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THE CATALYTIC DECOMPOSITION OF HYDRAZINE ON GOLD, NICKEL, AND A GOLD/NICKEL BRAZING ALLOY

L. A. DEE, T. W. OWENS

A. K. WEBB, AND J. T. NAKAMURA

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AIR FORCE ROCKET PROPULSION LABORATORY
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NOTICES

FOREWORD

A gold/nickel (82:18) brazing alloy is presently specified for use in several missile systems wherein the alloy will be in direct contact with the liquid propellant, hydrazine, or with hydrazine blends. Available chemical compatibility data for these materials are conflicting. The Air Force Rocket Propulsion Laboratory Specifications and Standards Branch requested that the Chemical and Materials Branch resolve the conflicting compatibility data. The NASA White Sands Test Facility requested that additional data on the compatibility of a gold/nickel (82:18) brazing alloy with UDMH/hydrazine (50:50) also be obtained. This work was accomplished in support of Project 060JSSZAT during the period September 1966 to September 1967.

The authors are indebted to Mr. P.O. Gants, NASA, White Sands, for providing a sample of the 82:18 Au/Ni alloy.

This report has been reviewed and approved.

W.S. ANDERSON
Chemical and Materials Branch
Propellant Division
Air Force Rocket Propulsion Laboratory

ABSTRACT

A laboratory study was conducted to resolve conflicting published data on the chemical compatibility of hydrazine with gold. Hydrazine and uns-dimethylhydrazine/hydrazine (50:50) were tested for compatibility with several metals including a gold/nickel (82:18) brazing alloy which is specified for use in several missile propellant systems designed for hydrazine and for hydrazine fuel blends. Gold, nickel, and the gold/nickel brazing alloy decompose hydrazine catalytically.

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I. INTRODUCTION

A gold/nickel (82:18) brazing alloy is presently specified for use in several missile systems wherein the alloy will be in direct contact with the liquid propellant, hydrazine, or with hydrazine blends. Available chemical compatibility data for these materials are conflicting. Technical Order 00-25-223, paragraph 1-33b, warns that "Gold, even in minute amounts, shall not be used in contact with hydrazine, uns-dimethylhydrazine (UDMH), ammonia, or ammonia-based fuels". AFRPL-TI-4-2-5 reflects a satisfactory rating for gold in the presence of a member of the general amine family, but provides no specific rating for hydrazine. The Defense Missile Information Center Memorandum 201 indicates that gold is satisfactory for use with the hydrazines. The AFRPL Specifications and Standards Branch requested that the Chemical and Materials Branch resolve the conflicting compatibility data. The NASA White Sands Test Facility requested that additional data on the compatibility of a gold/nickel (82:18) brazing alloy with UDMH/hydrazine (50:50) also be obtained.

II. EXPERIMENTAL PROCEDURE

Two methods were used for determining the compatibility of various metals with hydrazine and UDMH/hydrazine. All metal test specimens were ultrasonically cleaned in trichlorofluoromethane, acetone, distilled water, and oven-dried at 70°C and 27 inches Hg vacuum.

A. Gas Chromatograph Method.

A thin ribbon of the test material was placed in the glass liner of a gas chromatograph flash vaporizer inlet (Beckman Model GC-4). The surface area and weight of the test specimen were measured prior to insertion into the inlet. Propellant-grade hydrazine and UDMH/hydrazine were injected into the inlet with the aid of a Hamilton syringe. The reaction products were separated from the unreacted propellant in the gas chromatograph column. The relative quantities of reaction products and residual unreacted propellant were related to the compatibility of the test specimen with that propellant. The temperature of the test specimen in the inlet was varied over the desired range while all other test conditions remained constant. Figure 1 is a schematic of the apparatus used for the gas chromatograph method. Table I lists the test conditions.

TABLE I. CHROMATOGRAPH TEST CONDITIONS

Column - 6 ft x 1/4 in O.D. S/S - 10% Dowfax 9N9 - 60/80 mesh Teflon 5	
Column Temp.	100°C
Inlet Temp.	60-200°C, variable
Helium Flow	55 cc/min.
Glass Liner Volume	0.22 cc
Propellant Sample Size	1 $\mu \ell$

B. Immersion Method.

Small samples of the alloy were placed in glass pressure vessels (Fisher-Porter Aerosol bottles), each fitted with a ball valve at the top. A ball valve was used to provide for extraction of a vapor sample through a septum with a long needle and a Hamilton gas syringe. The vapor samples were analyzed with a gas chromatograph equipped with the column described in Table I. With this technique the temperature was fixed and exposure time was the variable. Figure 2 illustrates the immersion apparatus. Table II describes the test conditions.

TABLE II. IMMERSION TEST CONDITIONS

Propellant Sample Volume	30 ml
Ullage Volume	61 ml
Test Temperature	140°F

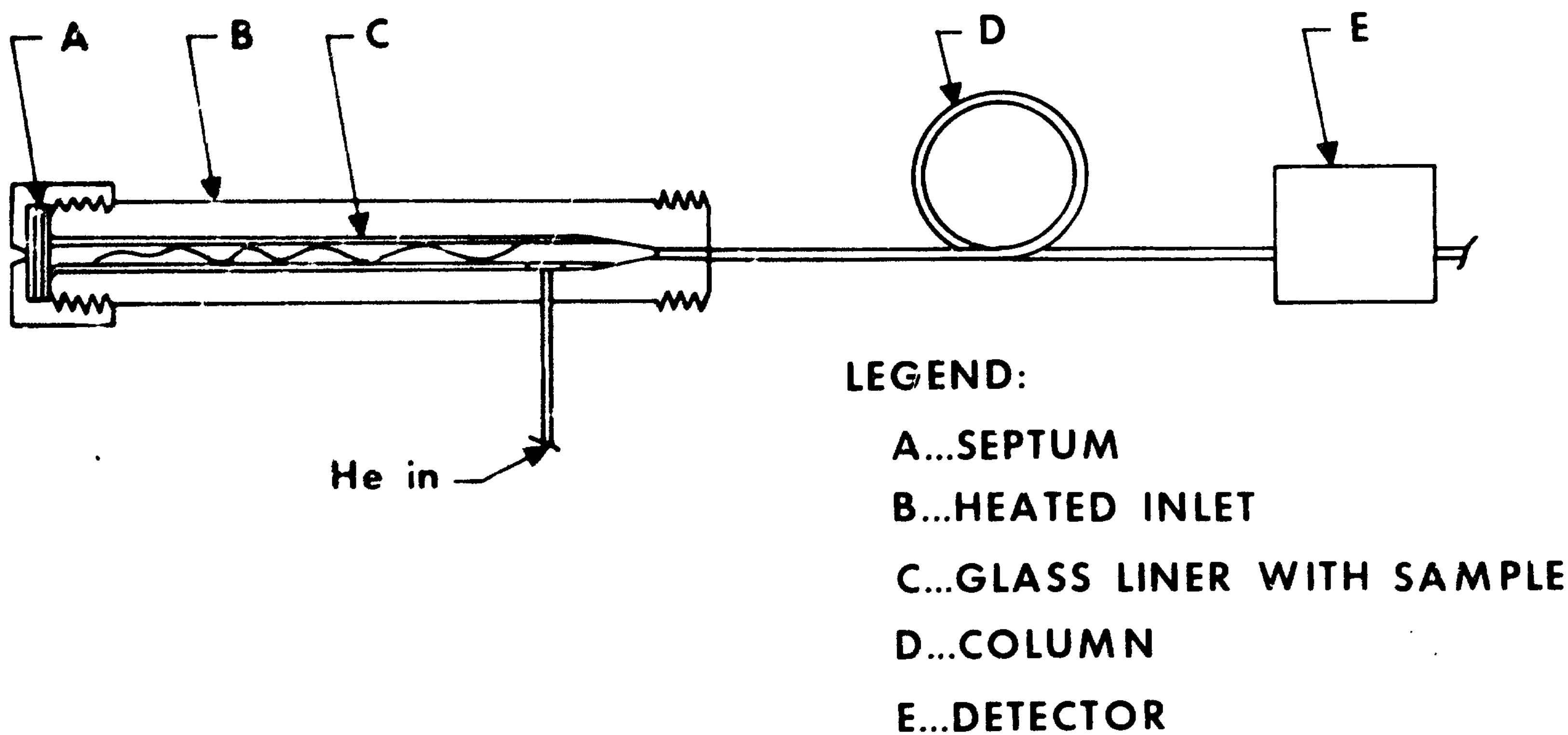

Figure 1. Gas Chromatograph and Inlet

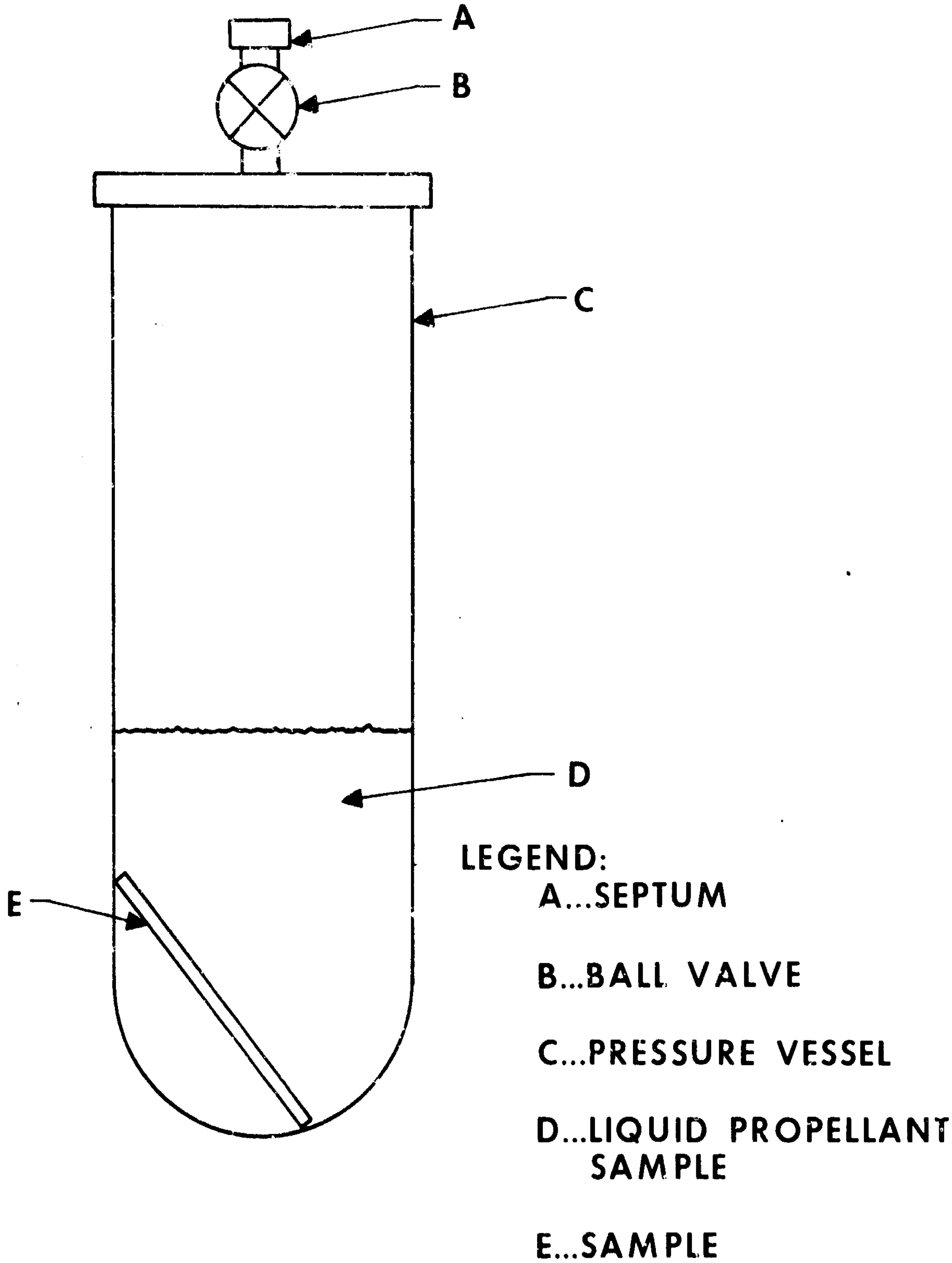

Figure 2. Immersion Test Apparatus

III. RESULTS AND DISCUSSION

A propellant blank determination was made for both hydrazine and the UDMH/hydrazine blend in the apparatus described. No significant reactions were noted. Table III lists the various materials tested in the gas chromatograph inlet and in the immersion test.

TABLE III. MATERIALS TESTED	
Material	Measured Surface Area (cm^2)
Gold	2.12
Aluminum	2.12
Nickel	2.12
82:18 Gold/Nickel Alloy	1.5
	3.7 [a.]
Glass	5.6 [b.]

a. Surface Area Used in Each Immersion Test
b. Empty Inlet Liner

Figure 3 shows the normalized results of gas chromatograph tests on the various metals with hydrazine. The N_2H_4 is considerably more unstable when in contact with gold, nickel, or the alloy that with the other materials. The decomposition temperature (the first significant slope change) is slightly higher than expected. Noticeable hydrazine decomposition occurred at a lower temperature (140°F) during the immersion tests. Probably this results from the short residence time of the propellant in the inlet (ca. 0.25 sec.). The decomposition products are hydrogen, nitrogen, and ammonia. Figure 4 shows the normalized results of the gas chromatograph tests of the gold/nickel alloy with UDMH/N_2H_4. The neat hydrazine test results are presented again for comparison. Figure 4 indicates that hydrazine in the UDMH/N_2H_4 blend is less stable than neat hydrazine. The curves cross at 170°C because the quantity of hydrazine available for reaction becomes significant at this point. Since no change

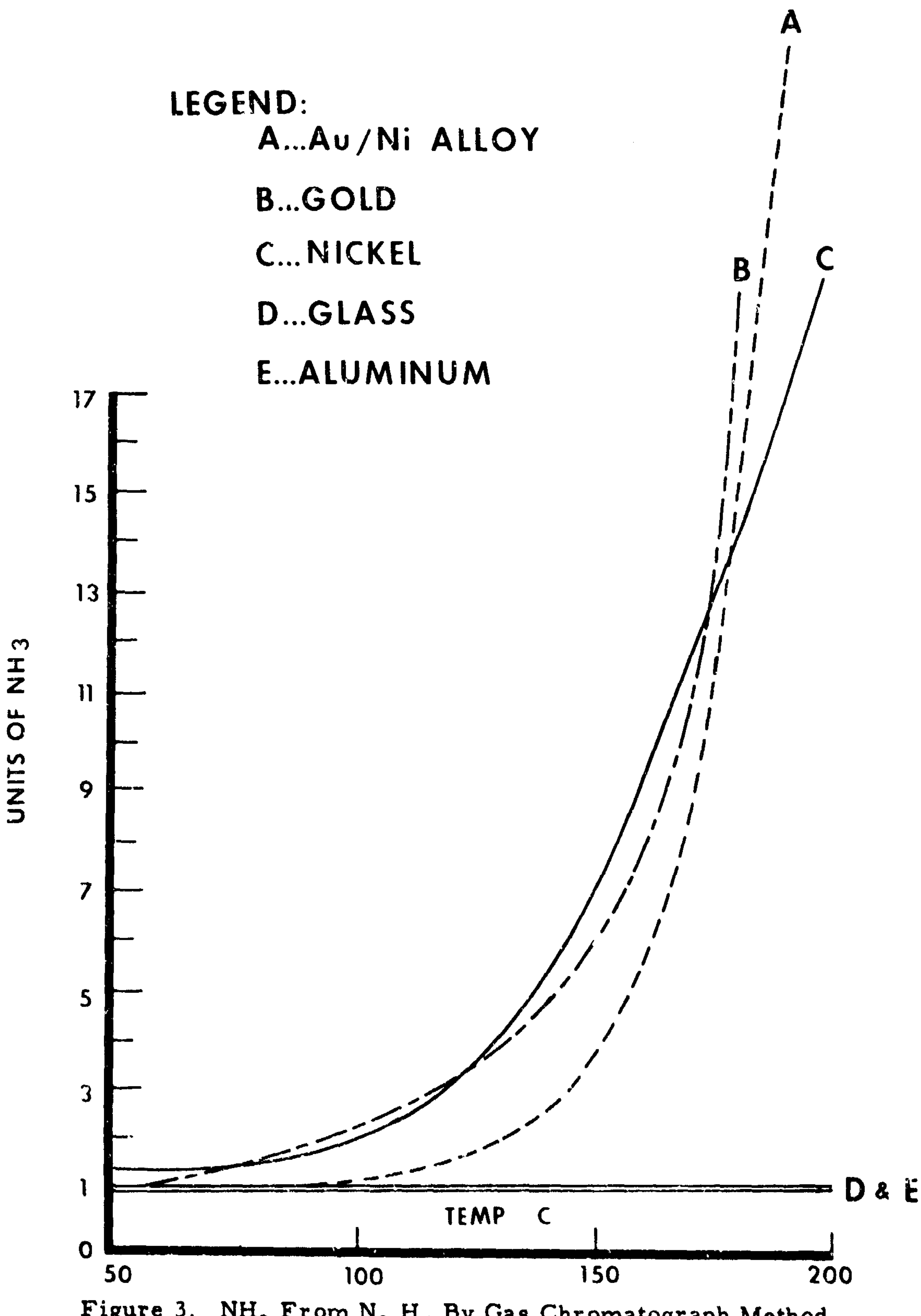

Figure 3. NH_3 From N_2H_4 By Gas Chromatograph Method

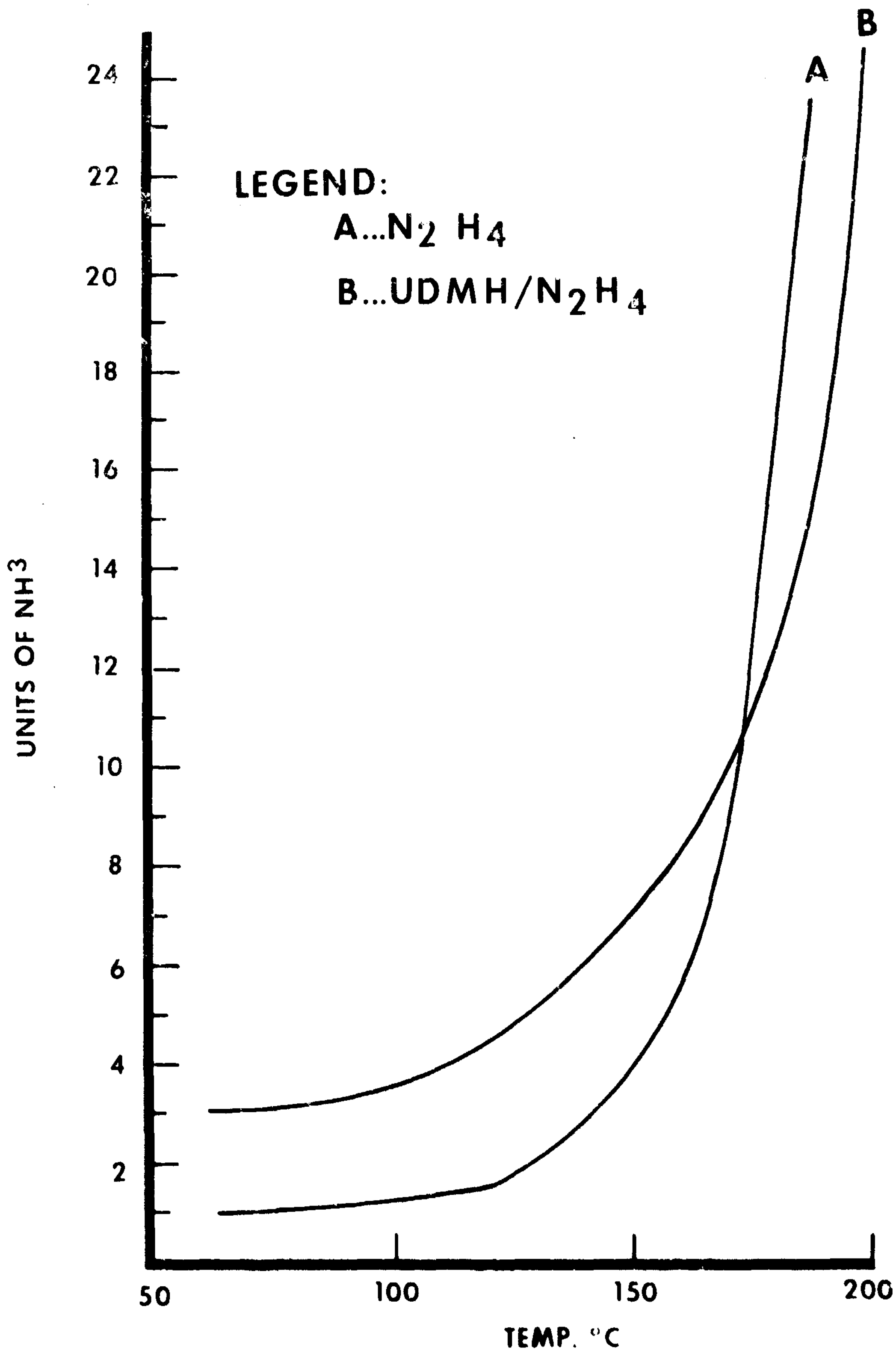

Figure 4. NH_3 From $UDMH/N_2H_4$ By Gas Chromatograph Method (Au/Ni Alloy)

in the dimethylamine or the UDMH content of the propellant was noted during the test it is concluded that only the hydrazine in the fuel blend had decomposed. Figure 5 depicts the results of the immersion tests on the gold/nickel alloy with hydrazine and with UDMH/hydrazine. Propellant blanks were determined simultaneously with the sample analysis. The surface areas of the alloy samples were 3.7cm^2 each. Although decomposition of the propellant was observed for both hydrazine and UDMH/hydrazine, the alloy samples did not change weight. A change in weight of 0.1 mg would have been detected. The hydrazine in the UDMH/hydrazine blend also decomposed more rapidly than neat hydrazine in the immersion test. The decomposition products of the N_2H_4 and UDMH/hydrazine, based on the chromatograph analyses, appear to be only ammonia, nitrogen, and hydrogen.

Hydrazine was also exposed to varying quantities of the Au/Ni alloy and decomposition rate appears to be directly proportional to the exposed surface area of the alloy. The hydrazine decomposition rates decreased noticeably after 8 to 12 hours of exposure to the alloy during the immersion tests with UDMH/N_2H_4 but not with neat hydrazine. This may have been the result of surface poisoning of the catalytic alloy.

IV. CONCLUSIONS

Gold, nickel, or the 82:18 gold/nickel alloy are definitely catalysts at 140^{o}F for the decomposition of hydrazine. These metals appear to be selective for hydrazine, however, the presence of UDMH enhances the rate of decomposition.

A new compatibility test method (gas chromatograph method) has been devised whereby materials can be rapidly screened to provide relative data for compatibility with fluids over a wide temperature range. Future compatibility work on other materials and propellants using this technique is anticipated.

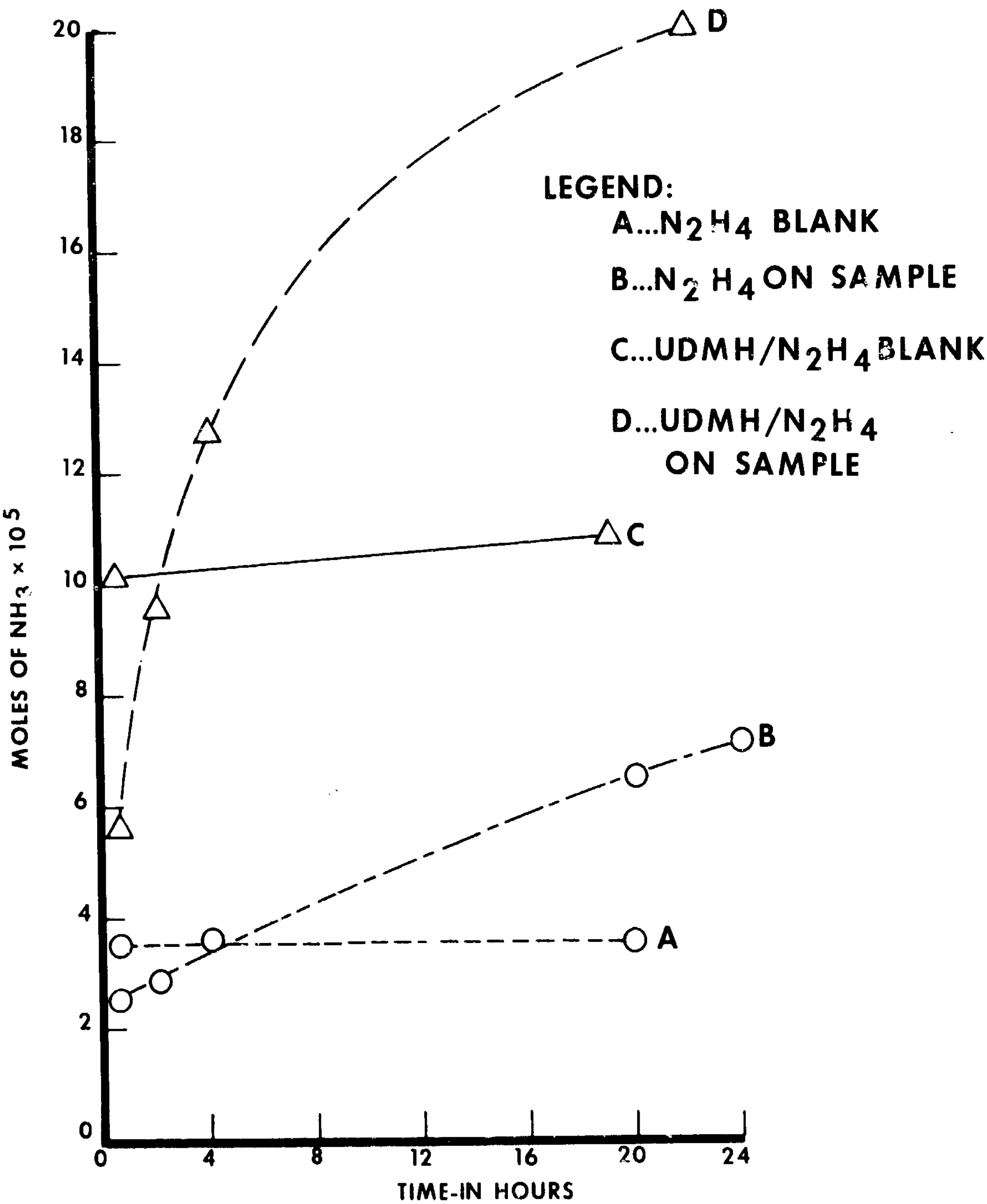

Figure 5. NH_3 From UDMH/N_2H_4 and N_2H_4 By Immersion Test Method (Au/Ni Alloy)

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Catalytic Decomposition						
Gas Chromatography						
Brazing Alloy						