NATIONAL BUREAU OF STANDARDS REPORT

9638

SURFACE PROTECTION OF MARAGING STEEL

By

V. A. Lamb, J. P. Young, and G. I. Reid

QUARTERLY PROGRESS REPORT No. 7

July 1 to September 30, 1967

For

Picatinny Arsenal Project

Order No. A1-8-RF034-01-D1-GG

To

Commanding Officer
Picatinny Arsenal, Dover, N. J. 07801
Attn: Code SMUPA DL-2
Liquid Rocket Propulsion Laboratory

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] provides measurement and technical information services essential to the efficiency and effectiveness of the work of the Nation's scientists and engineers. The Bureau serves also as a focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To accomplish this mission, the Bureau is organized into three institutes covering broad program areas of research and services:

THE INSTITUTE FOR BASIC STANDARDS . . . provides the central basis within the United States for a complete and consistent system of physical measurements, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. This Institute comprises a series of divisions, each serving a classical subject matter area:

—Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Physical Chemistry—Radiation Physics—Laboratory Astrophysics[2]—Radio Standards Laboratory,[2] which includes Radio Standards Physics and Radio Standards Engineering—Office of Standard Reference Data.

THE INSTITUTE FOR MATERIALS RESEARCH . . . conducts materials research and provides associated materials services including mainly reference materials and data on the properties of materials. Beyond its direct interest to the Nation's scientists and engineers, this Institute yields services which are essential to the advancement of technology in industry and commerce. This Institute is organized primarily by technical fields:

—Analytical Chemistry—Metallurgy—Reactor Radiations—Polymers—Inorganic Materials—Cryogenics[2]—Office of Standard Reference Materials.

THE INSTITUTE FOR APPLIED TECHNOLOGY . . . provides technical services to promote the use of available technology and to facilitate technological innovation in industry and government. The principal elements of this Institute are:

—Building Research—Electronic Instrumentation—Technical Analysis—Center for Computer Sciences and Technology—Textile and Apparel Technology Center—Office of Weights and Measures —Office of Engineering Standards Services—Office of Invention and Innovation—Office of Vehicle Systems Research—Clearinghouse for Federal Scientific and Technical Information[3]—Materials Evaluation Laboratory—NBS/GSA Testing Laboratory.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

[2] Located at Boulder, Colorado, 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT 3120465

October 1, 1967

NBS REPORT 9638

SURFACE PROTECTION OF MARAGING STEEL

BY

V. A. Lamb, J. P. Young, and G. I. Reid

QUARTERLY PROGRESS REPORT No. 7

July 1 to September 30, 1967

for

Picatinny Arsenal Project
Order No. A1-8-RF034-01-D1-GG

to

Commanding Officer
Picatinny Arsenal, Dover, N. J. 07801
Attn: Code SMUPA DL-2
Liquid Rocket Propulsion Laboratory

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

SURFACE PROTECTION OF MARAGING STEEL

A. Objectives of Project

1. To investigate the effect of various metallic coatings on Maraging steel for their ability to protect the steel from contact with mixed hydrazine fuel, for their ability to resist corrosion by mixed hydrazine fuel, and for freedom from catalytic effect on the decomposition of mixed hydrazine fuel.

2. To develop procedures for applying coatings, disclosed as satisfactory under part (1), to the interior surfaces of rocket and missile fuel tanks of complex shape.

B. Summary of Progress in Preceding Quarter

1. Decomposition of MHF-3 fuel in contact with various materials

a. "Background" measurement. Average rate of generation of gas by fuel decomposition due to inherent factors in the test unit other than the metal specimen decreased slightly from the preceding period. The average for two units, nos. Hg-2 and Hg-15 at 160°F was 0.0043 cm^3/day.

b. Decomposition rates due to various metals at 160°F. Silver, cadmium, electroless nickel, zinc, tin, tin-nickel alloy, and stainless steel continued to show very low activity, including duplicates of the first three recently placed under test.

Maraging steel, molybdenum and iron were very active in promoting decomposition.

Six new tests had been started, including additional duplicates of the most promising coatings, as well as one new metal, 50-50 lead-tin solder.

Modified procedures were described for filling and leak-testing of units to insure absolutely against leaks.

c. Decomposition rates at room temperatures. The four metals under test at room temperature showed no significant change in trends. Cobalt and Maraging steel maintained their rates. Cadmium and zinc continued to show a slow-down, approaching very low rates.

C. Progress During the Current Report Period

1. Decomposition of MHF-3 fuel in contact with various materials

a. "Background" rate at 160°F. The rate for unit No. Hg-2 has essentially stabilized at 0.0078 cc/day. The temporary rate of zero, noted in the last report for unit No. Hg-15, is now seen to be illusory. Because the rate of gas evolution is so low, temporary small fluctuations in temperature and atmospheric pressure can cause deviations in apparent system volume that are larger than the real volume change. Over a longer period these uncertainties disappear. The unit has now run long enough so that its rate appears to have stabilized at an average of 0.0038 cc/day. The average of these two, 0.0058 cc/day, was used where applicable to correct metal rates shown in Tables 1, 2, and 5.

b. Decomposition rates at 160°F. Table 1 shows cumulative results to the end of September, 1967. Data for the tests previously terminated are still shown for comparison. For most of the metals,

no significant changes from previous results occurred. The high activities for Maraging steel, molybdenum, and iron (units Hg-23, Hg-24, and Hg-25, respectively) have decreased but are still high. The new units, Nos. Hg-27 through Hg-33, have now run long enough to provide significant data. The two units with cadmium show even lower activity than previous ones. The low activity of cadmium appears to be unequivocally proved. This is also true for 347 stainless steel. Tin in the duplicate unit (No. Hg-32) shows a higher activity than the original unit (No. Hg-11), but still low. The low activity of lead-tin solder has potential practical value.

Data from the Teflon valve units are given in Table 2. Units PA-19, PA-21, and PA-26, containing, respectively, zinc, molybdenum, and nickel, are still in operation. Results for zinc show a small rise in rate. The data shown for molybdenum are the same as reported previously. During the current period the rate of gas accumulation in the molybdenum unit has been erratically variable, explainable only as a varying leak. The data were, therefore, not useable. Nickel shows a significant increase in rate. The most likely explanation of its change is that the previous results were too low due to a leak.

Data from the bomb-type units are shown in Table 3. No significant changes from previous trends have occurred.

c. Decomposition rates at room temperature. Data from the four room temperature units are given in Table 4 and Figure 1. The trend for cobalt and Maraging steel has remained about the same, but the rates for cadmium and zinc have decreased further. The rates

shown in Table 4 are the average over the total period of approximately 1 1/3 yr. However, the actual final rates for cadmium and zinc over the last quarter have fallen to 0.0013 and 0.0011 $cm^3/day/cm^2$, respectively, approximately 1/4 and 1/7 of the average rates.

The tests with these four units have been terminated. The fuel from the units is undergoing chemical analysis and detailed examination of the specimens is under way, with respect to corrosion behavior. Partial results are now available and will be reported when complete.

2. Results of experiments performed to provide information on the kinetics of fuel decomposition.

a. Effect of porosity of coatings. We have assumed in making rate coefficient calculations and in projecting tank pressures that decomposition rate is proportional (after correction for "background" factors) to the area of metal specimen in contact with the fuel. It seemed important to test this assumption on both a micro- and macro-scale. The micro-scale is important because a small proportion of basis metal may be exposed to fuel through pores in a coating, not practicable to eliminate completely.

Degree of porosity in a plated coating is very variable, depending on the condition of the basis metal, type of bath, identity of coating metal, degree of freedom of bath from suspended insoluble particles, e.g., fine anode sludge, and, most importantly, deposit thickness. For a deposit 0.1 to 0.2 mils thick, under unfavorable plating conditions, there might be as many as 100 pores of 1 mil diameter per cm^2. For a deposit 2 mils thick, porosity should be essentially zero.

In the present application of coatings to the interior of fuel tanks, the most likely cause of porosity is imperfections in the basis metal due to such factors as roughness and pits resulting from scale removal, incomplete scale removal, or defects in welds. Synthetic porosity specimens were designed in part on the basis of the above considerations and, in part, on the basis of the criteria that they should bear a reasonable relationship to probable actual porosity in production tanks and at the same time yield gas evolution rates in an experimentally reasonable measurement range. We decided to use specimens of silver-plated Maraging steel, pore-free as plated, and to introduce synthetic pores by drilling through the coating. If the Maraging steel exposed through pores were to have the same specific activity as 100% Maraging steel specimens, an exposed area of the order of 0.1 cm^2 is required. This is about ten times larger than the area of 100 pores/cm^2, 0.001 inch diameter, on a specimen of 20 cm^2 area. However, pores due to the types of flaws enumerated above, in fuel tanks, are likely to be larger than pores in typical electroplated ware. A pore area of 0.1 cm^2 therefore seemed a logical compromise around which to design the specimens. Their description is given in Table 5, Nos. Hg-34A to 34D. Pore diameter and total pore area were varied. A minimum pore diameter less than 0.013 inch may be desirable, but this was the smallest drill readily available. Actual area of Maraging steel exposed is not exactly proportional to the number of pores because hole depth varied slightly. Depth of each hole was measured with a microscope and true Maraging steel area was calculated from these data.

The results to date are shown in Table 5. The rate coefficient is calculated on the basis of the area of exposed Maraging steel. The over-all rate was corrected for background to obtain the rate due to pores. If we omit consideration of Hg-34A for the moment, it is seen that the rate of gas evolution for Hg-34B, C, and D is roughly proportional to pore area, with an average rate coefficient of 0.83 cm^3/day/cm^2. The surprising fact is that this is about 8 times the rate for massive Maraging steel (based on the most reliable value, from unit No. Hg-23). The acceleration for unit Hg-34A is even larger, with a ratio of about 30 compared with Hg-23. It would appear that some factor related to the bi-metal combination causes an acceleration of decomposition. Silver is strongly cathodic to Maraging steel, as will be discussed in a subsequent paragraph, and this may be a significant factor. To check it, we propose to make a similar experiment with pores in a cadmium coating, which is anodic to Maraging steel.

From a practical standpoint, it does not appear that this accelerated rate at pores would be a hazard. For example, an absolute porosity of the order of 10 times that in specimen Hg-34D would be an extremely large porosity for a 1 cubic foot tank and would be readily visible to optical inspection. Yet, such gross porosity would only produce about 1800 cc of gas per year and would only increase the pressure in the hypothetical tank used in Table 1 by about 10 psi per year.

b. Effect of area of glass, relative areas of glass exposed to liquid and vapor, and effect of fuel volume. Three special test units were made, designed to give large variations in area of glass exposed to liquid and vapor, and large variations in volume of liquid and vapor, to determine if possible the relative degree of fuel decomposition at the various interfaces and in the liquid and vapor phases. No metal specimen was present in these units. The regular background units, Nos. Hg-2 and Hg-15 constitute a 4th variant for comparison with the three new units. Data from these units are given in Table 6. The rate of gas evolution in units Hg-2 and Hg-15 is approximately the same as that in unit Hg-35, in which the volume of liquid fuel is similar, but in which vapor volume, and glass-vapor interface are very much larger. On the other hand, the rate of gas evolution in Hg-36 is almost exactly six times the rate in Hg-35. This ratio is closely related to the relative volumes of liquid fuel, even though the vapor volume and the glass-liquid and glass-vapor areas are widely different. The comparative liquid volume and rate ratios are as follows:

$$\frac{\text{Volume of liquid, Hg-36}}{\text{Volume of liquid, Hg-35}} = \frac{155}{25} = 6.2$$

$$\frac{\text{Rate, Hg-36}}{\text{Rate, Hg-35}} = \frac{0.028}{0.0046} = 6.1$$

It thus appears that the background rate is dependent almost entirely on the volume of liquid fuel, and that no appreciable reaction occurs in the vapor phase or at a glass-liquid or glass-vapor interface. Data from unit No. Hg-37 are so far indicating agreement with this conclusion, but a longer observation period will be required.

We should consider these conclusions tentative in any case since data from Hg-35 and Hg-36 span less than one month. If these results are confirmed by longer observation, they provide data for estimating the contribution to the pressure in a long-term storage tank due to the inherent decomposition rate of the liquid fuel. The data indicate a specific rate of 0.00018 cm^3 of gas per cm^3 of fuel per day. Applying this rate to the hypothetical one cubic foot tank with 10% ullage that we have used in Table 1, we can calculate the pressure developed in one year due to inherent liquid fuel decomposition as follows:

Volume of gas evolved at 1 atm. and 160°F =

$$(0.00018)(25{,}500)(365) = 1670 cm^3$$

Assuming initial pressure is 1 atm.,

$$p_{final} = 1 \text{ atm.} \frac{(2{,}832 + 1690)}{2{,}832} = 1.6 \text{ atm.}$$

(Note: 25,500 and 2,832 are, respectively, cm^3 of liquid and gas in 1 cu.ft. with 10% ullage.)

Thus, pressure is increased by only 0.6 atm. or approximately 9 psi. Inherent liquid fuel decomposition is, therefore, not a significant factor in development of storage pressure.

c. Effect of contact between metal and fuel vapor. Unit Hg-38 is shown schematically in Figure 2. It was designed to determine the fuel decomposition rate at the vapor-metal interface. Based on the short period of 28 days, the rate, shown in Table 6, is much less than that obtained from units 347-4 and Hg-23 (Table 1) for liquid-metal exposure. We give primary weight to the value from Hg-23, since unit No. 347-4 is more prone to error due to leakage. On this basis

the rate at the vapor interface is only 0.0063/0.099 = 0.064 or 6.4% of the rate at the liquid interface. This relative inertness of the vapor interface is in a sense not surprising, since, unless there were a difference in mechanism, the ratio of the rates at the vapor and liquid interfaces should be approximately proportional to the relative concentrations of fuel molecules in contact with the surface. Assume that reaction is proportional to the surface concentration of a monomolecular layer. It can be readily shown that the surface concentration of a monomolecular layer is proportional to the 2/3 power of the density of the fuel. The density of the vapor phase of MHF-3 at 160°F is 0.0011 g/cm^3, and of liquid is 0.89 g/cm^3. Hence,

$$\frac{S_v}{S_l} = \frac{0.0011^{2/3}}{0.89^{2/3}} = 0.012$$

where S_v and S_l respectively, represent surface concentration of fuel molecules in the vapor and liquid states. Thus, on the above assumption, the rate at the vapor interface should be a little more than 1% of the rate at the liquid interface. Actually, it is about 6%. However, this degree of agreement can be considered to be good, since the two values are of the same order of magnitude; better agreement might be obtained with a more refined theory. However, we should expect that the real vapor-metal interfacial reaction rate should be somewhat higher than on an ideal basis, because there is probably some condensation of liquid. This is the direction observed.

3. Plating of Cylindrical Maraging Steel Tank, 26 inches long by 3.46 inch ID.

An attempt was made to plate the indicated tank, which we had on hand, with 0.002 inch of electroless nickel. We failed on the first attempt to obtain sufficient thickness. An over-plate, applied to bring the thickness up to that desired, failed to adhere perfectly, as indicated by a few small blisters that were seen on inspection after applying the over-plate. It was, therefore, necessary to remove the plate completely by stripping. Concentrated nitric acid normally strips electroless nickel without attack of a steel base. This had been verified for Maraging steel in preliminary tests. Due to an error, stripping of the electroless nickel from the tank was done with 50% nitric acid, resulting in severe etching of the interior of the tank.

The damaged tank has itself been used to verify the safety of the concentrated nitric acid strip and has also been used to test electroless plating with a continuously circulated electrolyte, replenished externally, so that the required thickness can be applied without interruption. The previous plate was applied without continuous circulation. Difficulties encountered with thickness control and solution replenishment showed that continuous circulation is required.

4. New Work

Most of the following activities, initiated during the current report period, have been undertaken as a result of a conference on August 18, 1967, with Mr. Wahling Ng.

a. Tests of special metals. Inco stainless Maraging steel, stainless steel types 301 and AM 355, Inco alloy 718, titanium alloys 6 Al-4V and B 120-VCA, vapor-deposited aluminum from Commonwealth Scientific Corporation, electroless nickel made from an alkaline type of bath, and electroless nickel made from a borohydride type of bath, are to be tested for activity in causing decomposition of MHF-3. All that require procurement from outside sources except the titanium alloys have been obtained, and the alkaline bath electroless nickel deposits have been prepared. New test units to accommodate these specimens have been made and loading of units is in progress.

b. Experiments on ratio of metal surface to fuel volume. Experiments on ratio of metal surface to fuel volume are closely related to the experiments on kinetic factors described above in paragraphs C-2a and C-2b. Experiments are under way in which macro-areas are compared, with A/V having values of 1, 5, and 10, with two different metals, electroless nickel and electroplated nickel.

c. Plating of tensile specimens. Six small cylindrical test specimens supplied by Mr. Ng were plated, three with electroless nickel and three with cadmium. Two of each were sent to Picatinny Arsenal on October 11, 1967.

d. Accelerated corrosion of Maraging steel. Mr. Ng, during his visit, showed some photomicrographs of cross-sections of Maraging steel coated with electroless nickel that had been exposed for an extended period to MHF-3. A few examples of marked pitting of the Maraging steel through pores in the coating were seen. The corrosion

in these locations appeared to be examples of electrolytic corrosion, with acceleration of local pitting due to an anodic base and a cathodic coating. Examination of our specimens when our test units are opened should add to the information on this point. If this hypothesis as to the character of the corrosion is borne out, it would tend to throw doubt on the long-term safety of cathodic type protective coatings. Anodic types of coatings, e.g., cadmium, might be safer. As part of the further study of this question, coatings that might be expected to be anodic, such as cadmium, should be observed specifically with a view to clarifying the question as to whether or not electrolytic corrosion is supported by MHF-3. Corrosion potential measurements should aid in such a study.

D. Appendix

1. Design of test unit.

Several changes in design of the test unit have been made over a period of time in response to deficiencies that have been revealed by experience. It now appears that further changes are not likely. Hence, the latest design is shown in Figure 3. Changes that have been made and their reason are indicated in the legend.

2. Reduction of original data from test units to the form of rate coefficients and projected pressures

We have been questioned as to how rate coefficients and projected pressures are obtained from original data. The calculations are explained as follows:

a. Units with fixed volume (bomb-type units).

Let p_o = standard atmospheric pressure (14.7 psi)

p_1 = initial gage pressure

p_2 = second gage pressure, etc.

V_1 = free volume (total volume in enclosed system minus the volume of fuel and specimen)

$V_{2,1}$ = V_1 plus volume of evolved gas corresponding to p_1, at 1 atm.

$V_{2,2}$ = V_1 plus volume of evolved gas corresponding to p_2, at 1 atm.

The concept of the last two quantities may not be clear without further explanation. Consider $V_{2,1}$. It would be equal to V_1 if the bomb were bled to atmospheric pressure. This is not feasible, because bleeding disturbs equilibrium within the bomb (of temperature, liquid-vapor equilibrium, etc.) so that a waiting period is required after bleeding before a reliable initial reading can be obtained. In general, this reading will be higher than atmospheric pressure. This pressure results from the bomb containing some quantity of fuel decomposition gases (H_2+N_2). Now imagine that a piston were attached to the bomb, initially in a fixed position, such that the system volume is V_1. By moving the hypothetical piston, the volume is increased and the pressure correspondingly falls. $V_{2,1}$ is the total internal volume attained by piston motion when the pressure has dropped to p_o. The difference between $V_{2,1}$ and V_1 is the volume, measured at 1 atmosphere pressure, that would be occupied by the amount of gas that caused the pressure to increase from p_o to p_1.

Similarly, $V_{2,2} - V_1$ is the volume, measured at 1 atmosphere pressure, that would be occupied by the amount of gas that caused the pressure to increase from p_o to p_2.

Now, consider conditions at p_1. The amount of fixed gas in the system (amount of hydrazine is disregarded since it maintains a fixed pressure through equilibrium with liquid) is constant, as is temperature; hence, the following simple form of the gas law applies:

$$(p_o + p_1)V_1 = p_o V_{2,1} \tag{1}$$

Likewise,

$$(p_o + p_2)V_1 = p_o V_{2,2} \tag{2}$$

From Eq. 1,

$$V_{2,1} = \frac{(p_o + p_1)V_1}{p_o} \tag{3}$$

From Eq. 2,

$$V_{2,2} = \frac{(p_o + p_1)V_1}{p_o} \tag{4}$$

Substracting (3) from (4):

$$V_{2,2} - V_{2,1} = \frac{V_1(p_2 - p_1)}{p_o} \tag{5}$$

Equation (5) is the final relationship used for actual calculations. $V_{2,2} - V_{2,1}$ is, from the definitions above, the total volume of gas evolved, as measured at 1 atmosphere pressure, that causes pressure in the bomb to increase from p_1 to p_2. Designate this as $\Delta V_{t,o}$. If the period of time over which $\Delta V_{t,o}$ is obtained is d_t days, then volume obtained per day is $\Delta V_{t,o}/d_t$. By making measurements in an identical manner with the same bomb containing no specimen, a quantity $\Delta V_{b,o}$ is obtained, the volume of gas evolved due to interaction of the fuel with the bomb itself. If the number of days of observation in this

case is d_b, then the background rate, volume per day, is $\Delta V_{b,o}/d_b$ and the volume per day due to the specimen is $\Delta V_{t,o}/d_t - \Delta V_{b,o}/d_b$. If this quantity be divided by the area of the specimen, the specific rate that we have used in Table 1 is obtained. Designate it as R_s. Then

$$R_s = \frac{V_{t,o}/d_t - V_{b,o}/d_b}{A_s} \tag{6}$$

where A_s is area of the specimen. Any convenient units may be used. We have used $cm^3/day/cm^2$. Pressure units used are immaterial since they cancel in eq. (5).

b. Units with variable volume (Manometer type units). With manometer-type units both pressure and system volume change, since, as the mercury is driven down on the system side of the manometer due to gas evolution, the volume of the system increases. Change of both pressure and volume must be taken into account to determine the amount of gas evolved.

Let V_1 = initial free volume at p_1 (free volume is total volume in the unit measured to the level of the mercury, minus volume of fuel and specimen).

V_2 = final free volume at p_2.

p_o = standard atmospheric pressure, 760 mm Hg.

p_1 = total initial pressure (pressure due to mercury head plus actual atmospheric pressure at time of measurement, since manometer is open to the atmosphere).

p_2 = total final pressure.

(V_2 and p_2 are not "final" in an absolute sense. They represent any one of a series of increasing volumes and pressures.)

Let $V_{1,o}$ = volume that the initial amount of gas would have at p_o.

$V_{2,o}$ = volume that the final amount of gas would have at p_o.

The simple form of the gas law involving only p and V can again be applied separately to the initial and final conditions, since at each point, amount of gas and temperature are constant. Thus:

$$V_1 p_1 = V_{1,o} p_o \tag{7}$$

and

$$V_2 p_2 = V_{2,o} p_o \tag{8}$$

From (7)

$$V_{1,o} = \frac{V_1 p_1}{p_o} \tag{9}$$

From (8)

$$V_{2,o} = \frac{V_2 p_2}{p_o} \tag{10}$$

Substracting (9) from (10);

$$\Delta V_{t,o} = V_{2,o} - V_{1,o} = \frac{V_2 p_2 - V_1 p_1}{p_o} \tag{11}$$

Equation (11) is the relationship used for actual calculations. $\Delta V_{t,o}$ is the total volume of gas evolved, measured at 1 atmosphere pressure, that will change the volume and pressure in the system from V_1 and p_1 to V_2 and p_2. By "total" is meant the amount due to both background and specimen. $\Delta V_{b,o}$ is the volume similarly determined due to background. If d_t and d_b are respective days of test and A_s is the area of the specimen, then R_s, the rate coefficient as defined in par. D-2a above, is:

$$R_s = \frac{\Delta V_{t,o}/d_t - \Delta V_{b,o}/d_b}{A_s} \tag{12}$$

Again, we have reported this as $cm^3/day/cm^2$.

The following data are required to obtain the V and p values needed for equation (11).

(1) Total interior volume measured to an arbitrarily defined manometer zero. We uniformly use a mercury level 5 cm below the cross-brace as the zero point and fill the manometer to this point with atmospheric pressure in the unit.

(2) Free gas volume to the manometer zero.

(3) Manometer volume calibration (cm^3/cm length).

(4) Manometer height calibration. Since the manometer shown in Figure 3 is not symmetrical, a calibration curve is constructed before the unit is put into use, with difference in mercury level plotted vs height of mercury in stem above zero point.

(5) Barometric pressure.

c. Calculation of tank pressure after 1 year in our "standard" tank. In Table 1 of this report and in preceding reports we have shown the pressure that would be developed in an assumed tank after one year, in order to permit easy visualization on a standard basis as to the meaning or consequences of the decomposition activity of the various metals being tested.

The assumed tank is a cube one foot on edge, sitting level, filled nine-tenths full with fuel. The entire interior surface consists of the metal in question. Initial pressure is assumed to be atmospheric pressure. The entire interior surface has been counted as active on the basis that vapor-metal interfaces would be wetted by condensation. (The data in this report, paragraph C-2c, indicate that this will exaggerate the calculated pressure. However, the assumption

will be more true in real storage, with variable temperature, than in a constant temperature test unit).

The calculation is as follows:

Let V_u = ullage volume = 2832 cm^3

ΔV_y = volume of gas evolved in 1 year in cm^3, measured at 1 atm.

= R_s . 365 days.5,574 cm^2 (from eq. 6 or 12)

p_o = standard atmospheric pressure, 14.7 psi

p_y = pressure developed in tank after 1 year, psi

Applying the gas law and the same reasoning as in paragraph D-2a above, we obtain:

$$(V_u + \Delta V_y)p_o = V_u p_y \tag{13}$$

Solving (13) for p_y, one obtains:

$$p_y = p_o + \frac{\Delta V_y p_o}{V_u} \tag{14}$$

$$= 14.7 + \frac{R_s \cdot 365 \cdot 5574 \cdot 14.7}{2832}$$

$$= 14.7 + 10560\ R_s \tag{15}$$

In equations (14) and (15), p_y is absolute pressure. Designate gage pressure (psig) after one year as $p_{y,g}$. Since gage pressure is one atmosphere less than absolute pressure, it is given by:

$$p_{y,g} = 10560\ R_s \tag{16}$$

TABLE 1

Summary of Test Data for Materials Exposed to MHF-3 at 160°F

Test unit number	Coating or metal	Area of specimen cm^2	Time under test days	Gas evolved* cm^3	Rate coefficient* $cm^3/day/cm^2$	Calculated tank pressure after 1 year** psig[xxx]
Hg-1[x]	Silver	16.0	123	None	Zero	None
Hg-3	Cadmium	13.0	328	6.6	0.0016	16
Hg-4	Electroless nickel	19.6	316	10.1	0.0016	16
Hg-5[xx]	Tungsten	24.8	306	27.2	0.0050	53
Hg-6[x]	Gold	22.9	222	48.5	0.0095	94
Hg-7[xx]	Zinc	15.6	306	10.2	0.0034	35
Hg-8[xx]	Tin-Nickel alloy(65-35)	24.0	290	27.0	0.0050	52
Hg-9[x,xx]	Cobalt	16.1	199	--	0.94	9,884
Hg-11	Tin	15.2	290	None	Zero	None
Hg-12[xx]	Electroless nickel	22.2	246	6.4	0.0012	13
Hg-13[x]	Cadmium	15.5	85	1.0	0.0019	20
Hg-14	347 Stainless steel[a]	13.2	243	None	Zero	None
Hg-16	Cadmium (thin)	9.4	218	None	Zero	None
Hg-22	Silver (thin)	16.0	184	14.5	0.0049	52
Hg-23[xx]	18% Maraging steel[a]	17.0	188	--	0.099	1050
Hg-24[xx]	Molybdenum[a]	4.8	186	--	0.158	1675
Hg-25[xx]	Iron[a]	4.4	183	--	0.058	610
Hg-27	Cadmium (thin)	10.6	79	0.3	0.00036	3
Hg-28	347 Stainless steel[a]	6.5	79	None	Zero	None
Hg-29	Silver	14.5	79	None	Zero	None
Hg-31	Cadmium	14.7	61	0.1	0.00011	1
Hg-32	Tin	13.0	81	5.3	0.0050	53
Hg-33	Solder, 50/50 lead-tin[a]	15.3	61	None	Zero	None

*Cumulatiye total, corrected for background rate and to 1 atmosphere pressure.

**Based on a tank in the form of a cube, 1 cu.ft. volume, 10% ullage.

[x]Discontinued.

[xx]Total days under test are not equal to number of days during which gas was collected, due to temporary leaks, or to interrupted collection due to high rate.

[xxx]Tabulated values erroneously given as absolute psi in preceding reports.

[a]These specimens are solid metal. All others are coatings on 18% Maraging steel.

TABLE 2

Results of Tests in Units Equipped with 4 mm Teflon Valves,

Supplied by Picatinny Arsenal.

Temperature, 160°F.

Test unit number	Coating or metal	Area of specimen cm^2	Time under test days	Gas* evolved cm^3	Rate* coefficient $cm^3/day/cm^2$	Calculated** tank pressure after 1 year psig[xxx]
PA-17[x]	Silver	17.3	55	Unable to obtain tight valve closure		
PA-18[x]	Lead	19.1	55	" "	" "	" "
PA-19[xx]	Zinc	15.8	211	44.4	0.019	196
PA-20[x,xx]	Iron	5.6	193	--	0.23	2,425
PA-21	Molybdenum	3.6	206	--	0.089	937
PA-26[xx]	Nickel	17.0	189	--	0.025	268

*Cumulative total, corrected for background rate and to 1 atmosphere pressure.

**Based on a tank in the form of a cube, 1 cu.ft. volume, 10% ullage.

[x]Discontinued.

[xx]Total days under test are not equal to number of days during which gas was collected, due to temporary leaks, or to interrupted collection due to high rate.

[xxx]Tabulated values erroneously given as absolute psi in preceding reports.

TABLE 3

Summary of Data for Materials Exposed to MHF-3 at 160°F

in Stainless Steel Bomb-Type Test Units

Test unit number	Coating or metal	Area of specimen cm^2	Time under test days	Gas evolved* cm^3	Rate coefficient* $cm^3/day/cm^2$	Calculated tank pressure after 1 year** psig***
316-1	Nickel	16.0	352	110	0.0195	206
347-1	Lead	20.5	343	34	0.0048	59
347-4	18% Maraging steel	14.0	112	93	0.060	629
347-Ni	Nickel	82	344	1074	0.038	402

*Cumulative total, corrected for background rate and to 1 atm. pressure.

**Based on a tank in the form of a cube, 1 cu.ft. volume, 10% ullage.

***Tabulated values erroneously given as absolute psi in preceding reports.

TABLE 4

Summary of Test Data for Materials Exposed to

MHF-3 at Room Temperature

Test unit number	Coating or metal	Area of specimen cm^2	Time under test days	Gas* evolved cm^3	Rate* coefficient $cm^3/day/cm^2$	Calculated** tank pressure after 1 year psig[xx]
Rt-1a[x]	Cadmium	17.0	413	34.2	0.0049	51
Rt-2a[x]	Zinc	14.8	454	51.5	0.0076	80
Rt-3a[x]	Cobalt	17.1	456	155	0.0194	210
Rt-4a[x]	18% Maraging steel	14.6	491	292	0.0407	430

*Cumulative total, corrected to 1 atmosphere pressure and 25°C.

**Based on a tank in the form of a cube, 1 cu.ft. volume, 10% ullage.

[x]Discontinued.

[xx]Tabulated values erroneously given as absolute psi in preceding reports.

TABLE 5

Data on Decomposition of MHF-3 Fuel at 160°F in Special Test Units

Effect of Porosity in Coatings of Silver on Maraging Steel

Test unit number	Description	Time under test days	Gas evolved cm^3	Rate coefficient $Cm^3/day/cm^2$ of exposed MS
Hg-34A	Silver on Maraging steel, 20 pores, 0.013" diam., MS area 0.049 cm^2	45	6.9	3.1
Hg-34B	Silver on Maraging steel 200 pores, 0.013" diam., MS area 0.42 cm^2	44	15.4	0.84
Hg-34C	Silver on Maraging steel, 200 pores, 0.026" diam., MS area 1.29 cm^2	33	20.6	0.48
Hg-34D	Silver on Maraging steel, 1 pore, 0.22" diam., MS area 0.39 cm^2	34	15.5	1.17

TABLE 6

Effect of Fuel and Vapor Volume and Interfacial Variables

on Rate of Decomposition of MHF-3

Unit No.	Description							Time under test	Gas evolved	Rate
	Bulb dimensions		Volume		Interface Area					
	diam.	length	Liquid	Vapor	Glass-liquid	Glass-vapor	Metal-vapor			
	cm	cm	cm^3	cm^3	cm^2	cm^2	cm^2	days	cm^3	cm^3/day
Hg-2))Av. Hg-15)	2.2	10	31	8	25	35	--	273	1.6	0.0058
Hg-35	5.0	10	25	137	25	171	--	28	0.13	0.0046
Hg-36	5.0	10	155	7	152	44	--	25	0.69	0.028
Hg-37	2.2	20	78	6	158	26	--	--	--	--
Hg-38	2.2	16	4	59	5	141	9.7*	28	1.7	0.0063*

*The metal is 18% Maraging steel. The rate is $cm^3/day/cm^2$ of Maraging steel area.

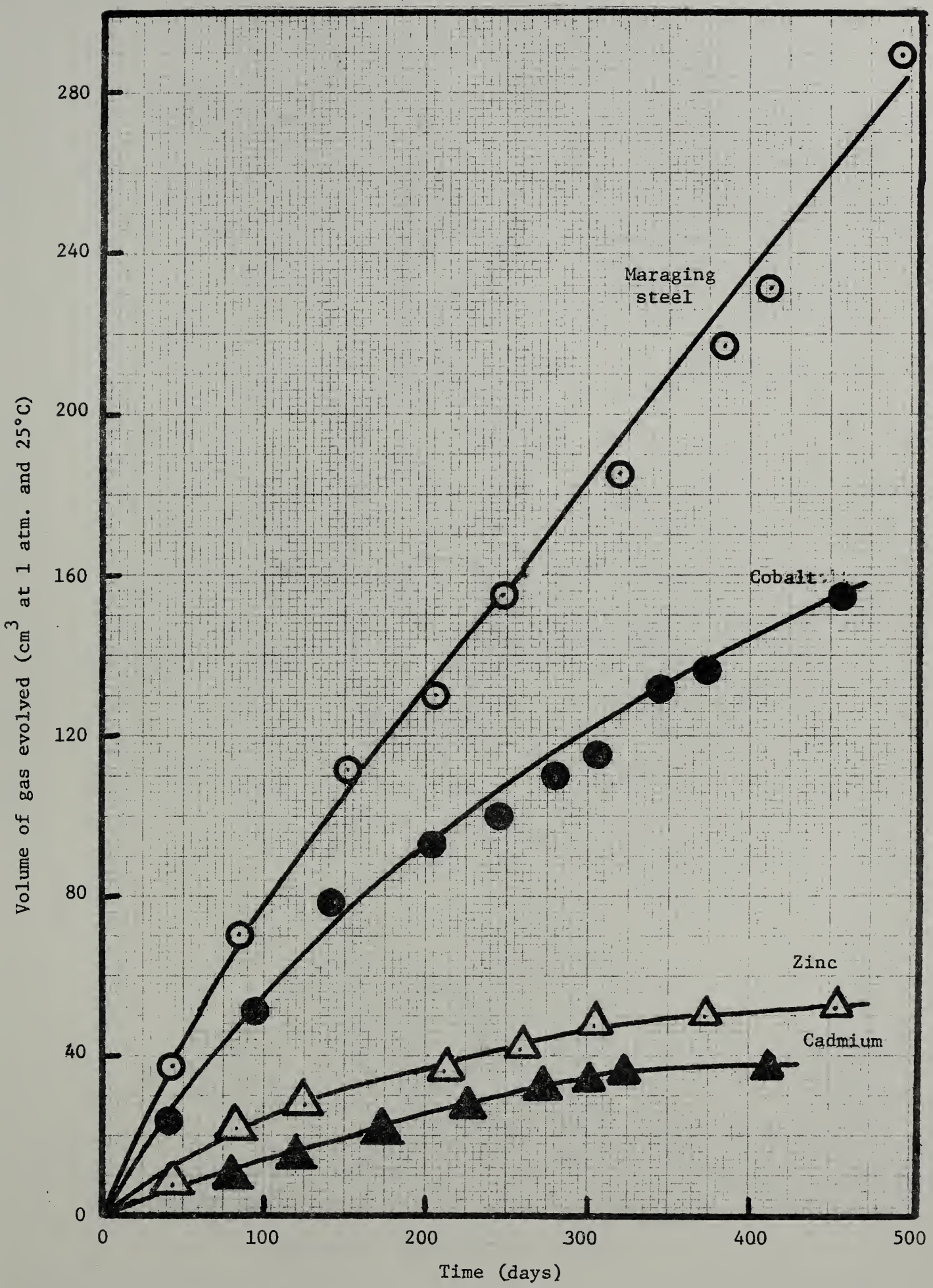


Figure 1. Rate of gas evolution from MHF-3 in contact with indicated metals at room temperature. Metal area approx. 15 cm^2.

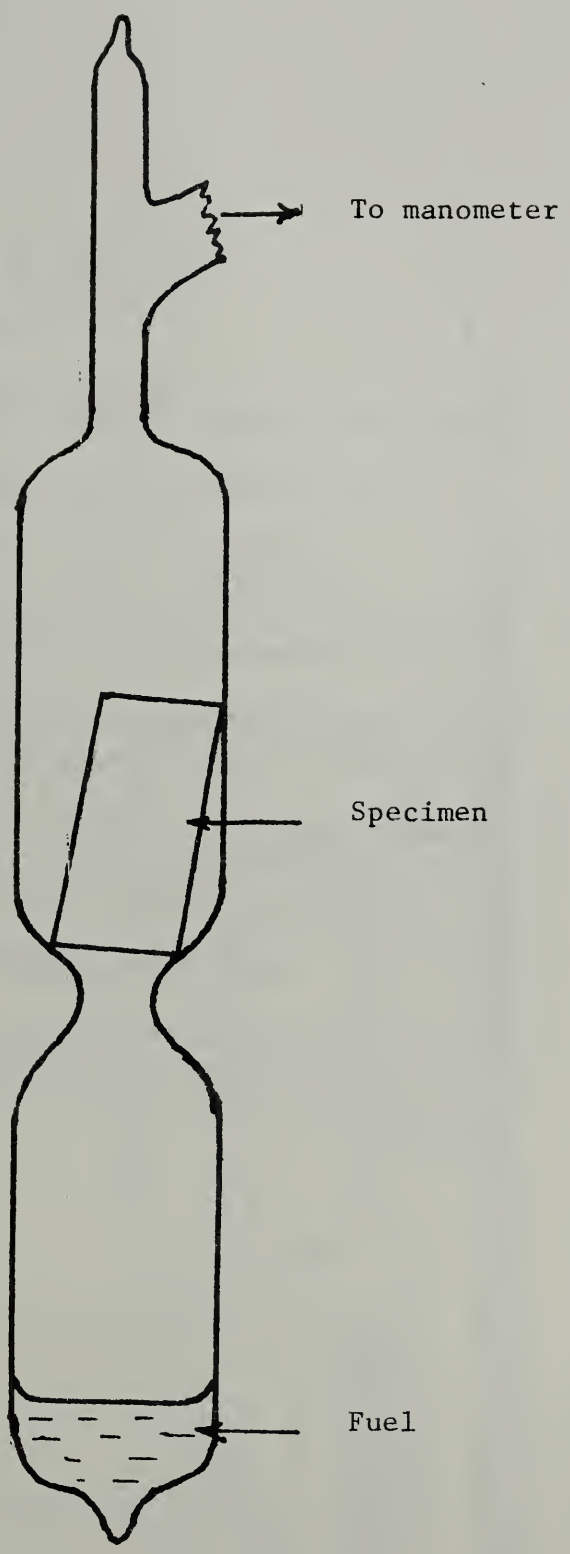


Figure 2. Arrangement of specimen in test unit for measuring rate of decomposition of fuel at metal-vapor interface.

Specimen: 18% Maraging steel.

Figure 3. Most recent design of glass test unit for measuring gas evolved from decomposition of fuel.

Features:

1. No part of bulb assembly projects from 160°F bath, reducing condensation in upper part.

2. Cross-arm slopes toward bulb, so any condensation in this portion of bulb assembly drains back to bulb.

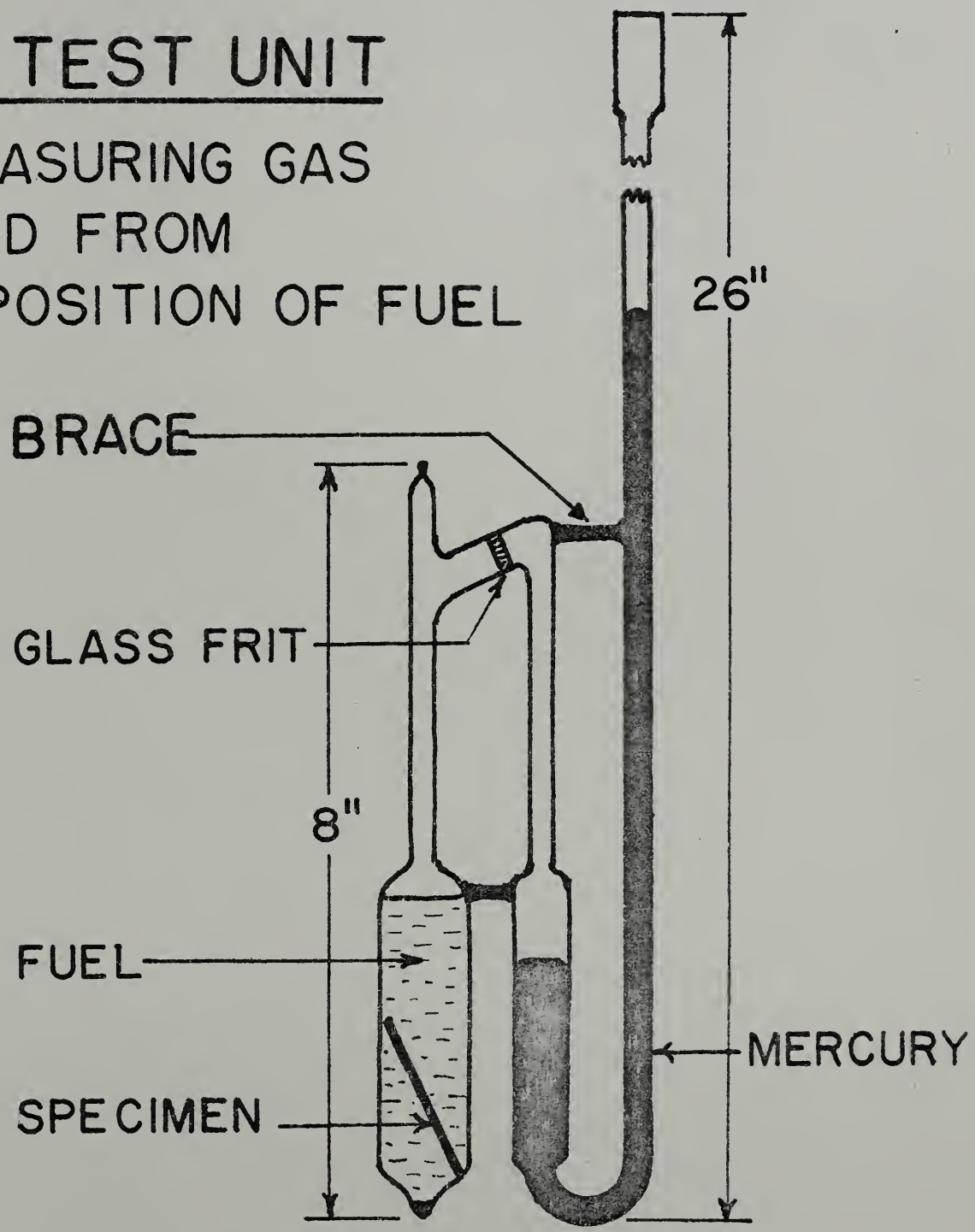
3. Glass frit retards diffusion to and condensation of vapor into manometer side. It also prevents accidental transfer of mercury to fuel bulb.

4. Completely sealed unit prevents leaks.

5. Initial flushing with nitrogen and periodic bleeding are accomplished through a 2 mm diameter Teflon tube inserted from the atmosphere side through the mercury column.

GLASS TEST UNIT

FOR MEASURING GAS
EVOLVED FROM
DECOMPOSITION OF FUEL



DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS