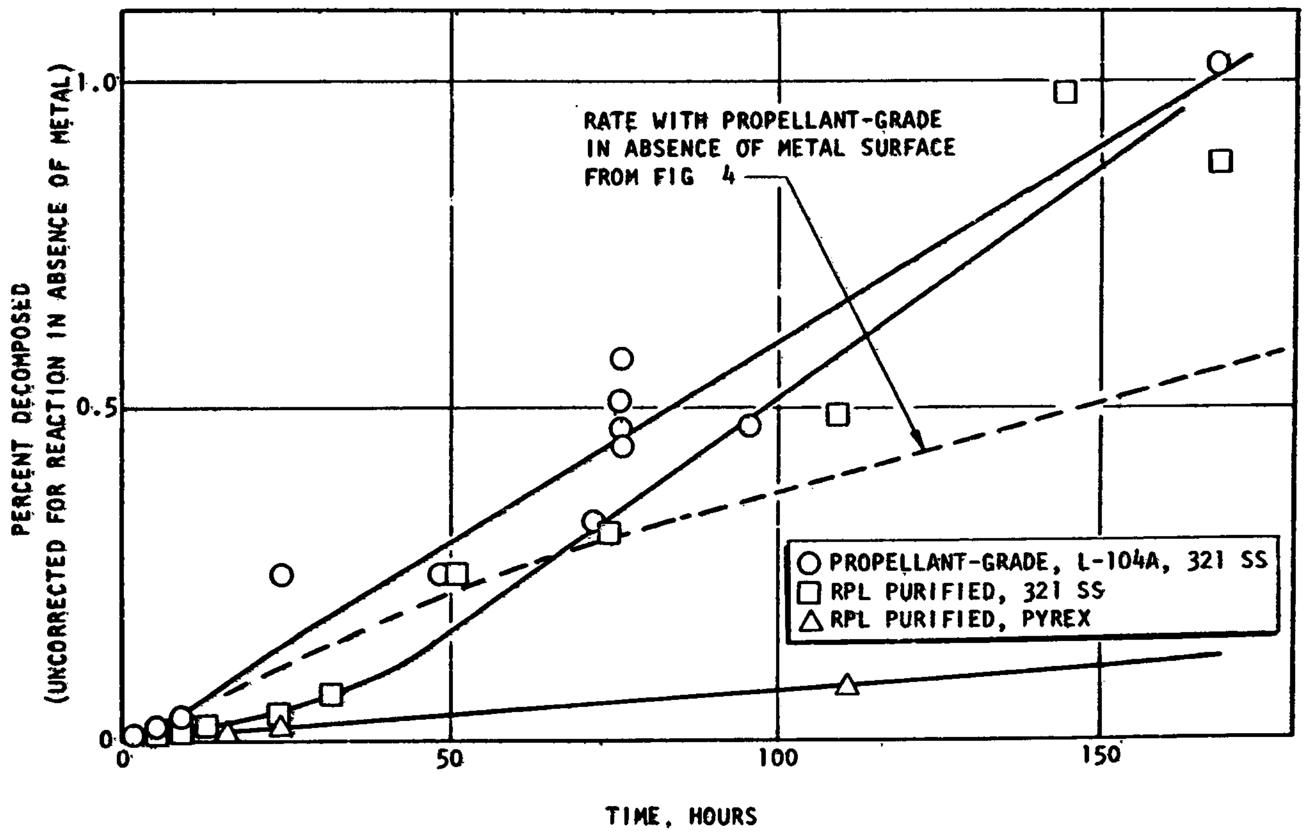


Figure 8. Hydrazine Decomposition Rate in Presence of Standard 321 Stainless-Steel Specimen at 128 C

Effect of Temperature

The remaining data with propellant-grade hydrazine in Table 7 , obtained at temperatures other than 128 C, are corrected for the blank decomposition rates as described in the footnotes of the table, and are also plotted in Fig. 6 . The corrected rates at 171 C (ninth column of Table 7) are approximately linear with time (within the scatter of the results) and have an average value of 0.067 percent per hour (which is plotted in Fig. 6). The heterogeneous rate at 187 C appears to increase with time with an average value of 0.13. The corrected rate is 0.19 at 203 C and the average value at 227 C is 0.91 percent per hour.

The single experiment at 90 C in which the area of the standard metal specimen was 1 cm^2 (Experiment 720 of Table 7), gave a heterogeneous decomposition rate of 1.5×10^{-4} percent per hour and this value is plotted in Fig. 6 using the symbol □. However, the three experiments at 90 C in which the size of the specimens were increased to a geometric surface area of 3 cm^2 gave an average corrected rate of 1.7×10^{-4}, which is about the same as was obtained with a 1 cm^2 specimen. This rate was divided by 3 before plotting in Fig. 6 because the rates listed there are in percent per hour per cm^2 of metal surface; the resulting value represented by the symbol Ⓧ, of course falls below the other point. This suggests the interesting possibility that the observed "heterogeneous" decomposition rate is not directly proportional to the area of the metal surface which is present. This effect was investigated in detail and the results, presented in the next section, indicate that this is the case.*

The activation energy for the heterogeneous decomposition of propellant-grade hydrazine on 321 stainless steel, obtained from Fig. 6 , is 22.7 kcal/mole (compared to a similar activation energy of 20.5 kcal/mole obtained in the absence of metal.

---

*To simplify the discussion, the term heterogeneous decomposition is used throughout this report even though part of the effect of a metal surface may result from the introduction of impurities which catalyze the homogeneous reaction.

Effect of Metal Surface Geometry

A series of experiments was conducted to determine the effect of varying the total surface area and geometry of the standard 321 stainless steel specimens upon the rate of decomposition of propellant-grade hydrazine at 128 C. It was of particular interest to determine whether the decomposition rate is proportional to the surface area of the metal and if the decomposition occurs more rapidly at the freshly cut end of the specimen. The procedure consisted of cutting a 1/16-inch 321 stainless steel tubing into sections having total surface areas of 1 and 3 cm^2, respectively. The surface area and geometry was varied by changing the number and size of sections added to each ampoule. The specimens and ampoules were cleaned and passivated with hydrazine in the usual manner for the standard conditions, and the ampoules were heated for 24 hours at 128 C. The results are presented in Table 8.

The results in Table 8 are somewhat inconclusive because of the scatter in the data and the rather large blank correction. When the number of 1-cm^2 sections is varied, the corrected rate is approximately proportional to the number of specimen sections present. However, the rate in the presence of one specimen with a total surface area of 3 cm^2 is about one-half that obtained with three 1-cm^2 specimens.

One explanation of these results would be that the decomposition occurs more rapidly on the ends of the specimen which were cut during their preparation (from long tubular stock). Another possibility is that all of the increase in rate when metal specimens are added does not come from simple heterogeneous surface decomposition but instead some of the increase results from the dissolution of trace metal impurities into the liquid. This latter process could occur more rapidly at the cut ends of the specimen.

The possibility that trace metal contaminants play a major role in the decomposition of hydrazine is in agreement with some of the results, reported in later sections, which relate to the role of impurities and to reaction mechanism.

TABLE 8

EFFECT OF METAL SURFACE GEOMETRY ON DECOMPOSITION OF PROPELLANT-GRADE HYDRAZINE (24 HOURS AT 128 C, STANDARD 321 STAINLESS STEEL)

Experiment	Total Area of 321 Stainless Steel, cm^2	Number of Sections	Percent Decomposed Per Hour	Corrected Percent Decomposed Per Hour*	Average
759	3	3	0.0092	0.0049	0.0054
760	3	3	0.0096	0.0053	
761	3	3	0.0083	0.0040	
762	3	3	0.0117	0.0074	
763	3	1	0.0071	0.0028	0.0028
764	3	1	0.0071	0.0028	
765	3	1	0.0071	0.0028	
766	2	2	0.0067	0.0024	0.0030
767	2	2	0.0079	0.0036	
768	1	1	0.0058	0.0015	0.0020
769	1	1	0.0063	0.0020	
770	1	1	0.0063	0.0020	
771	1	1	0.0067	0.0024	
772	1	1	0.0063	0.0020	
773	0	0	0.0046		
774	0	0	0.0042		
775	0	0	0.0042		

*Obtained by subtracting rate in absence of metal, 0.0043, from measured rate.

Stoichiometry

It may be seen from Table 7 that, with the exception of one experiment, the percent hydrogen formed from propellant-grade hydrazine in the presence of a standard 321 stainless-steel specimen ranged from 3 to 12 percent. This corresponds to 0.5- to 2.4-percent ammonia decomposed.

RESULTS: PURIFIED HYDRAZINE ON STANDARD 321 STAINLESS STEEL

The results obtained with the RPL purified (distilled) hydrazine at 128 C with 321 stainless steel are listed in Table 7. The total percent decomposed in each experiment (uncorrected for reaction in the absence of the metal specimen) are plotted in Fig. 8. As shown in Fig. 8, the purified hydrazine decomposes more slowly than propellant-grade for about 1 day and then its decomposition rate becomes about the same as that of propellant-grade hydrazine. It may be recalled that in the absence of the metal surface, the purified hydrazines decomposed at rates which were nearly an order-of-magnitude lower than those obtained with propellant-grade hydrazine. Data from Table 2 are plotted in the lower curve of Fig. 8. It may be seen that only in the absence of a metal surface does the distilled hydrazine give a significantly lower decomposition rate than propellant-grade.

The fact that the rate with purified hydrazine in the presence of a metal surface increases after about 1 day (Fig. 8) presents again the possibility that some very effective trace impurity is being leached out of the alloy during this period. It might reach its "solubility limit" after 1 day at which time the purified hydrazine would then behave as does propellant-grade.

Another possible explanation, which does not easily account for the low initial rate with purified hydrazine, is that the rate of the heterogeneous decomposition reaction on metal is independent of the purity of the hydrazine whereas the decomposition which occurs in the absence of the metal surface is impurity-catalyzed. If this explanation is correct, it is merely a coincidence that propellant-grade hydrazine decomposes at about the same rate and with the same activation energy both in the presence and absence of a metal surface. However, this would not appear very probable. Also, it will be shown later that the rate in the presence of a metal surface can be reduced by about an order-of-magnitude by pretreating the hydrazine with BaO.

Stoichiometry

It may be seen from Table 7 that the percent hydrogen formed from RPL purified hydrazine in the presence of 321 stainless steel ranges from 3 to 29 percent. This corresponds to 0.5- to 8-percent ammonia decomposed (Eq. 6).

RESULTS WITH VARIOUS METAL SURFACES

During the course of this investigation, data was obtained pertaining to the rate of hydrazine decomposition on a variety of metal surfaces other than the standard 321 stainless-steel surface for which the results have already been presented. The results obtained with various metals are presented and discussed in this section. No effort was made to optimize the cleaning and passivation procedure for any of the metals. Therefore, the results presented here for a given metal or alloy should not be taken as having established its utility for use with hydrazine. This is particularly true because it was found that the cleaning and passivation techniques employed with a given metal surface could markedly affect the hydrazine decomposition rate.

The results with various metals will be presented in approximately the order in which they were obtained, because some changes were incorporated in the procedure employed during the course of the investigation.

Beryllium/Propellant-Grade Hydrazine, 93 C

Initial experiments were conducted with "as-received" beryllium wire. It was found that the wire was covered with a coating which flaked off when placed in hydrazine. When the hydrazine was outgassed, bubbling occurred both at the surface of the wire and on the flakes of coating which had fallen to the bottom of the tube. Three of the tubes were sealed after outgassing and stored at room temperature. They were opened after 2, 17, and 840 hours and had undergone 0.07-, 0.04-, and 0.65-percent decomposition, respectively, indicating that a slow reaction continued at room temperature. A fourth ampoule was heated for 2 hours at 93 C and then held at room temperature for 35 days (gas measuring system was being remodeled). It underwent 1.8-percent hydrazine decomposition.

These results with "as-received" beryllium are not considered particularly significant because it became obvious that some type of coating was initially present on the wire.

Al, Ni, Fe/Olin Purified Hydrazine, 171 C

A series of experiments was conducted to determine the rate of decomposition of liquid Olin purified hydrazine on the surfaces of high-purity Ni, Fe, and Al wires. A 3-centimeter length of wire was immersed in 0.3 milliliter of the purified hydrazine in each glass ampoule (four ampoules for each metal).

The wires were 1 millimeter in diameter. Two different wire cleaning procedures were compared to determine if they affected the decomposition rates: (1) after 1 hour in concentrated nitric acid, rinse with distilled water and oven dry, and (2) scrape with emery cloth and wipe clean. The ampoules were all heated to 171 C for 15 hours.

The ampoules containing Ni or Fe wire all broke during this heating period, indicating that considerable decomposition had occurred (greater than 5 to 10 percent). However, all of the ampoules containing Al wire remained intact and gave the following results:

Run	Treatment	Percent Decomposed	R_1/R_2*
139	Nitric Acid	0.32	3.5
140	Nitric Acid	0.30	3.3
141	Emery Cloth	0.58	6.4
142	Emery Cloth	0.56	6.2

*R_1 is rate in the presence of metal, R_2 is rate in the absence of metal (Fig. 8)

The geometric surface area of the aluminum wire in the preceding experiments was 0.95 cm^2 compared to the 4 cm^2 of glass in contact with the liquid. Therefore, the purified hydrazine decomposes approximately 10 times faster (per unit geometric area) on the nitric acid cleaned Al wire than on the pyrex reactor wall

Al, Ni, Fe, and Stainless Steels/ Propellant-Grade Hydrazine, 171 C

The rate of decomposition of liquid propellant-grade hydrazine (L-104A) was measured on several metal surfaces at a temperature of 171 C. The metals were high-purity Fe, Ni, and Al, and 304, 316, 321, and 347 stainless steels, and the experiments were conducted in 3-millimeter ID pyrex tubing with the metal submerged in the liquid phase. The pure metals were in the form of 1-millimeter diameter wire, and the stainless steel was 1/16-inch OD tubing; the metal surfaces were cleaned with concentrated nitric acid. The heating time was limited to 0.6 hour at this temperature to prevent the ampoules from breaking from excess pressure buildup in the presence of the most active metal surface (which was Ni in this series).

The results of this series of experiments are presented in Table 9 . As the metal samples were not all of the same diameter, the percent decompositions in the presence of metal were corrected to a geometric metal surface

TABLE 9

DECOMPOSITION OF PROPELLANT-GRADE HYDRAZINE ON VARIOUS METAL SURFACES

(171 C, 0.6-Hour Heating Time)

Experiment No.	Metal Surface	Percent Decomposed	Percent Hydrogen
156	None	0.012	30.6
159	None	0.013	- -
166	None	0.014	- -
155	Fe (pure)	1.37	0.8
157	Fe (pure)	1.30	0.8
158	Fe (pure)	0.37	2.0
160	Ni (pure)	3.00	1.5
161	Ni (pure)	*	- -
162	Ni (pure)	2.08	3.1
163	Al (pure)	0.016	33.9
164	Al (pure)	0.007	- -
165	Al (pure)	0.015	28.0
167	304 Stainless Steel	0.16	- -
168	304 Stainless Steel	0.13	- -
169	304 Stainless Steel	0.089	4.3
170	304 Stainless Steel	0.15	3.5
171	316 Stainless Steel	*	- -
172	316 Stainless Steel	*	- -
173	316 Stainless Steel	0.32	- -
174	316 Stainless Steel	1.76	1.7
175	321 Stainless Steel	0.15	- -
176	321 Stainless Steel	0.13	2.8
177	321 Stainless Steel	0.13	2.8
179	347 Stainless Steel	0.44	- -
180	347 Stainless Steel	0.56	0.8
181	347 Stainless Steel	0.55	1.7
182	347 Stainless Steel	0.49	1.9

*Ampoule broke

area of 1 cm^2. In the absence of added metal, the propellant-grade hydrazine gave only 0.013-percent decomposition under these conditions, in this series of experiments, and the noncondensable product was about 30-percent hydrogen and 70-percent nitrogen.

The presence of the pure aluminum wire did not increase the decomposition rate of the propellant-grade hydrazine. It was reported above that the same aluminum wire did increase the decomposition rate of the Olin purified hydrazine at 171 C, but only by a factor of about 2.4 (a direct comparison cannot be made because the heating time was 15 hours with the purified hydrazine).

As may be seen from the data in Table 9 the wires of pure Fe and Ni increased the decomposition rate by factors of about 100 and 200, respectively. The percent hydrogen in the gaseous product was small (1 to 3 percent) in these experiments.

The various stainless steels were found to show marked differences in their effect on the rate of hydrazine decomposition (Table 9). The rates in the presence of the 304 and 321 stainless steel were about 10 times those in the absence of metal. This factor was about 40 with 347 stainless steel. The 316 stainless steel gave the highest rate of the stainless steels (a factor of 130 in one experiment), but the results with this metal were erratic and two of the ampoules broke, presumably from excessive pressure buildup. The rate obtained with 321 stainless steel under these conditions (nitric acid cleaned and not passivated with hydrazine) are higher by more than a factor of 3 than the rates obtained at 171 C with the standard 321 stainless steel surface (Table 7).

347 and 321 Stainless Steel/Propellant-Grade Hydrazine, 95 C.

A series of experiments was conducted at 95 C to determine the decomposition rate of propellant-grade hydrazine on 347 stainless steel as a function of heating time. The metal was cleaned in trichloroethylene and treated with nitric acid but was not passivated with hydrazine. This alloy was found (Table 9) to have an activity greater than that of 304 and 321 stainless steel, but less than that of 316 stainless steel (0.6 hour at 171 C). The data points (Fig. 9) were obtained from 4 to 264 hours at 95 C. The results fall on an approximate straight line, with zero intercept and a slope of 0.005 percent per hour. The average scatter in the data around the line is ±15 percent.

Two experiments with 321 stainless steel were included in the series at 95 C for comparison with 347 stainless steel under these conditions (Fig. 9). At 94 hours, the percent decomposed was the same with 321 stainless steel as with 347 stainless steel, and at 264 hours the propellant-grade hydrazine had decomposed 0.44 percent with 321 stainless steel compared to 0.56 percent with 347 stainless steel.

The rate for 321 stainless steel in Fig. 9 is higher than that obtained at 90 C under standard conditions (Table 7) by about a factor of 30. Presumably, this results mainly from the difference in the method of surface preparation. Also, the blank rates in Fig. 9 are higher than those obtained in passivated ampoules (Fig. 6) by about a factor of three. However, these blanks were not high enough to interfere with the surface reaction being measured.

The above experiments, conducted at 95 C to determine the most convenient temperature at which to conduct detailed kinetic studies on these metal surfaces, made it evident that the rate is inconveniently slow at 95 C. Calculations based on these results indicated that approximately 130 C would be the most convenient temperature.

Al, Ni, Fe, Be, and Stainless Steels/ Propellant-Grade Hydrazine

A series of 28-hour experiments was conducted at 128 C with propellant-grade hydrazine to compare various metals at this temperature. Triplicate tests

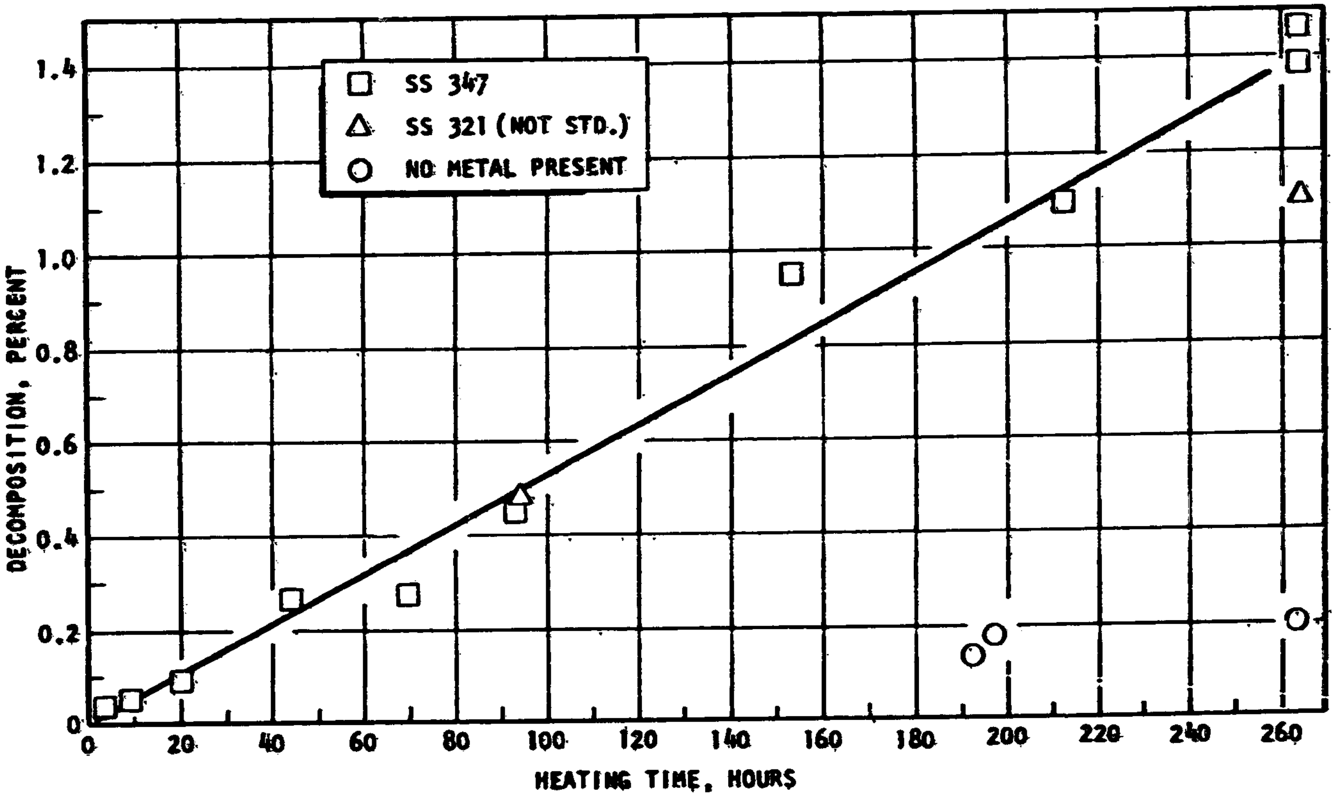


Figure 9. Decomposition of Propellant-Grade Hydrazine on 347 and 321 Stainless Steel at 95 C

were run with each of the following metals: Ni, Fe, Al, Be, and 304, 316, 321, and 347 stainless steel. A general description of the 300-series stainless steels used on this program is given in the Appendix. The metals were cleaned with trichloroethylene and treated with nitric acid. All of the ampoules which contained Ni, Fe, 316, or 347 stainless steel were found broken after 28 hours of heating. Two of the ampoules containing 321 stainless steel and one of the ampoules containing 304 stainless steel were broken. The measurement of the products in the remaining intact ampoules gave rates which were much higher than expected; in fact, the rates were approximately those expected at 170 C. It appears very likely, therefore, that the oven overheated during the night and returned to the correct temperature by morning. (The blank runs in this series are also in agreement with this conclusion.) A temperature recorder was employed in later experiments.

Despite the temperature control problem, the metals rated in this series as they had in the previous experiments at 170 C. On this basis, one result obtained is potentially very significant. Beryllium which had been cleaned with nitric acid was investigated for the first time in this series and gave decomposition rates approximately equal to those obtained with 304 stainless steel (about 2-percent hydrazine decomposed after 28 hours of heating). In Table 9, 304 stainless steel is shown to be one of the least active stainless steels. This suggests that the problems involved in the use of hydrazine in interregeneratively cooled bipropellant engines may be eventually overcome.

347 Stainless Steel/Propellant-Grade Hydrazine, 128 C

The decomposition of propellant-grade hydrazine on 347 stainless steel (acid-treated) was determined as a function of heating time at 128 C. The results are shown on the following page.

Experiment No.	Time, hours	Percent Hydrogen	Percent Decomposed	Percent Decomposed Per Hour
229	4.5	8.5	0.073	0.016
231	11.5	3.5	0.18	0.016
232	23	(2)	2.16	0.094
233	31	1.4	0.86	0.028
234	48	(2)	1.28	0.027
235	72	1.1	3.88	0.054
236	144	2.0	2.06	0.014

It is apparent from the last column in the above table that these data have a very poor reproducibility even though a similar series of experiments at 95 C (Fig. 9) had given an excellent linear plot.

A series of experiments was run with 347 stainless steel at 128 C with a constant heating period of 40 hours to determine the reproducibility on an acid-cleaned 347 stainless steel surface with propellant-grade hydrazine. The following results were obtained:

Experiment No.	Percent Decomposed	Percent Decomposed Per Hour
248	4.5	0.11
251	1.5	0.038
252	0.86	0.021
253	1.8	0.045
254	2.3	0.058

The scatter of the results was again excessive.

It was discovered after these experiments had been run that the blank rate in the absence of metal specimen was often excessive at 128 C if the pyrex ampoules were not prepassivated with hydrazine. This effect was discussed earlier in this report (Fig. 4 and Table 1). Three of the experiments in Table 1 with unpassivated ampoules (Experiments 321, 322, and 323) gave rates in the absence of metal of about 0.025 percent per hour. It may be seen that erratic blanks of this order of magnitude could account for the data scatter in the above two tables.

347 Stainless Steel/Purified Hydrazine, 128 C

Three ampoules containing the Olin purified hydrazine with a 347 stainless-steel specimen were included in the above series of 40-hour experiments at 128 C. The following results were obtained:

Experiment No.	Percent Decomposed	Percent Decomposed Per Hour
240	0.30	0.0075
241	1.23	0.031
242	0.58	0.014

The reproducibility was again poor.

These rates, obtained with Olin purified hydrazine on acid-treated 347 stainless steel, are about three times higher than the rates obtained at the same temperature with either propellant-grade or RPL purified hydrazine on the standard 321 stainless-steel surface (Fig. 8). This difference probably results from the difference in the method of preparation of the surface. It is possible that the poor reproducibility of these experiments also results from high blank rates, but for this to be the case the rates must fluctuate to values higher than those of Experiments 255 and 256 in Table 2.

347 Stainless Steel--Effect of Surface Treatment

A series of 48-hour experiments was run at 110 C with propellant-grade hydrazine (L-104A) and 347 stainless steel to investigate the effect of the method of cleaning the metal surface. The pyrex ampoules were not prepassivated. In the first six experiments, the metal was cleaned with boiling nitric acid and rinsed with distilled water; the average decomposition was 2.1 ±1.1 percent. In the other six experiments, the surface was cleaned with trichloroethylene; the average decomposition was only 0.67 ±0.21 percent. The scatter in the data was excessive in each series, but the acid cleaned specimens gave the higher average rates.

Experiments were conducted at 128 C with propellant-grade hydrazine (L-104A) to determine the effect of various treatments of the 347 stainless-steel surface. The results are presented in Table 10. The results obtained with acid-treated 347 stainless steel in Experiments 229 through 236 and 248 through 254, which were presented in previous tables, are included at the top of Table 10 for comparison.

In the 17-hour experiments, the metal was boiled in trichloroethylene, rinsed in trichloroethylene, rinsed in acetone, boiled in acetone, rinsed in acetone, boiled in distilled water, rinsed in distilled water, and dried. Very high decomposition rates were obtained in these experiments (Table 10).

The hydrazine passivation technique which was found to be effective for the glass ampoules was used with the metal specimens in the first series of 64-hour experiments in Table 10. The specimens were cleaned in boiling trichloroethylene, dried, passivated with propellant-grade hydrazine for 24 hours, rinsed with distilled water, and dried. Much lower rates were obtained than with the previous cleaning techniques, but additional experiments would be required at 128 C with trichloroethylene alone to establish definitely the effect of prepassivation with hydrazine.

The lack of reproducibility from ampoule to ampoule in these experiments could result from an actual nonuniformity of the surfaces of the metal specimens. To test this, the metal specimens used in the 64-hour experiments were recleaned in boiling trichloroethylene, passivated in hydrazine (3 hours), and rerun with propellant-grade hydrazine (Table 10). A direct correlation could not be established between the relative activities of

TABLE 10

EFFECT OF SURFACE TREATMENT ON DECOMPOSITION RATE OF HYDRAZINE ON 347 STAINLESS STEEL AT 128 C

Propellant	Time, hours	Percent Decomposed	Percent Decomposed Per Hour	Average	Surface Treatment	
					Metal	Ampoule
Propellant Grade (Lot-104)	4.5	0.073	0.016	0.038	Wash in trichloroethylene, concentrated HNO$_3$ at RT for 1 hour, rinse with distilled water and dry	Aqua regia
	11.5	0.18	0.016		↓	↓
	23	2.2	0.094			
	31	0.86	0.028	↓		
	40	4.5	0.11	0.054		
	40	1.5	0.038			
	40	0.86	0.021			
	40	1.8	0.045			
	40	2.3	0.058	↓		
	48	1.28	0.027	0.032		
	72	3.9	0.054			
	144	2.1	0.014	↓		
Propellant Grade (Lot-104)	17	4.6	0.27	0.41	Boil in trichloroethylene, boil in acetone, boil in water, rinse with distilled water and dry	
	17	7.2	0.42			
	17	8.8	0.52			
	17	6.2	0.36			
	17	8.5	0.50	↓		↓
Propellant Grade (Lot-104)	64	0.90(A)*	0.014	0.020	Boil in trichloroethylene, Hz passivated for 24 hours, rinse with distilled water and dry	Aqua regia, Hz passivated
	64	1.09(B)	0.017			↓
	64	1.10(C)	0.017			
	64	1.22(D)	0.019			
	64	1.72(E)	0.027			
	64	1.72(F)	0.027	↓		
Propellant Grade (Lot-104)	64	0.27(A)	0.0042	0.0052	Rerun of above specimens after recleaning and passivating in hydrazine	
	64	0.31(C)	0.0049			
	64	0.34(D)	0.0053			
	64	0.34(E)	0.0053			
	64	0.40(F)	0.0063	↓		↓
Purified (Olin Mathieson)	40	0.30	0.0075	0.018	Same as other 40-hour experiments at top of table	Aqua regia
	40	1.23	0.031			
	40	0.58	0.014	↓		↓

*Letter designates individual metal specimen given specimens in the first and second runs. It was found, however, that the average decomposition rate in the second series of 64-hour experiments was only one-fourth that of the first 64-hour runs. It appears that contacting the metal with hydrazine and/or its decomposition products at 128 C further passivates the surface. The average rate obtained in the second series of 64-hour experiments (0.0052 percent per hour) is 1 order of magnitude lower than the rate with acid-cleaned specimens, and 2 orders of magnitude lower than with trichloroethylene/acetone-cleaned 347 stainless-steel specimens. Note that the rate obtained in this final series of 64-hour experiments is only slightly higher than would be expected in the absence of a metal specimen (Fig. 4).

The results of Experiments 240 through 242, presented previously, with Olin purified hydrazine and acid-treated 347 stainless steel are listed at the bottom of Table 10 for comparison. A very large scatter in the results was obtained. Comparison of these experiments with the 40-hour experiments using propellant-grade hydrazine (Table 10) indicates that the purified hydrazine gives a lower rate when compared under identical conditions.

Chromel-A, Cu, Al, Stainless Steels/ Propellant-Grade Hydrazine, 128 C

A final series of experiments was run at 128 C to compare the relative catalytic activities of several metal surfaces which had been passivated in hydrazine for three days at room temperature (after cleaning in boiling trichloroethylene). Results obtained with propellant-grade hydrazine (L-104A) with a heating time of 75.5 hours are shown on the following page.

The rate obtained with 321 stainless steel (after subtracting the blank) is that which would be expected (Fig. 8) under these standard conditions.

Specimen	Percent Decomposed	Specimen	Percent Decomposed	Specimen	Percent Decomposed
Chromel-A	1.09	321 Stainless Steel	0.47	Fe	Broke
	2.64		0.45		
	2.13		0.57		
	2.12		0.51	Ni	Broke
Cu	1.10	316 Stainless Steel	3.40		
	0.89		2.67	None	0.26
	0.90		2.92		0.36
	0.97		4.12		0.32
Al	0.97	304 Stainless Steel	0.92		
	0.57		0.60		
	0.38		0.87		
	0.74		1.12		
	0.84				
	0.68				

It was unexpected that aluminum would be more active than 321 stainless steel because aluminum had shown no effect over pyrex at 171 C (Table 9). It appears that aluminum requires a nitric-acid passivation. It was also unexpected that copper would give results similar to those obtained with the stainless steels because copper is reportedly incompatible with hydrazine (perhaps this is the case at higher temperatures).

The percent hydrogen in the noncondensable product was measured in a few of the experiments listed in the above tables. The values were: Chromel A, 3.6; copper, 9.3; aluminum, 14.2; 321 stainless steel, 3.8; 316 stainless steel, 1.9 and 3.4; and no metal (blank), 4.6. These values for percent hydrogen again give very low calculated values (Eq. 6) for the percent ammonia decomposed.

Sodium Hydroxide Passivation

Hydrazine was shown to be an effective passivating agent for glass and 321 stainless-steel surfaces. Experiments were conducted to determine if a stronger base, 5M NaOH, might not be an even more effective passivating agent (the decomposition of hydrazine will be shown later to be acid-catalyzed). The results of these experiments indicate that hydrazine is more effective in passivating a 321 stainless-steel surface than is concentrated NaOH. Ampoules containing 321 stainless-steel specimens which had been passivated with propellant-grade hydrazine (24 hours at room temperature) gave decomposition rates at 128 C, which were approximately one-third lower than those obtained with specimens which had been passivated in 5M NaOH. However, experiments conducted at 171 C in glass ampoules alone (no metal present) indicated that 5M NaOH was slighly more effective than hydrazine in passivating glass.

Conclusions on the Effect of Metal Surface

It may be concluded that the rate of the heterogeneous decomposition of hydrazine can vary by one or two orders of magnitude, depending on the type of metal used and the type of pretreatment employed. These results indicate that detailed passivation studies should be conducted with alloys of interest to ensure that reliable storability of hydrazine can be obtained and to determine the optimum conditions for long-term storage.

ROLE OF IMPURITIES

One of the major goals of this program was to determine the effects of hydrazine impurities on the kinetics of the homogeneous and heterogeneous decomposition reactions. If such effects were found, the reaction mechanisms involved were to be investigated. In addition to the known impurities in hydrazine, the effects of potential impurities must also be established so that the thermal stability of hydrazine can be predictably controlled. This applies also to additives which might be used for various purposes (such as to increase the electrical conductivity) and to other components which might be added in a mixed hydrazine fuel.

It was shown in the first section of this report that propellant-grade hydrazines decompose in pyrex ampoules (in the absence of a metal surface) at rates which are nearly an order of magnitude greater than are obtained with samples of purified hydrazine under the same conditions. This would indicate that the homogeneous decomposition of propellant-grade hydrazine is an impurity-catalyzed reaction.

It was shown in the second section of this report that the rate of the heterogeneous decomposition of hydrazine on a metal surface is a function of the purity of the sample under some conditions, but with a well passivated surface and at long reaction times, the rate is nearly independent of the purity of the sample (Fig. 8).

Two possible explanations were suggested for the limited effect of sample purity on the heterogeneous decomposition rate: (1) the major heterogeneous reaction mechanism is simply not markedly dependent on the purity of the hydrazine, and (2) the purified hydrazine leaches impurities out of the metal surface and becomes "impure" hydrazine--at least with respect to the critical impurities. The first explanation is weakened by the fact that the kinetic parameters are about the same for the heterogeneous decomposition of propellant-grade hydrazine as for the impurity-catalyzed homogeneous decomposition in the absence of a metal surface (this includes the pre-exponential factor and activation energy, Fig. 6, and the overall stoichiometry). The second explanation is in agreement with other observed phenomena (e.g., effect of specimen geometry, Table 8, and the reduction in rate when the metal samples are rerun, Table 10).

The first approach to establishing the role of impurities with respect to the thermal stability of hydrazine was to determine the major impurities and investigate their effect on the decomposition rate. The results of the analyses performed on a variety of hydrazine samples were presented in Table 3, and the details of these analyses are presented in a later section of this report. The impurities identified in the propellant-grade hydrazines are: water, ammonia, aniline, toluene, iron, and carbazic acid (N_2H_3COOH, the reaction product of hydrazine and CO_2).

The effect of NH_3 was reported earlier because it is also a decomposition product of hydrazine. It was found not to affect the decomposition rate under the conditions investigated. The results obtained relating to the other impurities, and also to potential impurities, are reported here.

EFFECT OF ANILINE

Aniline is present at a concentration of about 0.5 weight percent in commercial hydrazines because it is added to azeotrope the water from the crude hydrazine. It may be seen from Table 3 that a single distillation (RPL purified) is not particularly effective in removing the aniline, but the process used to prepare the Olin purified sample (fractional crystallization) reduces the aniline content to about 50 ppm. Aniline contents as low as 5 ppm have been obtained by double distillation from CaH_2 (Ref. 15).

Three experiments were conducted at 171 C with 0.5 weight percent aniline added to the Olin purified hydrazine and two were conducted with 1.2-percent aniline. The results are plotted in Fig. 7. The upper curve drawn in Fig. 7 is copied from Fig. 3 for comparison, and represents the average decomposition rate for the propellant-grade hydrazines. It may be seen that within the normal scatter of these experiments, the aniline did not affect the decomposition rate appreciably. The rates with added aniline were, on the average, slightly higher than were obtained without added aniline, but the rates certainly did not approach those obtained with propellant-grade hydrazine.

The values for percent hydrogen in the noncondensable products obtained when aniline was added were 18.1, 15.6, 10.9, and 18.1.

EFFECT OF WATER

The effect on the decomposition rate during the first 20 hours at 128 C of adding distilled water to the Olin purified hydrazine is shown in Fig. 7. The addition of 0.5 or 2.1 weight percent water markedly increases the decomposition rate but not to that of propellant-grade hydrazine. For some reason, the addition of 1.2 percent water had little effect on the rate.

Two experiments of 92 hours duration with 0.5 and 2.1 percent added water gave decomposition values of 0.84 and 0.91 percent, respectively. These values cannot be plotted in Fig. 7, but comparison of these values with Fig. 2 demonstrate that although the addition of water appreciably increases the decomposition rate, the rate is only about one-half that of propellant-grade hydrazine.

It is possible, of course, that the increase in rate which does occur results from impurities in the distilled water rather than from the water itself. Two experiments were conducted in which 0.72-percent tap water was added (Fig. 7). These gave rates in the same range as was obtained with added distilled water.

The values for percent hydrogen obtained in the experiments with added water were 22.4, 12.1, 24.1, 19.1, and 9.5.

COMBINED EFFECT OF WATER AND ANILINE

Because neither water nor aniline increased the decomposition rate of purified hydrazine to values approaching that of propellant-grade hydrazine, water and aniline were added together to determine if they exhibit a synergistic effect. The three experiments with 1.0-percent water and 0.5-percent aniline in combination (Fig. 7) showed no evidence of a synergistic interaction. The effect was about the same as with added water alone.

EFFECT OF TOLUENE

Toluene was added to the purified hydrazine at a concentration of 400 ppm in three experiments. The results (Fig. 7) showed a possible small catalytic effect of toluene, but it was not sufficient to account for the observed lower thermal stability of propellant-grade hydrazine.

EFFECT OF SODIUM CHLORIDE

An analysis of propellant-grade hydrazine conducted at Edwards Rocket Propulsion Laboratory did not disclose the presence of many metal ions. It did, however, reveal in one sample the presence of sodium and chloride ions at concentrations of approximately 20 ppm each. Therefore, six 32-hour experiments were conducted at 171 C in which an aqueous solution of NaCl was added to the purified hydrazine. The first two, in which 0.5 percent water and 20 ppm Na Cl were introduced, resulted in decompositions of 0.22 and 0.20 percent. In the other four experiments, 1.2-percent water and 43-ppm NaCl were added. These resulted in decompositions of 0.27, 0.24, 0.27, and 0.31 percent, respectively.

Comparison of these values with Fig. 7 indicates that the addition of NaCl did not increase the decomposition rate; in fact, the rates did not increase as much as would have been expected for the addition of these amounts of water. It will be seen in the later section on mechanism investigation (Fig. 14) that increasing the ionic strength by the addition of these amounts of NaCl would decrease the rate by 30 percent and 50 percent, respectively (because of the type of ionic reaction which is occurring if the RPL purified and Olin purified materials decompose by the same mechanism). This apparently mitigates the effect of the added water in these experiments.

EFFECT OF SOLUBLE IRON

It may be seen from Table 3 that 1.0 ppm of iron was found in the L-104A and L-104D propellant-grade hydrazines but none was detected in the RPL propellant-grade samples. To determine the effect of added soluble iron, $FeCl_3$ was added to the RPL purified hydrazine and the percent decomposition measured after 17 hours at 171 C in the absence of a metal surface. The following results were obtained:

Experiment No.	Concentration of $FeCl_3$, millimolar	Concentration of Iron, ppm	Percent Hydrazine Decomposed
973	1.01	56	1.5
974	1.01	56	3.2
975	1.43	80	4.6

These results indicate that the ferrous ion is a catalyst for the decomposition of hydrazine; it is expected that the ferric ion will be reduced to ferrous in hydrazine and a rapid evolution of gas was noted during sample preparation. An ionic mechanism is proposed later in this report which could account for catalysis by the ferrous ion.

If the rate of the iron-catalyzed reaction is directly proportional to the concentration of added $FeCl_3$, the above results predict the percent hydrazine decomposed in 17 hours will be about 0.05 percent per ppm of iron. The blank rates under these conditions give about 0.07-percent decomposition in 17 hours, indicating that 1 to 2 ppm of iron impurity would need to be present to account for the decomposition rate of purified hydrazine in the absence of a metal surface; about 15 ppm would be required to decrease the thermal stability to that of the propellant-grade hydrazine. It can be seen from Table 3, however, that the iron content of the RPL purified hydrazine is likely to be less than 0.1 ppm, and that of the propellant-grade hydrazine is only 1 ppm or less.

If dissolved iron itself is involved, several possibilities exist with regard to its potential detrimental role. The first possibility is that the effect of iron is not a linear function of concentration, the first traces of iron being relatively more effective than higher concentrations. Another possibility, based on the ionic mechanism proposed later in this report, is that the iron impurity reacts synergistically with acidic impurities and the overall effect of added iron is not a simple function of the amount of iron present.

It is possible that another trace metal impurity, such as nickel, has a similar catalytic effect toward the decomposition of hydrazine but is effective at lower concentrations.

EFFECT OF SOLUBLE COPPER

A similar series of experiments was conducted with $CuCl_2$ added to the RPL purified hydrazine to determine if soluble copper affected the decomposition rate. Audrieth (Ref. 16) found that dissolved copper is a specific catalyst for the oxidation of hydrazine. The following 17-hour experiments at 171 C were conducted to determine if copper had a similar effect on the thermal decomposition in the absence of oxygen:

Experiment No.	Concentration of $CuCl_2$, millimolar	Concentration of copper, ppm	Percent Hydrazine Decomposed
920	0.43	27	0.09
921	0.43	27	0.10

Because blank rates of 0.05 to 0.10 percent are usually obtained under these conditions, added $CuCl_2$ does not affect the decomposition rate appreciably.

EFFECT OF CARBAZIC ACID

It was reported previously that carbazic acid, N_2H_3COOH, is a common impurity in propellant-grade hydrazine (Ref. 17). Because CO_2 reacts rapidly with hydrazine to form carbazic acid, the carbazic acid could come from the contact of hydrazine with air. It can be calculated, however, that hydrazine must contact considerable amounts of air to accumulate appreciable quantities of carbazic acid because air contains only 315 ppm CO_2.

A sample of carbazic acid had been synthesized and purified for another purpose under a Rocketdyne IR&D program by reacting an excess of CO_2 with an aqueous solution of hydrazine (Ref. 18). This available material was used on the present program to determine the effect of the potential impurity, carbazic acid, on the thermal stability of hydrazine.

The effect of adding 1 weight percent carbazic acid to the RPL purified hydrazine was investigated in a series of 66-hour experiments at 171 C in prepassivated pyrex ampoules. The following results were obtained:

Experiment No.	Percent Hydrogen in Noncondensable Product	Percent Hydrazine Decomposed
450	23.3	2.00
451		Ampoule Broke
452		Ampoule Broke
453	24.0	2.04

Two of the ampoules broke, presumably from strains in the glass, and the sample in the remaining two had undergone 2-percent decomposition. The blank runs in this series were Experiments 454 through 457 in Table 2 These gave an average decomposition of 0.39 percent in 66 hours in the absence of added carbazic acid. Thus, the addition of 1 percent weight carbazic acid increases the decomposition rate by a factor of 5 in the absence of a metal surface. The rate obtained with 1-percent carbazic acid in purified hydrazine is about the same as that obtained with propellant-grade hydrazine (Fig. 2) under the same conditions.

All acids, including carboxylic acids such as carbazic, are expected to react completely in hydrazine (Ref. 19) to form the $N_2H_5^+$ ion and the corresponding anion (e.g., $N_2H_3COO^-$ from carbazic acid). The possibility had been suggested previously that the presence of the $N_2H_5^+$ ion is involved in the decomposition of hydrazine (Ref. 15).

The addition of 1 weight percent carbazic acid to hydrazine should result in the same solution as would be obtained by allowing 0.58 weight percent CO_2 to react slowly with hydrazine. The concentration of the $N_2H_5^+$ ion would be 0.13 molar in this solution.

A method of measuring carbazic acid in hydrazine was developed and the results obtained are included in Table 3. The method, described in detail later in this report, is similar to that employed in Ref. 16 and is not necessarily completely specific to carbazic acid. Therefore, the carbazic acid values in Table 3, 250 and 150 ppm, can only be considered upper limits. Data will be presented which indicate that the actual carbazic acid concentrations are even lower than these values.

A series of experiments was conducted at 128 C with the RPL-purified hydrazine to determine the effect of the concentration of added carbazic acid both in the absence and presence of the standard 321 stainless-steel surface.

It may be seen from the results in Fig. 10 that in pyrex ampoules at 128 C, the addition of 0.12-percent carbazic acid to the RPL-purified hydrazine decreased the decomposition rate slightly at the shorter heating times, and had little effect at longer times. The addition of 1.2-percent carbazic acid under these conditions (128 C) increased the rate of

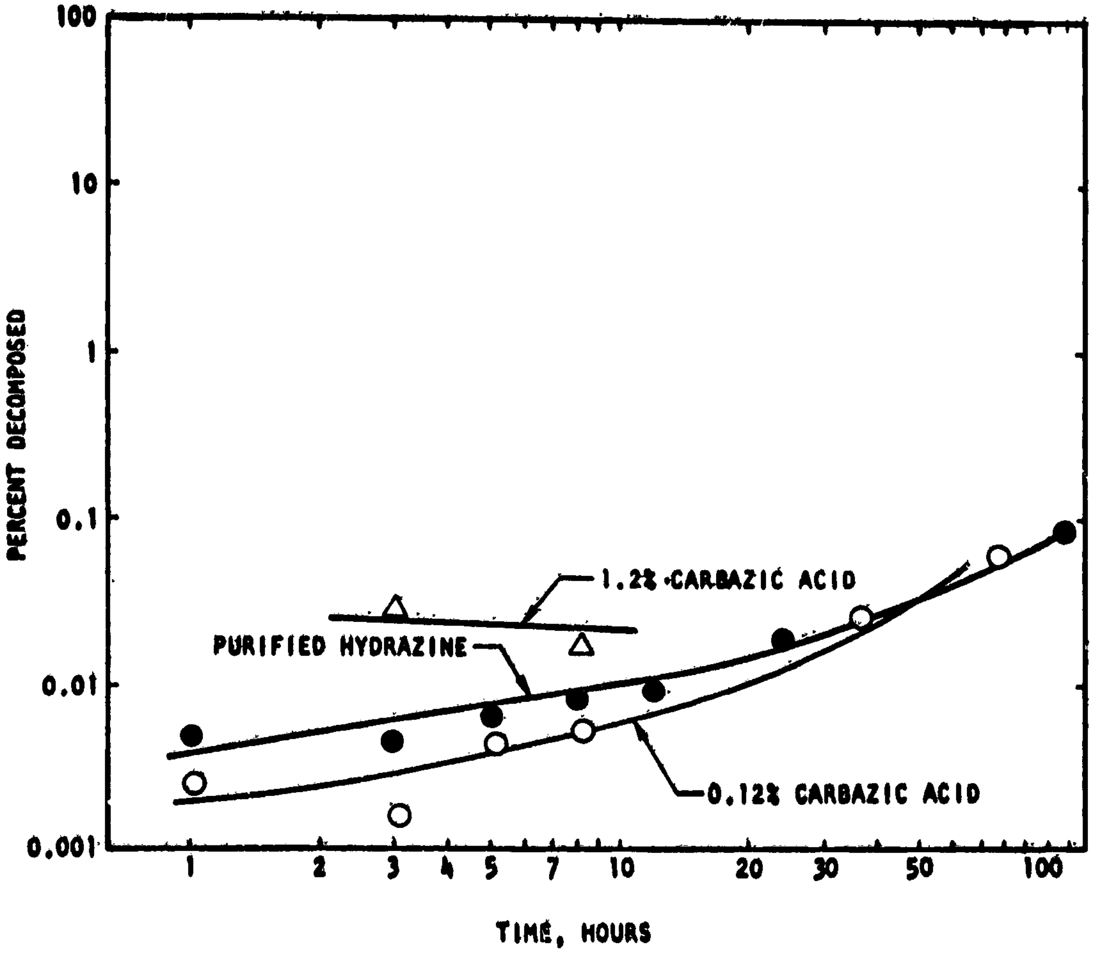


Figure 10. Effect of Added Carbazic Acid on Decomposition Rate of RPL-Purified Hydrazine in Pyrex Ampoules at 128 C

decomposition by a factor of about three. The scale chosen in Fig. 10 is the same as that of Fig. 4 , for comparison. Logarithmic scales were used in these figures because a wide range of concentrations and decomposition rates were to be compared.

In the presence of the standard passivated 3 stainless-steel surface, the effect of added carbazic acid (Fig. 11) was much greater. At a concentration of only 0.12-percent carbazic acid, the rate at 128 C increased by more than a factor of 100. The addition of 1.2-percent carbazic acid increased the decomposition rate on 321 stainless steel by more than a factor of 1000. The rate at the higher carbazic acid concentration was increasing exponentially with time and would have reached 100-percent decomposition in a few more hours. The values for percent hydrogen in the noncondensable product were only 1.5, 1.2, and 1.3 in the experiments with 1.2-percent carbazic acid in the presence of a metal surface.

The results with added carbazic acid in Fig. 10 and 11 demonstrate that the increase in rate is much greater in the presence of a metal surface. It appears that, with a metal surface, only about 100 ppm of carbazic acid would be required to increase the decomposition rate of the purified hydrazine to that of propellant grade at the shorter heating time (Fig. 8).

The presence of a metal surface could promote the effect of carbazic acid either through an acid-catalyzed heterogeneous reaction on the metal surface or by introducing a trace metal impurity into the liquid, if this impurity enhances the effect of the acid (as will be shown later to probably be the case).

The catalytic effect of other acidic materials and the possible mechanisms involved will be presented in later sections.

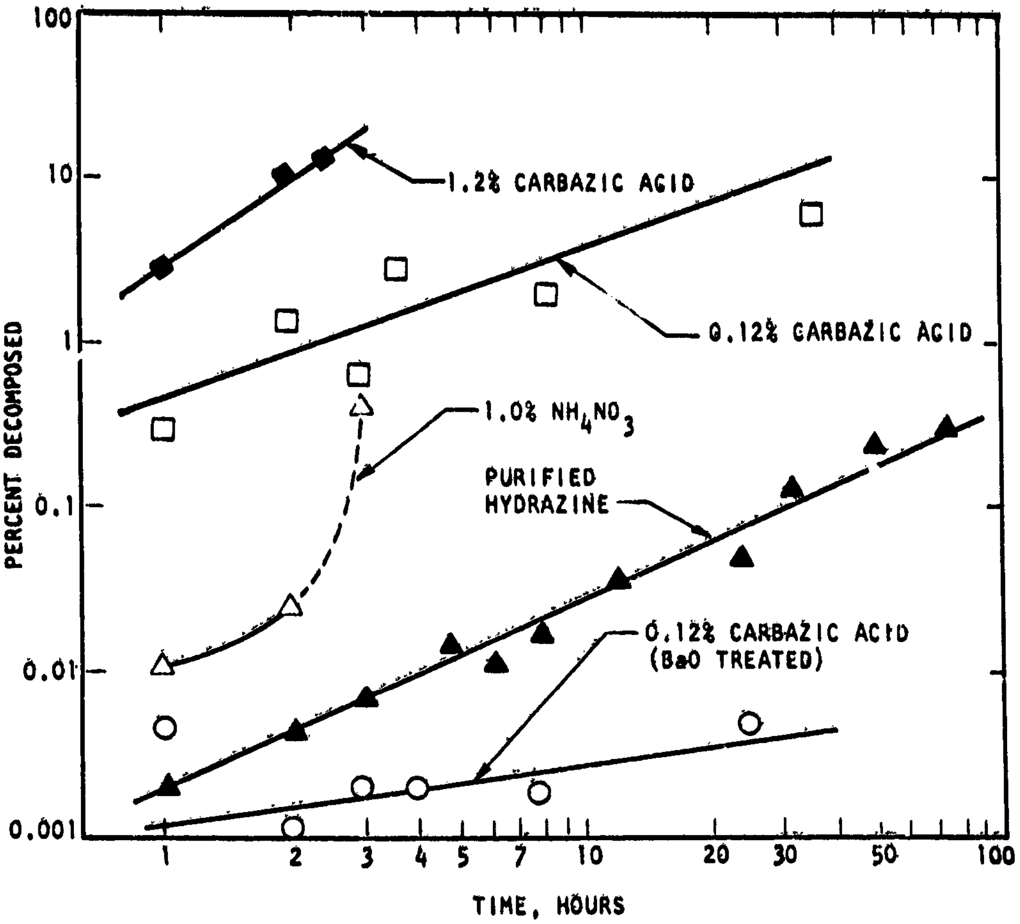


Figure 11. Effect of Added Carbazic Acid and Ammonium Nitrate on Decomposition Rate of RPL-Purified Hydrazine on Standard 321 Stainless Steel at 128 C

METHODS OF CONCENTRATING IMPURITIES

Stability of the Olin Mother Liquor

A sample was received of the mother liquor from the Olin purification process (fractional crystallization). This material would be expected to contain more impurities than even propellant-grade hydrazine. It was run in six passivated ampoules for 20 hours at 171 C. Three of the ampoules broke and the remaining three gave decompositions of 1.3, 1.6, and 1.3 percent, respectively. This is nearly twice the rate at which propellant-grade hydrazine decomposes under these conditions (Fig. 3).

An analysis of this mother liquor gave the following results (Table 3): 94.5-percent hydrazine, 4.7-percent water, 0.03-percent ammonia, 0.74-percent aniline, and 26-ppm toluene. Although this decrease in purity from that of propellant-grade hydrazine would appear to be compatible with the lower thermal stability, the situation is the same as with propellant-grade hydrazine in that none of the identified major impurities would be this deterimental (based on the results obtained on this program). It is likely, therefore, that an acidic or trace metal impurity is also concentrated in the mother liquor and this (these) species determine(s) the thermal stability.

Partial Evaporation of Propellant-Grade Hydrazine

Two 1-hour experiments were conducted in which 40 percent of the hydrazine was pumped off before the ampoules were sealed. These experiments, at 171 C in the absence of a metal surface, gave a rate about twice that of two blank experiments which were run at the same time.

EFFECT OF ACIDIC ADDITIVES

It was shown in the previous section that added carbazic acid markedly lowers the thermal stability of liquid hydrazine, particularly in the presence of a metal surface. It was possible that this is a specific effect with carbazic acid. However, the experiments reported in this section demonstrate that all acidic additives are capable of reducing the thermal stability of hydrazine. Had carbazic acid been unique in this respect, a mechanism involving the decomposition of the $N_2H_3COO^-$ anion would have been indicated (with the released CO_2 reacting again with hydrazine to form carbazic acid). Because it was found instead that all acids are detrimental, a mechanism involving the $N_2H_5^+$ ion is indicated.

ADDED HCl AND AMMONIUM CHLORIDE

Solutions containing 1-weight percent HCl were prepared by adding concentrated HCl (Allied 37.5 percent) to the Olin purified hydrazine. Because the addition of 1-percent HCl by this method entailed the incidental addition of 1.6-percent H_2O, two samples also were prepared containing this concentration of H_2O. After 2.8 hours at 171 C in passivated pyrex ampoules, one acidified sample had undergone 4.6-percent decomposition and the other ampoule had broken from excessive pressure, while the unacidified samples had decomposed only 0.08 percent. A "blank" sample which contained no added HCl or H_2O gave only 0.02-percent decomposition (in agreement with Fig. 7). Thus, the addition of 1-weight percent HCl increases the percentage decomposition by a factor of 50 over that for a sample containing an equivalent amount of water, and a factor of 200 over that for the neat propellant-grade hydrazine.

Because 1-weight percent HCl is 0.28 molar, the addition of 1-percent HCl introduces about twice as many "protons" ($N_2H_5^+$) as does the addition of 1-percent carbazic acid. Even taking this into account, it appears that HCl is more effective than carbazic acid in reducing the stability of hydrazine. Also, hydrazine samples purified by different processes were used in the two series of experiments upon which this comparison is based. If the $N_2H_5^+$ ion should react synergistically with a trace impurity, the two samples of purified hydrazine might not be equally susceptible to acid catalysis.

A series of experiments was conducted at 128 C to determine the effect of 1 weight percent NH_4Cl on the rate of decomposition of RPL-purified hydrazine. The addition of NH_4Cl should be equivalent to the addition of HCl if the ammonia which is added with the HCl (in NH_4Cl) does not affect the results. The equilibrium constant for the reaction:
$NH_3 + N_2H_5^+ \rightleftharpoons NH_4^+ + N_2H_4$ favors NH_4^+ because ammonia is more basic than hydrazine but the high hydrazine concentration favors $N_2H_5^+$. Also, most of the ammonia will migrate to the vapor phase at reaction temperature. It was reported erroneously in the Fifth Quarterly Progress Report, and elsewhere, that the NH_3 was pumped off during the degassing procedure. However, liquid nitrogen was used as the coolant during degassing rather than CO_2, so that the NH_3 was not removed. The only experiments in which CO_2 was employed as the coolant were conducted during the first two quarters of the program.

The percentage decomposition was followed as a function of time at 128 C. The results are presented in Fig. 12. The addition of 1-percent NH_4Cl (0.20 molar) increases the rate in the absence of a metal surface (passivated ampoules) by about a factor of 20. Comparing Fig. 10 and 12, NH_4Cl has a larger effect than carbazic acid in RPL purified hydrazine even if the difference in molar concentration is taken into account. This suggests that the carbazic acid may not be completely ionized in hydrazine.

It may be seen from Fig. 12 that the effect of NH_4Cl is much greater on the standard 321 stainless-steel surface than in the absence of a metal surface. The decomposition after 3 hours on 321 stainless steel is increased

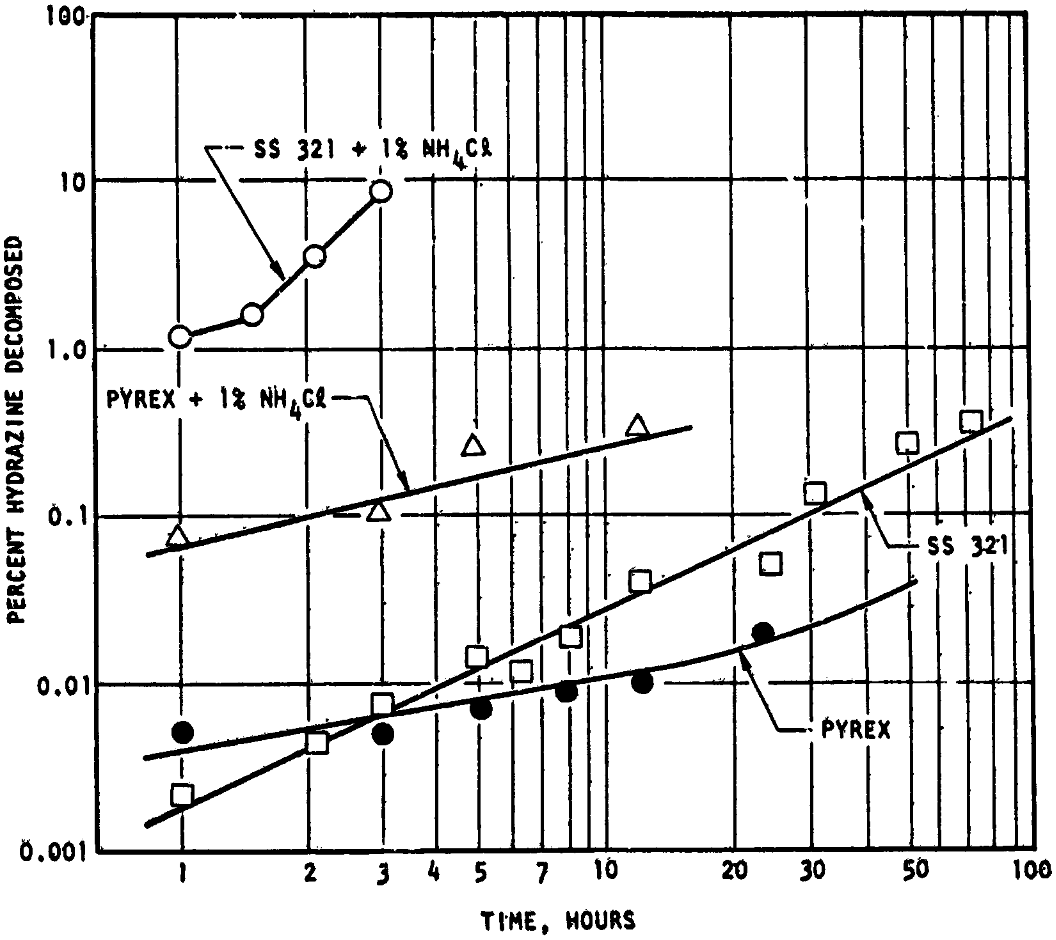


Figure 12. Effect of Added NH_4Cl on Decomposition Rate of RPL-Purified Hydrazine on Pyrex and Standard 321 Stainless Steel at 128 C

by about a factor of 1000 by the addition of 1-percent NH_4Cl. The rate in the presence of the additive is increasing nearly parabolically with time (slope equal to 2) indicating that all of the hydrazine would have decomposed in a few more hours. Comparing these results with those in Table 11, carbazic acid is slightly more effective than NH_4Cl in the presence of the metal surface.

The values measured for percent hydrogen in the noncondensable product when 1-percent NH_4Cl was added were 0.8, 2.9, and 3.0 in the absence of a metal surface, and 1.3 and 0.8 in the presence of the metal surface. Similarly, low amounts of hydrogen were produced with 1 percent added carbazic acid (metal surface).

Some additional experiments with added NH_4Cl are reported in later sections of this report.

ADDED AMMONIUM NITRATE

Because hydrazinium nitrate, $N_2H_5NO_3$, is a component of some mixed hydrazine fuels, it was of interest to determine if added NH_4NO_3 gives effects similar to added NH_4Cl (as was discussed for NH_4Cl, the addition of NH_4NO_3 is expected to be equivalent to the addition of $N_2H_5NO_3$ or HNO_3).

It may be seen from Fig. 11 that 1.0-percent added NH_4NO_3 (0.12 molar) increases the decomposition rate of the HPL-purified hydrazine on the standard 321 stainless steel but not to as great an extent as do NH_4Cl and carbazic acid. Based upon the single data point at 3 hours, the rate appears to be increasing rapidly with heating time (a fourth experiment not shown in Fig. 11 gave 0.021-percent decomposed at 0.5 hour.

A series of experiments was conducted to determine the effect of added 1-percent NH_4NO_3 on the thermal stability of propellant-grade hydrazine (L-104A). The results of these 128 C experiments are shown in Table 11.

TABLE 11

EFFECT OF 1-PERCENT AMMONIUM NITRATE (AN) ON STABILITY OF PROPELLANT-GRADE HYDRAZINE AT 128 C

Heating Time, hours	Passivated Pyrex (blank)	Passivated Pyrex + AN	321 SS* (blank)	321 SS* + AN
1.5				0.16
3.0				0.34
4.0	0.019	0.020	0.012	0.48
6.0	0.029	0.022	0.022	2.30

*Standard 321 stainless-steel specimen with 1-cm^2 surface area; values have been corrected for reaction in absence of metal surface

These data demonstrate that hydrazine nitrate has little effect upon the rate of hydrazine decomposition in glass ampoules (up to 6 hours heating time). However, in the presence of a passivated 321 stainless-steel surface, a considerable acceleration in rate is observed which becomes pronounced at longer heating times.

It thus appears that ammonium nitrate behaves as the other "acidic" impurities in that its effect is dependent on the presence of a metal surface. The ammonium nitrate is somewhat different, however, in that it is less effective at shorter heating times (in the presence of metal) but its effectiveness increases more rapidly than the other acidic impurities at longer heating times.

ADDED AMMONIUM CHLORIDE IN PRESENCE OF ADDED SOLUBLE COPPER

It was shown previously in this report that the addition of $CuCl_2$ to the RPL-purified hydrazine at a concentration of 0.43 millimolar did not increase its decomposition rate. These were 17-hour experiments at 171 C in passivated ampoules without metal specimens. Additional experiments were conducted under these same conditions to determine if an acidic impurity would interact synergistically with added soluble copper. The results are presented in Table 12.

TABLE 12

EFFECT OF THE SIMULTANEOUS ADDITION OF SOLUBLE COPPER AND NH_4Cl TO RPL-PURIFIED HYDRAZINE AT 171 C

Experiment No.	Concentration of Copper, ppm	Concentration of NH_4Cl, ppm	Percent Hydrazine Decomposed*
920	27	--	0.09
921	27	--	0.10
922	--	117	0.30
923	--	117	0.11
916	27	20	0.21
917	27	20	0.16
918	27	153	0.17
919	27	153	0.20

*17-hour experiments

Blank rates of 0.05 to 0.10 percent decomposed are usually obtained under these conditions. There was considerable scatter in the results, but it appears that the added NH_4Cl increased the rate slightly. Its effect was not enhanced by the addition of the $CuCl_2$.

ADDED OXALIC ACID

Oxalic acid $(COOH)_2$ at concentrations of about 1 percent has been proposed for use as an electrolyte in hydrazine so that it may be electrolyzed for propulsion purposes (Ref. 20). It was of interest, therefore, to determine if this carboxylic acid is as detrimental toward thermal stability as is carbazic acid. Experiments were conducted at 128 C with propellant-grade hydrazine (L-104B) to which had been added 0.1-weight percent oxalic acid (0.011 molar). The results, obtained in the presence of the standard 321 stainless-steel surface, are presented in Table 13.

TABLE 13

EFFECT OF ADDED 0.1-PERCENT OXALIC ACID ON DECOMPOSITION RATE OF PROPELLANT-GRADE HYDRAZINE ON STANDARD 321 STAINLESS STEEL AT 128 C

Experiment No.	Time, hours	Percent Hydrazine Decomposed	Blank Percent Decomposed
976	4	2.9	0.02
977	8	4.8	0.05
978	12	2.9	0.07
979	24	6.3	0.10

The average increase in the heterogeneous decomposition rate from the added acid is a factor of 80. It may be seen from the last column of Table 11 that 0.1-percent added oxalic acid is more detrimental than 1-percent ammonium nitrate (at heating times of around 6 hours). Comparing the data in Table 13 with Fig. 11, it may be seen that propellant-grade hydrazine containing 0.1-percent oxalic acid decomposes slightly faster on 321 stainless steel than does purified hydrazine which contains 0.12-percent carbazic acid. It should be noted that oxalic acid contains two protons per molecule.

EFFECT OF PROPELLANT PURITY

As shown by the following examples, the effect of acids on the homogeneous decomposition rate appears to decrease with decreasing purity of the hydrazine; this is in agreement with the postulate mentioned previously which states that the effects of impurities may not be a linear function of concentration. In the absence of a metal surface, the addition of 0.2 percent NH_4Cl to the BaO-treated hydrazine increases the rate by a factor of 20

(Fig. 16) while the addition of 0.12 percent carbazic acid to the distilled hydrazine does not increase the rate (Fig. 10). The addition of 1 percent NH_4Cl, carbazic acid, or HCl to purified hydrazine (distilled or fractional crystallization) increases the rate by factors of 3 to 50, while the addition of 1 percent NH_4NO_3 to propellant-grade hydrazine has no effect in the absence of a metal surface (Table 11). Additional data are required to determine if this trend is real (or results from using different acidic materials in the various experiments) and to establish the importance of low concentrations of acidic impurities in determining thermal stability.

EFFECT OF AMMONIUM CHLORIDE ON SENSITIVITY

Hydrazine is a high-energy compound which has the fortunate property of not propagating a detonation in the liquid phase. However, when the liquid is adulterated by the addition of an additive, extreme caution should be exercised until it has been established that the liquid has not become sensitive. This is always done when new mixed hydrazine fuels are formulated.

Under a Rocketdyne IR&D program, a detonation propagation test was conducted with propellant-grade hydrazine to which had been added 5-percent ammonium chloride. The results indicate that this liquid is borderline with respect to detonation propagation; the sample tube was completely fragmented, but the witness plate was not damaged.

It thus appears that caution should be used whenever several percent of acidic additives are to be introduced into hydrazine for any purpose.

APPENDIX C

SUMMARY OF ELASTOMER PHYSICAL PROPERTIES

I. INTRODUCTION

This appendix provides a summary listing of physical property data which is available at JPL on elastomeric materials considered candidates for hydrazine system application. The sources of this data include numerous internal JPL memoranda reporting the results of specific tests usually run to evaluate the effect of some process or environmental variable or to compare a critical property of two or more candidate materials. Therefore, the data does not constitute a systematic, consistent documentation of all the physical properties listed. Some of the data reports referred to do not include all of the test parameters of interest, and followup queries are in process where such data is of general interest.

II. PHYSICAL PROPERTY DATA*

A. Permeability

(1) Helium through EPT-10 (0.0686/0.0723-in.-thick sample; source TBD) at 25°C and 49.5 psid: 9.28×10^{-4} cm^3/in.^{2}-h-psid; at 25°C and 25.0 psid: 9.53×10^{-4} cm^3/in.^{2}-h-psid (Ref. 1).

(2) Nitrogen through EPT-10 (0.0686/0.0723-in.-thick sample; source TBD) at 25°C and 74.0 psid: 1.18×10^{-4} cm^3/in.^{2}-h-psid; at 25°C and 44.0 psid: 1.24×10^{-4} cm^3/in.^{2}-h-psid (Ref. 1).

(3) Hydrazine through EPT-10 (0.0686/0.0723-in.-thick sample; source TBD) at 25°C: <0.0003 mg/in.^{2}-h (Ref. 1).

(4) Hydrazine through EPT-10 (0.0091-in.-thick sample made at JPL) at 25°C after 100-200 h: 0.39 mg/h-in.^{2} exposure to hydrazine (Ref. 2).

(5) Hydrazine through EPT-10 (0.0079-in.-thick sample made at JPL and extracted with benzene for 24 h in a Soxhlet extraction apparatus).

(6) Hydrazine through AFE-102-(1) (0.0078-in.-thick sample; source TBD) at 25°C after 100-200 h: 1.04 mg/h/in.^{2} (Ref. 2).

---

*Herein, TBD = to be determined.

(7) Hydrazine through DuPont LD-2613 (0.0072-in.-thick sample; lot TBD) at 25°C after 100-200 h: 0.004 mg/h/in.^{2} (Ref. 2).

(8) Permeation phenomena (Ref. 3).

(9) Hydrazine through copolymer of tetrafluoroethylene and perfluorovinylmethylether, unfilled (0.030-in.-thick sample; sample size and source and test method TBD; Ref. 4).

(10) Hydrazine through copolymer of tetrafluoroethylene and perfluorovinylmethylether, filled (0.028-in.-thick sample; sample details and source and test method TBD; Ref. 4).

B. Swelling

(1) EPT-10 in hydrazine and hydrazine/hydrazine nitrate after 1, 2, 4, and 8 weeks (samples cut from bladder whose mandrel was removed by immersion in NaOH; Ref. 5).

(2) Parker E515-8 in hydrazine and hydrazine/hydrazine nitrate after 3 weeks (Ref. 6).

C. Weight Change

(1) EPT-10 in hydrazine and hydrazine/hydrazine nitrate after 1, 2, 4, and 8 weeks; also subsequent recovery (samples cut from bladder whose mandrel was removed by immersion in NaOH; Ref. 5).

(2) Parker E515-8 in hydrazine and hydrazine/hydrazine nitrate after 3 weeks (Ref. 6).

(3) Weight loss of EPT-10 upon vacuum drying after 168-h soak in hydrazine and 4-day wash in distilled water (Ref. 7).

D. Hardness

(1) Parker E515-8 before and after 3 weeks in hydrazine and hydrazine/hydrazine nitrate (Ref. 6).

(2) EPT-10 exposed to gamma radiation (approximately 1 megarod) while immersed in N_2H_4; no apparent effect on hardness (Ref. 8).

(3) DuPont tetrafluoroethylene perfluorovinylmethylether copolymer, with and without accelerator and 5% TFE filler, exposed to

gamma radiation (approximately 1 megarod) while immersed in N_2H_4; no apparent effect on hardness (Ref. 8).

(4) Change in hardness of EPT-10 consequent with compression set testing in air, nitrogen, isopropyl alcohol, and hydrazine (Ref. 9).

(5) Change in hardness of DuPont ECD-006 consequent with compression set testing in hydrazine (Ref. 9).

(6) Change in hardness of AFE-102 consequent with compression set testing in air, nitrogen, isopropyl alcohol, and hydrazine (Ref. 10).

(7) Change in hardness of AFE-332 in air, nitrogen, isopropyl alcohol, and hydrazine (whether -9 or -11 formulation TBD; Ref. 10).

E. Propellant Decomposition Products

Results after elevated temperature soak which was preceded by a 168-h ambient temperature soak and bath change; EPT-10 in hydrazine (samples prepared at Pressure Systems, Inc., under Contract 952864; Ref. 7).

F. Captured Volume Pressure Rise

Results following 168-h ambient temperature soak of EPT-10 in hydrazine and pressure rise during subsequent elevated temperature soak (samples prepared at Pressure Systems, Inc., under Contract 952864; Ref. 7).

G. Extractables

Results of 168-h presoak followed by elevated temperature soak of EPT-10 in hydrazine. Sulfur was found in presoak hydrazine but none in soak hydrazine. Water and NVR (mostly silicon) were found in the soak hydrazine (samples prepared at Pressure Systems, Inc., under Contract 952864; Ref. 7).

H. Mold Shrinkage

Percent linear shrinkage from mold dimensions (Ref. 12):

EPT-10 (material compounded and molded at JPL with 4-h postcure at 330°F in closed oven instead of the usual 4 h at 350°F in a forced air oven; unacceptable charring occurred at 350°F):

Before postcure -2.80%

After postcure -1.44%

DuPont LD-2614 (material cured and postcured at JPL):

Before postcure -1.94%

After postcure -6.32%

AFE-102-(1) (material compounded and molded at JPL):

Before postcure -2.10%

After postcure -2.32%

I. Stress Relaxation

(1) EPT-10 in nitrogen at 125°C and in air at 125, 140, and 155°C; at 10% elongation (Ref. 9).

(2) EPT-10 in air at 125, 140, 155, 170, and 185°C; at 10% elongation; in nitrogen at 125 and 155°C; and in air at 125 and 155°C after being soaked in hydrazine for 30 or more days. Temperatures during hydrazine soak TBD (Ref. 10).

(3) EPT-10 in dry nitrogen at 125, 155, 170, and 185°C; at 10% elongation; in isopropyl alcohol at 125, 140, and 155°C; and in air at 125, 140, 155, 170, and 185°C after being soaked in hydrazine. The soak time and temperatures TBD (Ref. 11).

(4) AFE-102 in air at 125, 140, 155, and 170°C; at 10% elongation (Ref. 11).

J. Compression Set

(1) EPT-10 in air, nitrogen, isopropyl alcohol, and hydrazine; per ASTM D-395, Method B (Ref. 9).

(2) DuPont ECD-006 in hydrazine (Ref. 9).

(3) AFE-332 in air, nitrogen, isopropyl alcohol, and hydrazine; test method TBD (Ref. 10).

(4) AFE-102 in air, nitrogen, isopropyl alcohol, and hydrazine; per ASTM D-391-6, Method B (Ref. 10).

K. Density

EPT-10 (material compounded and molded at JPL with 4-h postcure at 330°F in closed oven instead of the usual 4 h at 305°F in forced air oven;

unacceptable charring occurred at 350°F): 1.14 gm/cm^3. DuPont LD-2613 (material cured and postcured at JPL): 2.03 gm/cm; AFE-102-(1) (material compounded and molded at JPL): 0.983 gm/cm^3; AFE-332 (material prepared at TRW): 1.08 gm/cm^3 (Ref. 12).

L. Tensile Strength

(1) DuPont LD-2613 at 22°C, per procedure of ASTM D-412-68, using O-ring samples, 20 in./min crosshead speed in the Instron tester (materials included samples prepared at JPL without filler from compound with no accelerator and from compound with accelerator, also samples prepared at JPL with various fillers from compound without accelerator and from compound with accelerator; Ref. 12, Table 2).

(2) Similar to item (L1) above, except in hydrazine following immersion in hydrazine for 100 h at 70 °C (Ref. 12, Table 3).

(3) EPT-10 at 22°C, per procedure of ASTM D-412-68, using O-ring samples (materials compounded at JPL and included two modifications: one was obtained by simply omitting the postcure; the other was obtained by substituting a peroxide cure for the sulfur cure; Ref. 12, Table 3).

(4) Same as item (L3) above, except in hydrazine following immersion in hydrazine for 100 h at 70°C (Ref. 12, Table 3).

(5) AFE-332 at 22°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 3).

(6) AFE-332 at 22°C, per procedure of ASTM D-412-68, using O-ring samples in hydrazine following immersion in hydrazine for 100 h at 70°C (samples prepared at TRW; Ref. 12, Table 3).

(7) AFE-102 at 22°C, per procedure of ASTM D-412-68, using O-ring samples (materials compounded at JPL and included a modification obtained by substitution of one filler constituent; Ref. 12, Table 3).

(8) Same as item (L7) above, except in hydrazine following immersion in hydrazine for 100 h at 70°C (Ref. 12, Table 3).

(9) AFE-332 at 22°C, per procedure of ASTM D-412, using O-ring samples, following immersion in refluxing isopropyl alcohol for 100 h at 82°C (Ref. 12, Table 4).

(10) Same as item (L7) above, except followed immersion in refluxing isopropyl alcohol for 100 h at 82°C (Ref. 12, Table 4).

(11) EPT-10 (not postcured) at 22°C, per procedure of ASTM D-412-68, using O-ring samples, following immersion in refluxing isopropyl alcohol for 100 h at 82°C; material compounded at JPL (Ref. 12, Table 4).

(12) Similar to item (L1) above, except followed immersion in refluxing in isopropyl alcohol for 100 h at 82°C (Ref. 12, Table 4).

(13) AFE-332 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 5).

(14) AFE-102 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 5).

(15) AFE-102 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (material compounded at JPL; Ref. 12, Table 5).

(16) EPT-10 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (material compounded at JPL; Ref. 12, Table 5).

(17) Similar to item (L1) above, except also at 48 and 79°C (Ref. 12, Table 5).

M. Elongation at Break

(1) DuPont LD-2613 at 22°C, per procedure of ASTM D-412-68, using O-ring samples, 20 in./min crosshead speed in the Instron tester (materials included samples prepared at JPL without filler from compound with no accelerator and from compound with accelerator, also samples prepared at JPL with various fillers from compound without accelerator and from compound with accelerator; Ref. 12, Table 2).

(2) Similar to item (M1) above, except in hydrazine following immersion in hydrazine for 100 h at 70 °C (Ref. 12, Table 3).

(3) EPT-10 at 22 °C, per procedure of ASTM D-412-68, using O-ring samples (materials compounded at JPL and included two modifications: one was obtained by simply omitting the postcure; the other was obtained by substituting a peroxide cure for the sulfur cure; Ref. 12, Table 3).

(4) Same as item (M3) above, except in hydrazine following immersion in hydrazine for 100 h at 70 °C (Ref. 12, Table 3).

(5) AFE-332 at 22 °C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 3).

(6) AFE-332 at 22 °C, per procedure of ASTM D-412-68, using O-ring samples in hydrazine following immersion in hydrazine for 100 h at 70 °C (samples prepared at TRW; Ref. 12, Table 3).

(7) AFE-102 at 22 °C, per procedure of ASTM D-412-68, using O-ring samples (materials compounded at JPL and included a modification obtained by substitution of one filler constituent; Ref. 12, Table 3).

(8) Same as item (N7), except in hydrazine following immersion in hydrazine for 100 h at 70 °C (Ref. 12, Table 3).

(9) AFE-332 at 22 °C, per procedure of ASTM D-412-68, using O-ring samples, following immersion in refluxing isopropyl alcohol for 100 h at 82 °C (Ref. 12, Table 4).

(10) Same as item (M7) above, except followed immersion in refluxing isopropyl alcohol for 100 h at 82 °C (Ref. 12, Table 4).

(11) EPT-10 (not postcured) at 22 °C, per procedure of ASTM D-412-68, using O-ring samples, following immersion in refluxing isopropyl alcohol for 100 h at 82 °C (material compounded at JPL; Ref. 12, Table 4).

(12) Similar to (N1) above, except followed immersion in refluxing isopropyl alcohol for 100 h at 82 °C (Ref. 12, Table 4).

(13) AFE-332 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 5).

(14) AFE-102 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 5).

(15) AFE-102 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (material compounded at JPL; Ref. 12, Table 5).

(16) EPT-10 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (material compounded at JPL; Ref. 12, Table 5).

(17) Similar to item (M1) above, except also at 48 and 79°C (Ref. 12, Table 5).

N. Modulus

(1) Modulus at 100% elongation: DuPont LD-2613 at 22°C, per procedure of ASTM D-412-68, using O-ring samples, 20 in./min crosshead speed in the Instron tester (materials included samples prepared at JPL without filler from compound with no accelerator and from compound with accelerator, also samples prepared at JPL with various fillers from compound without accelerator and from compound with accelerator; Ref. 12, Table 2).

(2) Similar to item (N1) above, except in hydrazine following immersion in hydrazine for 100 h at 70°C (Ref. 12, Table 3).

(3) EPT-10 at 22°C, per procedure of ASTM D-412-68, using O-ring samples (materials compounded at JPL and included two modifications: one was obtained by simply omitting the postcure; the other was obtained by substituting a peroxide cure for the sulfur cure; Ref. 12, Table 3).

(4) Same as item (N3) above, except in hydrazine following immersion in hydrazine for 100 h at 70°C (Ref. 12, Table 3).

(5) AFE-332 at 22°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 3).

(6) AFE-332 at 22°C, per procedure of ASTM D-412-68, using O-ring samples in hydrazine following immersion in hydrazine for 100 h at 70°C (Ref. 12, Table 3).

(7) AFE-102 at 22°C, per procedure of ASTM D-412-68, using O-ring samples (materials compounded at JPL and included a modification obtained by substitution of a filler constituent; Ref. 12, Table 3).

(8) Same as item (N7) above, except in hydrazine following immersion in hydrazine for 100 h at 70°C (Ref. 12, Table 3).

(9) AFE-332 at 22°C, per procedure of ASTM D-412-68, using O-ring samples, following immersion in refluxing isopropyl alcohol for 100 h at 82°C (samples prepared at TRW; Ref. 12, Table 4).

(10) Same as item (N7) above, except followed immersion in refluxing isopropyl alcohol for 100 h at 82°C (Ref. 12, Table 4).

(11) EPT-10 (not postcured) at 22°C per procedure of ASTM D-412-68, using O-ring samples, following immersion in refluxing isopropyl alcohol for 100 h at 82°C (material compounded at JPL; Ref. 12, Table 4).

(12) Similar to item (N1) above, except followed immersion in refluxing isopropyl alcohol for 100 h at 82°C (Ref. 12, Table 4).

(13) AFE-332 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 5).

(14) AFE-102 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (samples prepared at TRW; Ref. 12, Table 5).

(15) AFE-102 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (material compounded at JPL; Ref. 12, Table 5).

(16) EPT-10 at 22, 48, and 79°C, per procedure of ASTM D-412-68, using O-ring samples (material compounded at JPL; Ref. 12, Table 5).

(17) Similar to item (N1) above except also at 48 and 79°C (Ref. 12, Table 5).

REFERENCES

1. Cannon, W., "N_2, He, and N_2H_4 Permeation Through EPT-10 Rubber Sample," IOM 382-311 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., Sep. 10, 1971.
2. Walmsley, D., "Hydrazine Permeability Through Selected Elastomer Films," internal document, Jet Propulsion Laboratory, Pasadena, Calif., June 23, 1971.
3. Rogers, C. E., "Permeation Phenomena Relating to Expulsion Bladders for Hydrazine Fuel Propulsion Systems," Consultant's Report, JPL P.O. GP-527347(2), Division of Macromoleculár Science, Case Western Reserve University, Cleveland, Ohio, Nov. 27, 1971.
4. Vango, S. P., "Permeation of Propellants Through DuPont Copolymers of Tetrafluoroethylene and Perfluorovinylmethylether," IOM 382-77 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., Feb. 23, 1970.
5. Cannon W. A., "Swelling of EPT-10 in Hydrazine and Hydrazine/Hydrazine Nitrate," IOM 382-269 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., June 19, 1970.
6. Cannon, W. A., "Compatibility of Parker Compound E515-8 with Propellants," IOM 382-338 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., July 29, 1970.
7. Vango, S. P., "Results of EPT-10 Soak Test," IOM 382-49 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., Feb. 7, 1972.
8. Ingham, J. D., "Monthly Technical Report: Advanced Expulsion Device Technology Report, Period September 16 to October 15, 1971," (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., Oct. 14, 1971.
9. Kalfayan, S. H., and Silver, R. H., "Evaluating of Valve Seat and Bladder Materials," IOM 382-187 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., June 3, 1971.
10. Kalfayan, S. H., and Silver, R. H., "Evaluation of Valve Seat and Bladder Materials," IOM 382-259 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., Aug. 3, 1971.
11. Kalfayan, S. H., and Silver, R. H., "Evaluation of Valve Seat and Bladder Materials," IOM 382-343 (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif., Oct. 5, 1971.
12. Walmsley, D., "Current Status of Liquid Propellant-Elastomer Work," (JPL internal document), Jet Propulsion Laboratory, Pasadena, Calif.

APPENDIX D

EPT-10 PROPERTIES AS A FUNCTION OF HYDRAZINE IMMERSION TIME

The material presented in this appendix is taken from Technical Memorandum 101, Pressure Systems, Inc., Los Angeles, Calif., Mar. 31, 1971.

RUBBER COMPOUND EPT-10 WITH HYDRAZINE

Long term hydrazine immersion tests are being conducted with ethylene propylene rubber compound EPT-10. The data contained in this report covers an exposure period of 1.5 years. Since the test is being conducted in Southern California, under ambient conditions, the mean test temperature has been approximately 65°F with extremes ranging from 35 to 110°F. The test began in September of 1969 and will continue for three years.

Figures 1 and 2 contain data on selected properties. Each point represents the mean of three values which were obtained from standard ASTM tensile samples. The data has been plotted on a semi-log scale to accentuate the short term aging where most of the changes occurred.

Figure 1 shows that mechanical properties are affected more within the first two days than during any subsequent period. It is interesting to note that the elongation shows an increase while both the tensile strength and 100% modulus show initial drops followed by an increase which appears to stabilize at approximately 60 days. The increase in elongation from 290 to 380% is, of course, desirable in diaphragm and bladder applications. Shore hardness values ranged from 75 to 80 with no trend. The latest value after 1-1/2 years was 77.

Figure 2 describes the change in length and weight after hydrazine immersion. Again, the major changes occurred during the early phases with stabilization at approximately 100 days.

The changes in properties are minimal and should not preclude the use of EPT-10 as a diaphragm material in hydrazine positive expulsion systems.

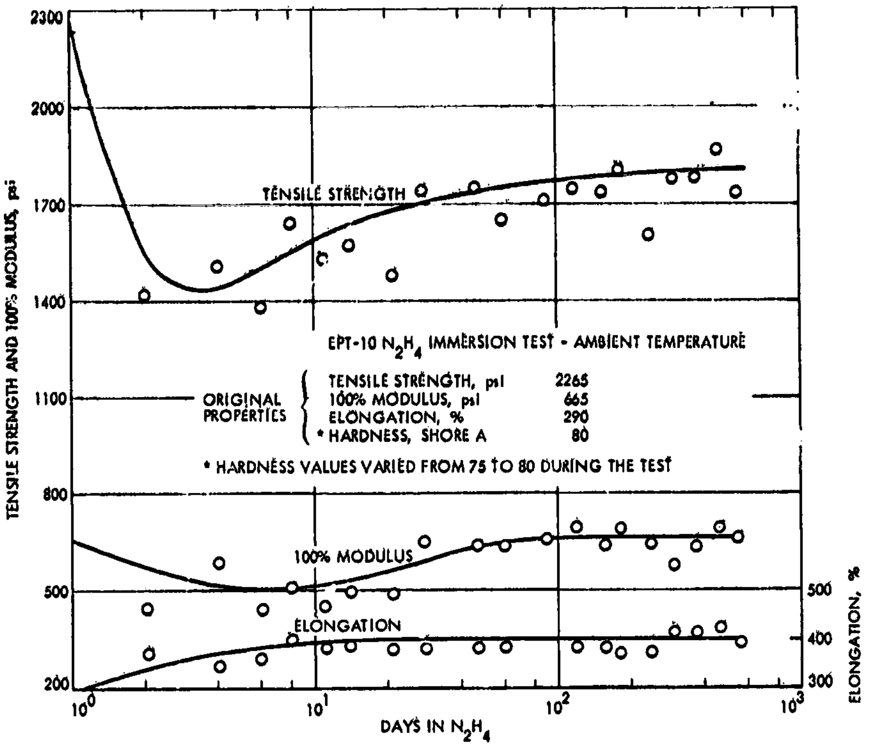


Fig. 1. Mechanical properties vs immersion time in hydrazine

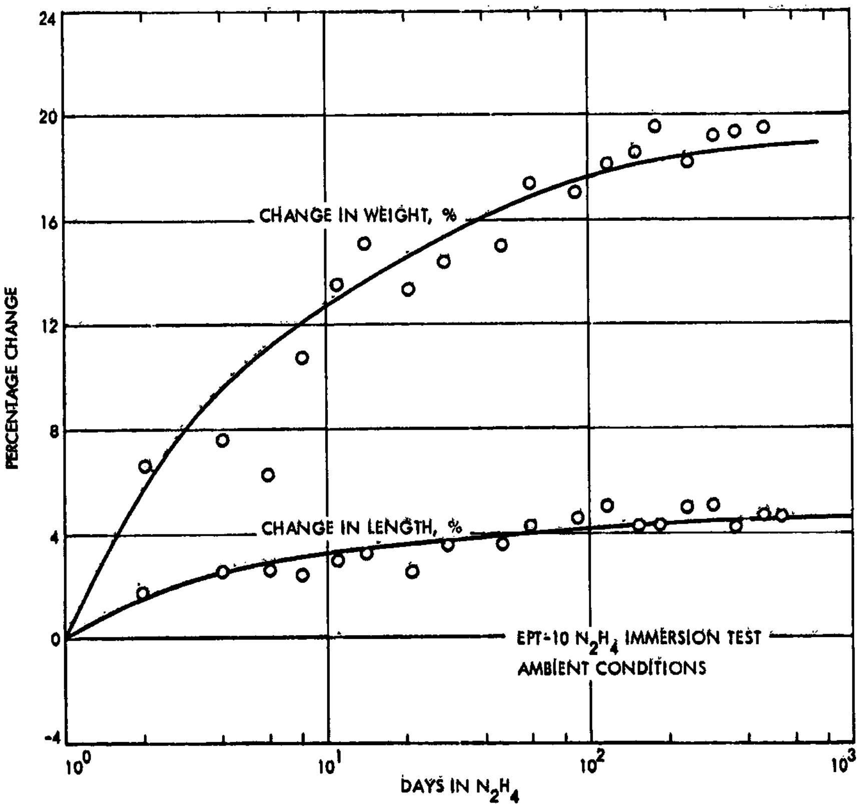


Fig. 2. Swelling characteristics of EPT-10 vs immersion time in hydrazine

NASA — JPL — Coml., L.A., Calif.