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PASSIVITY EXPERIMENTS ON HYDRAZINE FUELED SATELLITE PROPULSION SUBSYSTEMS

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Small-scale test results were compared with those from two full-scale conditionings made on flight propulsion subsystems following completion of experiments on the critical materials for those particular units. Comments are presented on the general credibility of the conditioning or passivation process and on methods of standardizing the technique when it is employed.

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PASSIVITY EXPERIMENTS ON HYDRAZINE FUELED SATELLITE PROPULSION SUBSYSTEMS

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ABSTRACT

The absence of a generally accepted state-of-art for conditioning or passivating monopropellant hydrazine satellite propulsion subsystems prompted the implementation of a small-scale program involving experimental and analytical efforts to assess the need for and effectiveness of procedures presently employed by contractors practicing the technique.

A specialized laboratory apparatus was used to test basic metals involved in fabricating satellite propulsion hardware such as tanks, manifold tubes, welds and brazes. Metal samples were immersed in military grade hydrazine at 48.9°C (120°F) for about 1000 hr while monitoring the pressure rise from evolved gases. The collected gases were analyzed for constituents so that the quantity of gases could be accurately determined. Test results were normalized to provide gas evolved per unit area then extrapolated to full size propulsion subsystems to predict anticipated pressure rises or volume changes under varying conditions of interest.

Small-scale test results were compared with those from two full-scale conditionings made on flight propulsion subsystems following completion of experiments on the critical materials for those particular units. Comments are presented on the general credibility of the conditioning or passivation process and on methods of standardizing the technique when it is employed.

I. INTRODUCTION

Passivity in metals is a condition generally related to the conversion of its external surfaces to a less reactive or even inactive state as a result of exposure to, or immersion in, appropriate gas or liquid solutions. In the specific case of monopropellant satellite propulsion subsystems, the process of passivation or conditioning has been associated with the conversion of internal, fuel wetted surface areas to a less reactive state by exposure to the fuel, either hydrogen peroxide or hydrazine, which will be used later when the unit is ready to fly. This process was considered necessary on hydrogen peroxide fueled subsystems because hydrogen peroxide decomposed to some degree in the presence of commonly used fabrication metals and was especially sensitive to contaminants on the metal surfaces. To a lesser degree, hydrazine also appears to react with many commonly employed metals, as well as with contaminants on the metal surfaces, therefore, conditioning or passivation has also been implemented on a number of hydrazine fueled subsystems.

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The rationale and techniques for the conditioning or passivation process, however, have not been well developed for hydrazine fueled subsystems. A wide diversity of procedures, all somewhat lacking in credibility, presently exist among propulsion subsystem contractors practicing the process. For example, there is no unanimity in regard to solution strength, solution temperature and exposure time. Similarly, subsystems have been passivated without propellant control valves or engines and in other cases with propellant valves and engines welded into place. In general, there is no basic agreement about the necessity or value of conditioning at all for hydrazine subsystems.

This absence of a generally accepted state-of-art directly impacted several satellite programs, especially those involving new materials and new unsubstantiated conditioning procedures such as the NATO-III subsystem. A small-scale program was therefore implemented which involved experimental and analytical efforts to (1) evaluate passivation or conditioning procedures, (2) verify the effectiveness of cleaning procedures prior to conditioning, (3) determine relative compatibility of selected propulsion subsystem materials with hydrazine and (4) determine the need for and applicability of success criteria for passivation or conditioning processes.

II. DISCUSSION

A. Present State-of-Art

The currently employed techniques for conditioning or passivating monopropellant hydrazine propulsion subsystems appear to be at least partially based upon traditions and emotions. A wide diversity in actual procedures, which ostensibly accomplish the same thing, should adequately attest to this. The basic process generally includes wetting critical internal surfaces of the subsystem such as tanks and feed lines with hydrazine and then disposing of the fuel. It has already been employed on a number of spacecraft subsystems such as the ComSat Corporation Intelsat IV, United Kingdom Skynet II, NASA Synchronous Meteorological Satellite, NATO-III, NASA Mariner, NASA Radio Astronomy Explorer-B and Canadian Telsat. Implementation of this process is also planned for other satellites.

Parameters which directly affected these previous passivations or conditionings, but which varied between spacecraft as shown in Table I, include the following:

a. single- or multiple-stage process

b. hydrazine solution strength

c. solution temperature

d. exposure time at temperature

e. percent of subsystem capacity filled with solution

f. primary subsystem materials

g. success criterion

h. propellant valves in place at time of process

For example, referring to Table I, the Intelsat IV qualification and flight subsystems, which are built by the Hughes Aircraft Company of titanium alloys, are conditioned in a single-stage process by filling the entire capacity of the hardware with military grade hydrazine. The filled subsystem is heated to 175°F, then stabilized at this temperature for 24 hr while a pressure rise is monitored in a small external ullage volume to verify that it does not exceed a specified level established as a success criterion.

Those who have already practiced conditioning or passivation appear, in general, to believe that the particular approach they selected was beneficial to their hardware. However, to further complicate matters, other contractors appear to be strongly opposed to the entire idea of exposing the subsystem to hydrazine prior to the final flight load of propellant largely on the basis that it is difficult to decontaminate the hardware. This position also appears to be at least partially based upon traditions and emotions.

This diversity of opinions and approaches in the industry, or the absence of a generally accepted state-of-art technique for conditioning or passivating monopropellant hydrazine propulsion subsystems, prompted the implementation of the efforts described in the remainder of this paper. Initial work in this area involved the NATO-III subsystem; consequently, this particular unit will be used throughout the paper as a representative example.

B. Representative Propulsion Subsystem

The Philco-Ford designed monopropellant hydrazine propulsion subsystem configuration for the NATO-III satellite is reasonably typical of those on which conditioning or passivation is planned or has already been implemented. The unit is assembled and tested by Marconi Space and Defence Systems Limited under subcontract to Philco-Ford. Primary components of this subsystem, shown in Fig. 1, include a pressure transducer, fill and drain valve, three propellant and pressurant tanks and four hydrazine rocket engine assemblies. The tanks are interconnected by manifolds on both the gas and liquid side and are connected to pairs of engines on the liquid side.

The propellant and pressurant tanks, which represent the largest fuel wetted internal surface area, are fabricated of cryogenically stretched 301 stainless steel. The spherical surface of each tank has a complete girth weld, three circular welds for mounting lug bosses and three circular welds for outlet port bosses. Each of the three outlet tubes on a tank have a transition weld between the 301 stainless steel tank material and the 304L stainless steel utilized for all subsystem manifolding. All tank and transition welds use a bead of 308L stainless steel. Sections of manifold tubing are joined together utilizing 304L stainless steel braze fittings. Braze alloy for the joint is 82 percent gold, 18 percent nickel.

Total internal surface area for all 301 stainless steel tankage in the NATO-III propulsion subsystem, as noted in Fig. 1, is about 9600 square centimeters (cm^2)*. Similarly, the internal surface area of the 308L

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*English and Metric measurement units will be intermixed in this paper. Propulsion subsystem designs and testing have generally been implemented in English units while the experiment and its extrapolation to these designs was made using Metric units.

Table I. Characteristics of Recent Conditionings or Passivations

Spacecraft / Characteristic	Mariner	Intelsat IV	Skynet II	SynMet Sat	NATO III	RadAst Exp-B	Telsat
Propulsion Subsystem Contractor	Boeing	Hughes	Marconi	Philco	Marconi	Hamilton Standard	Hughes
Primary Materials	titanium alloys	titanium alloys	titanium alloys	stainless steels	stainless steels	stainless steels	titanium alloys
Steps or Stages in Process	one	one	one	three	one	two	one
Hydrazine Solution Strength	military grade	military grade	15% N_2H_4 85% H_2O	10% then 40% N_2H_4 with water then mil grade	military grade	35% N_2H_4 65% H_2O then mil grade	military grade
Solution Temperature	ambient	175°F	110°F	ambient	122°F	ambient then 120°F	175°F
Time at Temperature	48 hr	24 hr	2 hr	1 hr then 1 hr then unspecified	10 hr	1 hr then 24 hr	24 hr
Percent Fill	10	100	50	100	100	100	100
Propellant Valves on Subsystem	yes	no	yes	yes	no	yes	no
Qualification and/or Flight Units	both	both	both	both	both	flight	both
Success Criterion Used	no	yes	no	no	yes	yes	yes

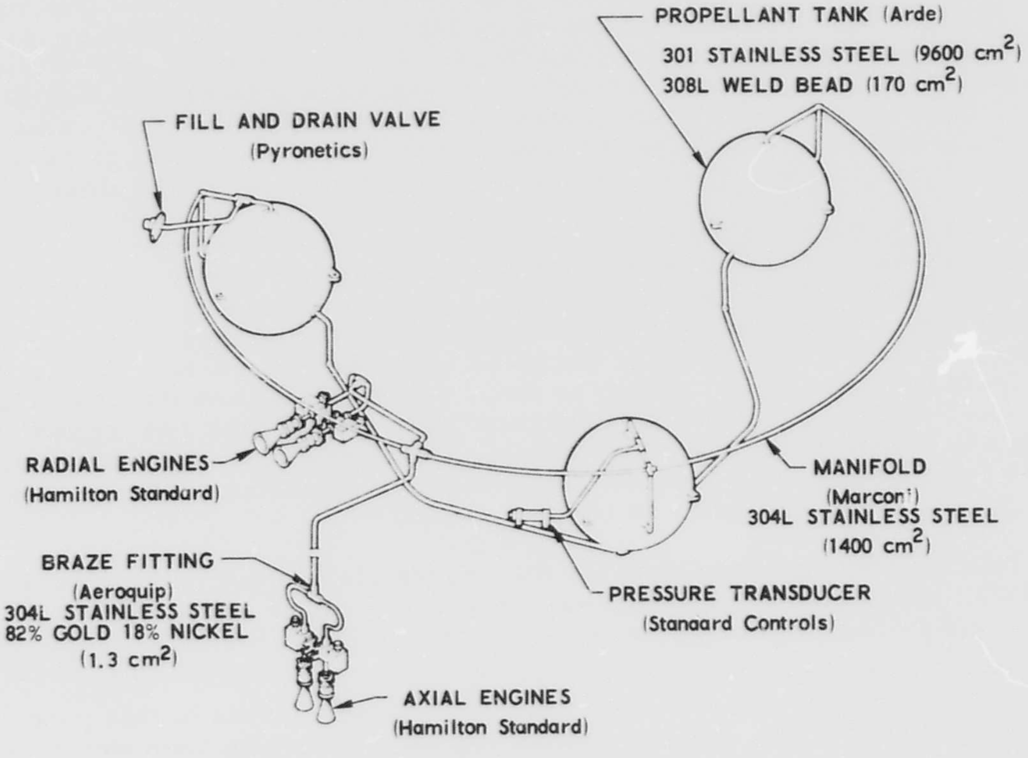

Fig. 1. NATO-III Propulsion Subsystem

stainless steel tank weld bead is estimated to be 170 cm^2. The internal area of the 304L stainless steel manifold tubing which can be wetted by hydrazine is about 1400 cm^2 and finally, the total subsystem internal surface area of the braze alloy is estimated to be 1.3 cm^2. The above metal surface areas will be referred to later in this paper when data from small scale experiments on these materials will be extrapolated to the full size NATO-III propulsion subsystem.

C. Experimental Hypothesis

A brief study of the data from earlier experimental efforts on compatibility of metals with hydrazine (see Ref. 1) indicated that the resulting curves of evolved gas per unit surface area versus time could be categorized into two basic types whose characteristics are illustrated in the simplified sketches of Figs. 2 and 3. This observation formed the basis for a hypothesis which was postulated in an attempt to interpret the general form of the gas evolution plots made during the earlier compatibility experiments and anticipated for the current passivity experiments.

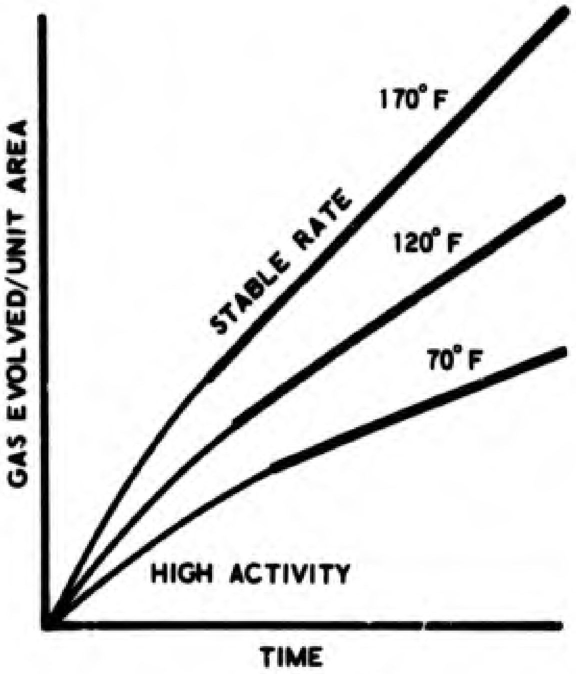

Fig. 2. High Initial Reaction Rates

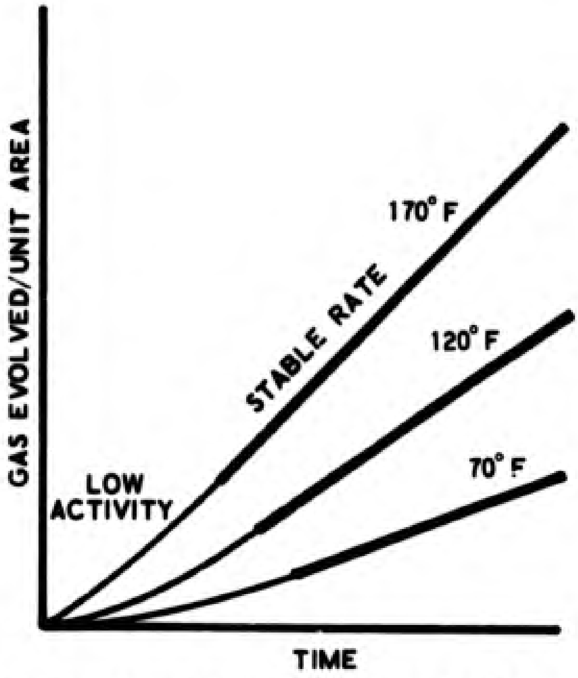

Fig. 3. Low Initial Reaction Rates

The basic hypothesis can be stated as follows: clean metals which are considered to be suitable for use with hydrazine exhibit a natural or stable gas evolution rate when immersed in hydrazine at a constant temperature. This is illustrated by the linear portions of both Figs. 2 and 3 which have been emphasized by a wide dark line. If the metal surface is coated with a consumable contaminant, the initial reaction rate may be greater than this stable rate, as illustrated by the early portions of all curves in Fig. 2. On the other hand, if the metal surface contains a suppressive coating, the initial reaction rate may be less than the stable rate, as shown by the early portions of all curves on Fig. 3.

However, regardless of whether the initial reaction is active and characterized by steadily decreasing rates or depressed and characterized by steadily increasing rates, the stable rate between the metal and hydrazine will predominate over any protracted time period and will be fully established when the reaction between all consumable coatings and hydrazine is completed. It should be noted that all of the metals presently considered suitable for use in contact with hydrazine possess some degree of incompatibility with the fuel and will therefore exhibit, as noted above, a stable gas generation rate even in a very clean condition. There appears to be no absolute compatibility of metals with hydrazine but only varying degrees of incompatibility.

D. Description of Test Apparatus

The experimental portion of this investigation was carried out in two parts, with each part utilizing a separate piece of equipment. The first apparatus involves a unique compatibility monitor which provides a thermally controlled environment for metal test samples immersed in military grade hydrazine. The device is used to monitor the rate of pressure increase in a closed system due to gas evolution caused by the decomposition of hydrazine in the presence of a test specimen. Figure 4 is a photograph of four samples being simultaneously tested. A more detailed description of the compatibility monitor is provided in Appendix A.

The second part of the test involved a specially designed gas analyzer where the evolved gases from the compatibility monitor were extracted and analyzed for constituents. Figure 5 is a photograph of the gas analysis equipment. This apparatus is required so that the quantity of gases trapped in the compatibility monitor can be accurately determined. Hydrazine is assumed to decompose as follows:

$$3\ N_2H_4 \rightarrow N_2 + 4\ NH_3$$

However, the ammonia may dissociate providing additional nitrogen and hydrogen

$$4\ NH_3 \rightarrow 2N_2 + 6\ H_2$$

If the fraction of ammonia which dissociates is designated by X, then the resulting equation for the reaction is as follows:

$$3\ N_2H_4 \rightarrow (1 + 2X)\ N_2 + 6XH_2 + 4(1-X)\ NH_3$$

A value for X is determined by analyses of the gases collected in each leg of the compatibility monitor. Once again, for those interested in more detail, a thorough description of the gas analysis equipment is provided in Appendix B.

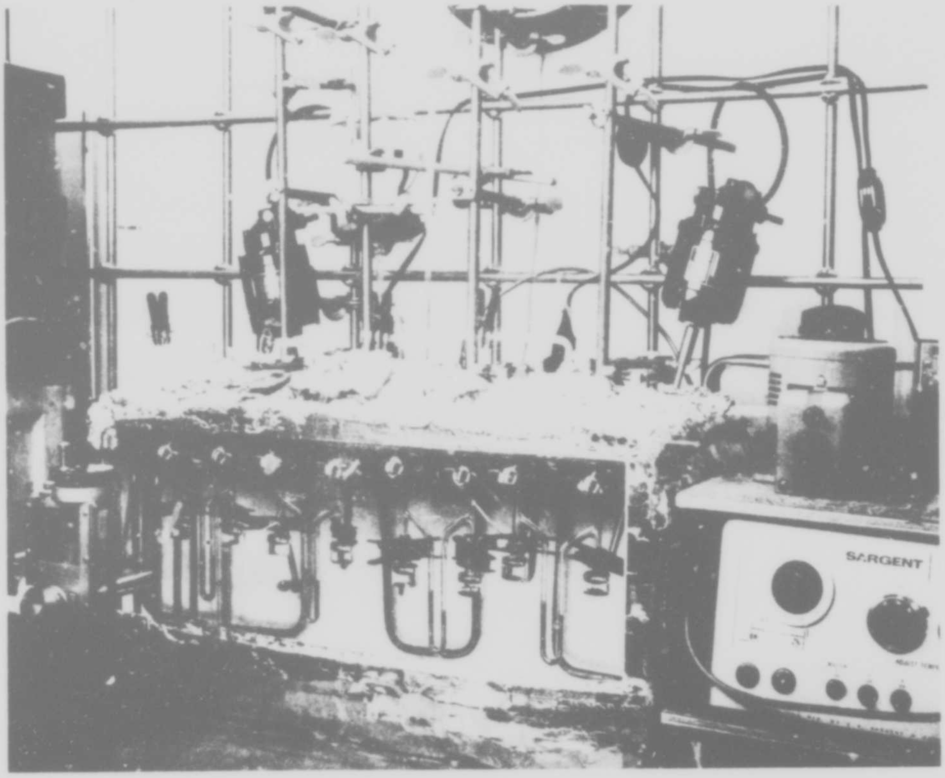

Fig. 4. Simultaneous Test of Four Samples

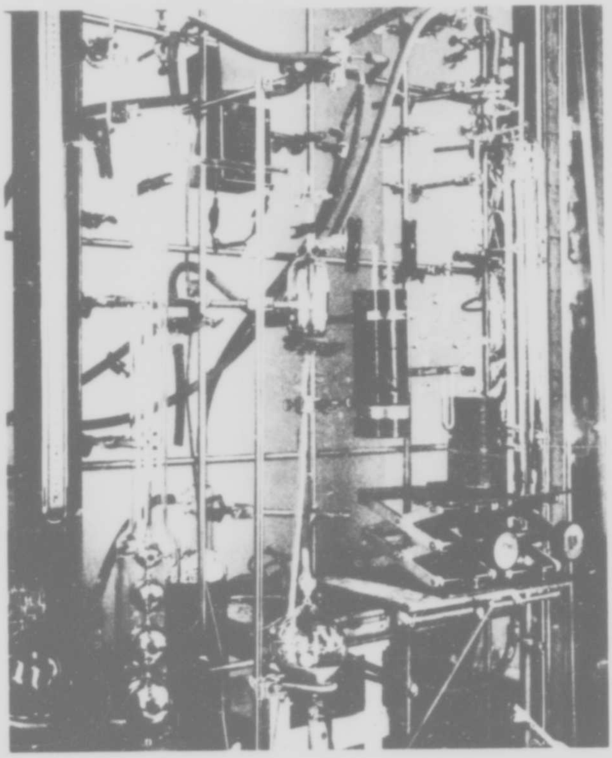

Fig. 5. Gas Analysis Equipment

E. Preparation of Test Samples

Four satellite prime contractors supplied metal samples from major portions of various propulsion subsystems for testing. Some of the samples were completely prepared by these contractors, that is, they were cut to size, cleaned, bagged and certified as clean. Other samples were prepared in a similar fashion in the laboratory from larger sections of material provided by the contractors.

The Philco-Ford NATO-III propulsion subsystem provided the first set of metal samples to be tested in this effort. Philco and their propulsion subcontractor, Marconi, supplied relatively large pieces of structural material from all critical portions of the NATO-III propulsion subsystem. For example, a part of a propellant and pressurant tank which had been burst tested was made available for a sample of tank wall and tank weld bead materials. Similarly, brazed sections of manifold lines provided representative samples of a brazed joint and manifold tubing. A summary of the appropriate characteristics of the four NATO-III test samples is shown in Table II.

Table II. Description of Test Samples

Part of Subsystem	Materials	Configuration	Wetted Surface Areas
Tank 0.014 in. wall thickness	301 stainless steel	six rectangles	7.66 cm^2 total
Manifold Tubing 0.020 in. wall thickness	304L stainless steel	two cylinder halves 0.250 in. outside diameter	6.09 cm^2 total
Welded Joint 0.020 in. wall thickness	301 stainless steel tube 304L stainless steel tube 308L weld bead	half cylinder 0.250 in. outside diameter	0.97 cm^2 301 0.60 cm^2 304L 0.47 cm^2 308L
Brazed Joint 0.020 in. wall thickness for tubing and braze fitting	304L stainless steel tube 304L stainless steel fitting 82 percent gold, 18 percent nickel braze alloy	two concentric cylinders 0.295 in. outside diameter fitting 0.250 in. outside diameter tube	7.20 cm^2 304L 0.03 cm^2 braze alloy

Following proper sizing, each NATO-III test sample was thoroughly cleaned to component and subsystem specifications. For example, the tank wall and weld were cleaned to the exact procedures utilized by the tank vendor for final cleaning of the component before delivery to Philco. This process was then followed by the cleaning procedures utilized by Marconi after installation of tanks at the subsystem level but prior to subsystem conditioning. Similarly, Philco specifications for cleaning stainless steel parts were followed in the case of the manifold tubing and again, Marconi procedures were utilized to finish the cleaning which would be implemented at the subsystem level. Finally, Marconi after-braze subsystem cleaning procedures were followed in the case of the brazed joint.

NATO-III tank and weld sample final preparation included repeated ultrasonic cleanings in a detergent solution followed in each case by hot water rinses; ultrasonic cleaning in a weak isopropyl alcohol/deionized water solution; repeated ultrasonic cleaning in deionized water and, finally, nitrogen drying. Similarly, manifold tube sample cleaning included ultrasonic cleaning with a mild potassium hydroxide solution; two rinses with deionized water; a flush with isopropyl alcohol; nitrogen drying; ultrasonic cleaning in Freon precision cleaning agent and a nitrogen drying. Marconi limits NATO-III cleaning at the subsystem level to filtered deionized water and isopropyl alcohol, therefore all samples received a final water and alcohol rinse followed by a nitrogen drying.

F. Small Sample Test Results

Three sets of metal samples from three different propulsion subsystems, such as the one shown in Fig. 1, have been tested in the compatibility monitoring apparatus with military grade hydrazine at 48.9°C (120°F). Exposure times to hydrazine have been in the vicinity of 1000 hr; however, some tests have been terminated early because of problems with the apparatus such as the evolved gases pushing the column of mercury to the limit of the manometer capability.

Basic raw experimental data from the compatibility monitor, in terms of pressure increase in millimeters of mercury versus exposure time in hours for the set of four NATO-III metal samples, is shown in Fig. 6. This figure simply provides trend lines from the many data points actually gathered over the long hydrazine exposure periods. It should be noted that the wetted surface area of the four samples vary considerably, as indicated in Table II; consequently, the quantity of evolved gases must be determined and normalized to a unit area basis before this information is really meaningful.

In the compatibility monitor, the ratio of ullage volume to liquid volume is relatively large therefore not all of the evolved ammonia is dissolved in the liquid hydrazine as it would normally be in an actual propulsion subsystem (see Ref. 2). As a consequence, analysis of the constituents in the evolved gases is necessary to determine the exact dissociation reaction of hydrazine so that the total quantity of generated gases can be determined on a unit area basis. For example, the fraction of ammonia which dissociates (see page 6) was found to be approximately 0.02 for the stainless steel samples. The resulting normalized data is presented in Figs. 7 and 8 for the NATO-III samples where the quantity of gases evolved in millimoles/cm^2 of wetted area versus exposure time in hours is plotted for the four materials. The dashed portions of both Figs. 7 and 8 are in areas where data was extrapolated or utilized from several samples. For example, in order to plot the curve for 308L weld bead material in Fig. 7, the effects of both 301 and 304L, which had been tested separately and exposed for a shorter time interval, had to be subtracted from the complete weld sample data. Similar calculations were made for the 82 percent gold/18 percent nickel braze alloy curve of Fig. 8.

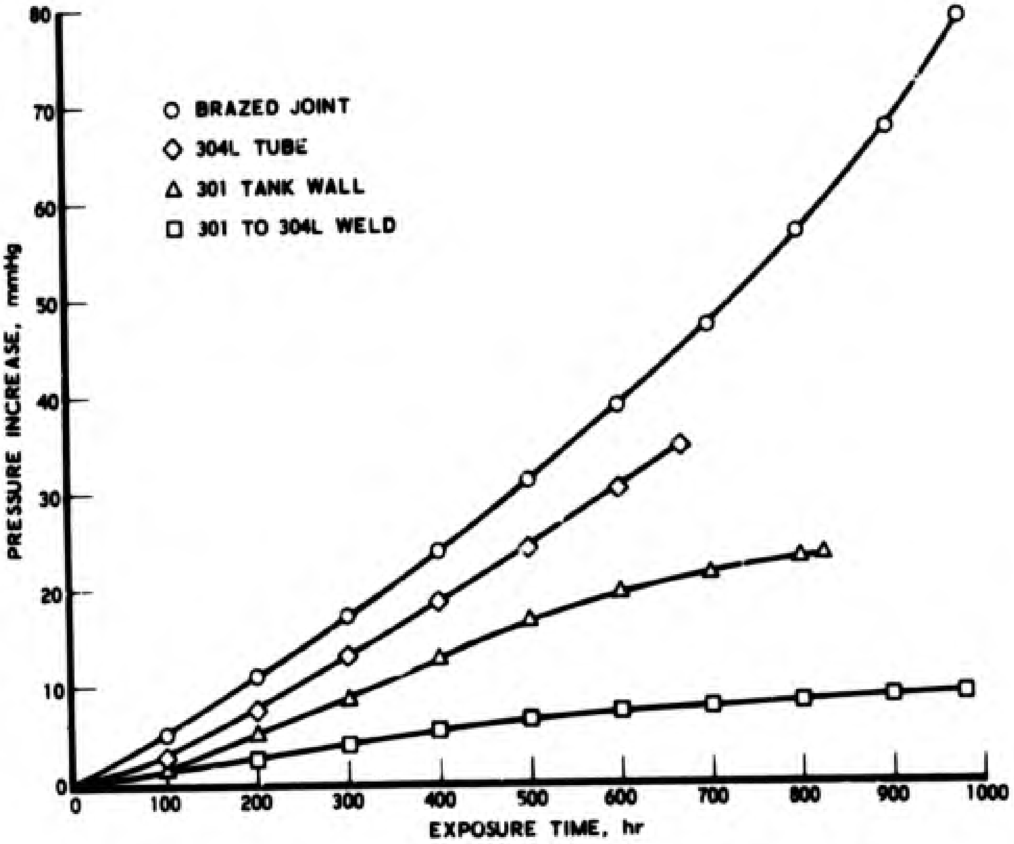

Fig. 6. Pressure Increase, NATO-III Test Samples

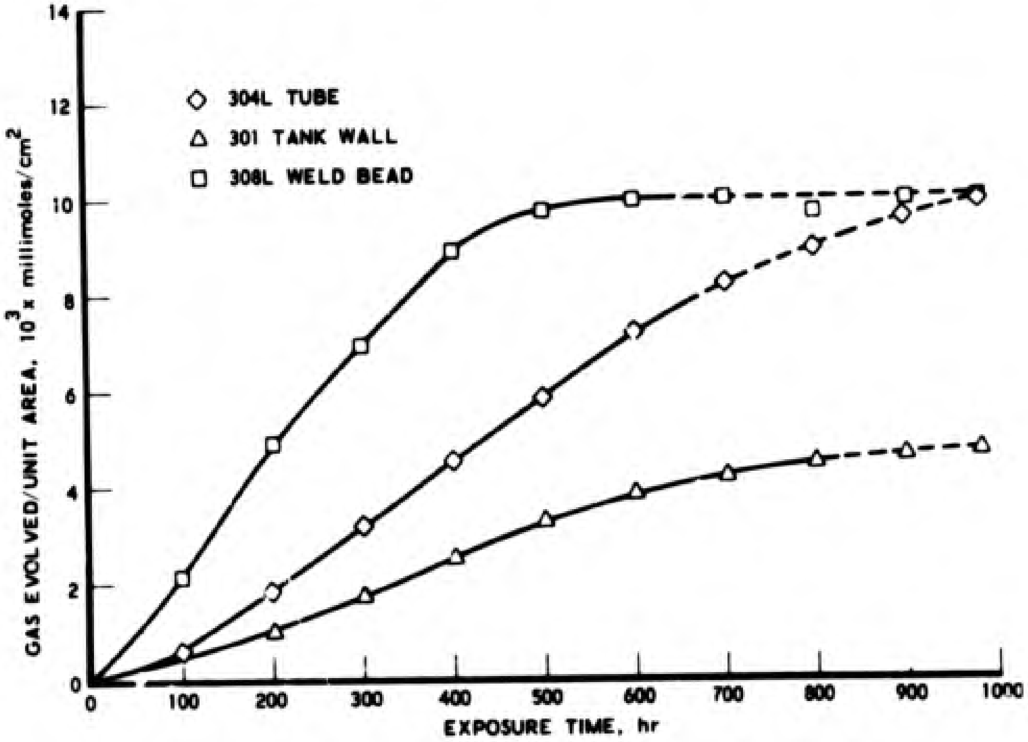

Fig. 7. Gas Evolved per Unit Area, NATO-III Steel Samples

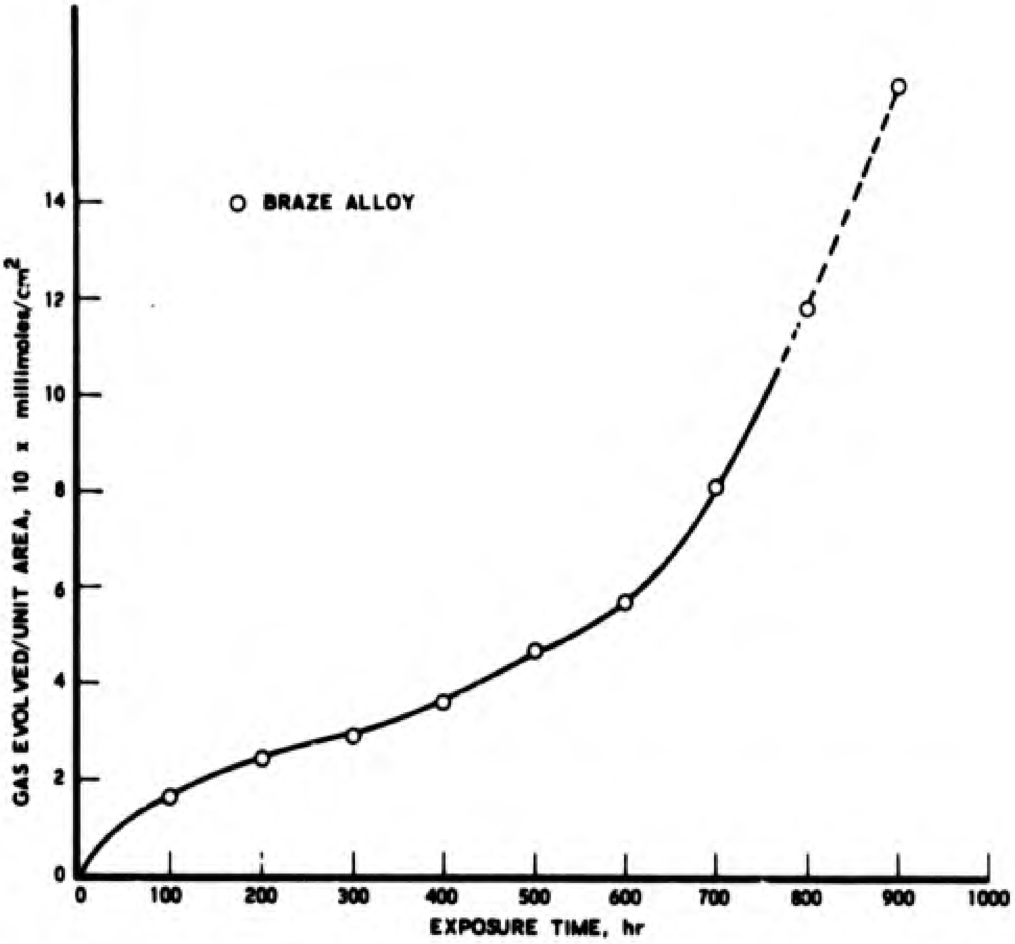

Fig. 8. Gas Evolved per Unit Area, NATO-III Braze Alloy Sample

The low initial gas evolution rates observed for test samples of the more critical portions of the NATO-III propulsion subsystem, such as tankage and manifolding, tend to indicate that they were reasonably free of consumable contaminants prior to hydrazine exposure. For example, although it is not perfectly clear because of the highly expanded time scale used on Fig. 7, these curves do not exhibit the initial characteristics of the Fig. 2 type curves which had been observed on earlier in-house metals compatibility studies reported in Ref. 1. It would therefore appear that the NATO-III piece part and subsystem cleaning procedures used on the metal test samples are probably adequate.

The removal of consumable type coatings from NATO-III test samples, as evidenced by the establishment of a reasonably stable minimum reaction rate, appeared to require as much as 800 hr of exposure to hydrazine at 48.9°C (120°F) as shown for example in Fig. 7. If complete removal of these consumables, that is, a thorough final cleaning, was the intended goal of the NATO-III conditioning process, then either the conditioning temperature or exposure time must be increased to accomplish it.

The compatibility of the braze alloy with hydrazine, relative to the other samples tested, is poor. Note the difference in gas generation rate scales in Figs. 7 and 8. The welded joint tested was considerably more compatible with hydrazine than the brazed joint. These results, however, were not unexpected in view of earlier efforts reporting the braze alloy to be catalytic (Ref. 3). The combination of a small total exposed braze alloy area and a large pressurant gas ullage volume in the actual NATO-III propulsion subsystem, however, make the adverse effects due to the application of brazed joints tolerable.

Figure 9 provides unit area normalized data for a set of three titanium alloy metal samples tested at 48.9°C (120°F). The samples included a portion of a tank wall, a piece of manifold tubing and a butt weld between two sections of tubing. The three samples of 6A14V titanium alloy were prepared and provided by Hughes Aircraft Company and are representative of the materials in a propulsion subsystem such as that on the Intelsat IV spacecraft.

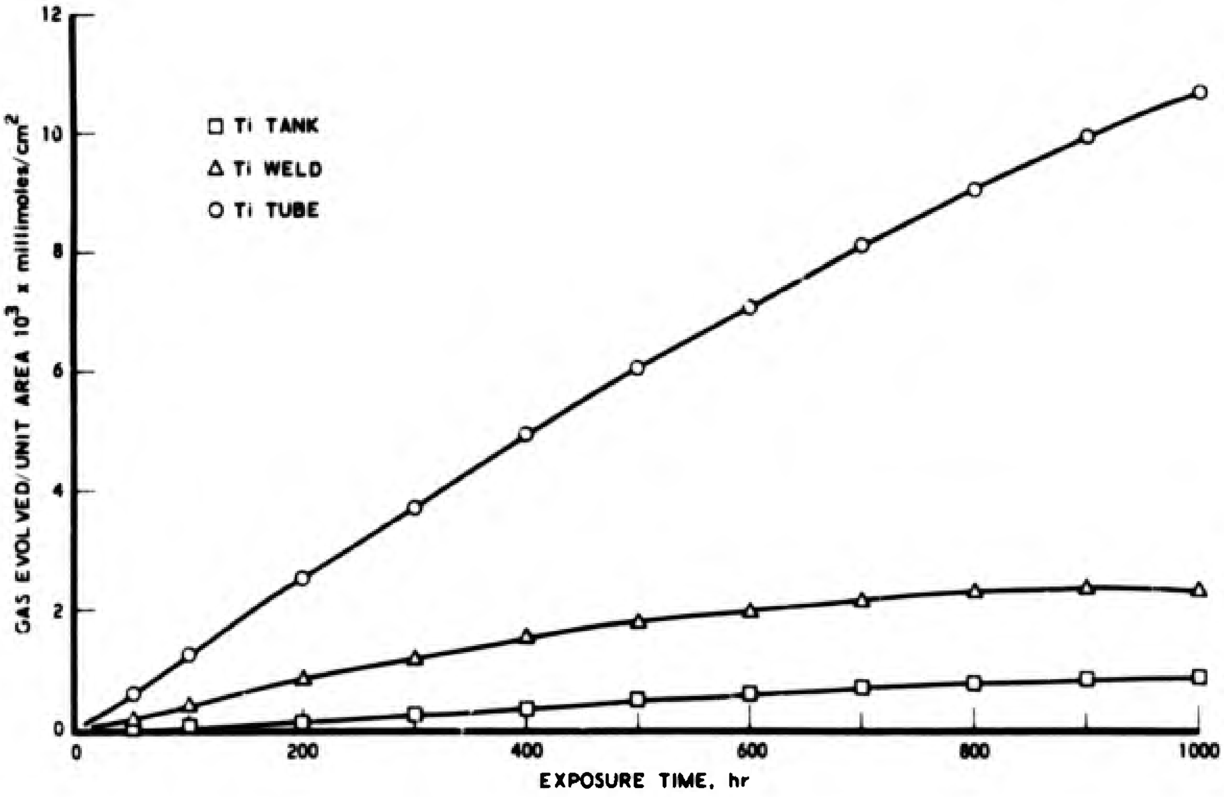

Fig. 9. Gas Evolved per Unit Area, Titanium Samples

The normalized data for all three samples was expected to provide about the same magnitude of gas evolution since the metal was essentially identical in each case. However, as shown in Fig. 9, the tube sample provided a gas generation rate approximately five times as high as the weld sample and about ten times as high as the tank sample. The reason for the high rate for the tube is unknown at this time. The tube test was repeated with a second sample and provided essentially the same results. No ammonia dissociation was found with the three titanium alloy samples.

Three of the comments made with regard to the NATO-III sample data on Fig. 7 are also valid for Fig. 9; for example, the cleaning procedures used to prepare test samples appear to be adequate, the butt weld appears to be very compatible with hydrazine and the removal of consumable type coatings appears to require as much as 800 hr of exposure to hydrazine at the test temperature. However, note on Table I that the Intelsat IV conditioning or passivation is implemented at 175°F for 24 hr which should go a long way towards removing virtually all consumable type coatings in a subsystem.

Aluminum alloys have also been employed on hydrazine propulsion subsystems; consequently, two typical samples were tested, again at 48.9°C (120°F). One sample was 2021-T81 aluminum alloy representative of tank wall material while the second sample was 6061 aluminum alloy brazed wire screen representative of surface tension type screen material. The wire screen is of 24 x 110 mesh dutch weave.

Normalized data for the aluminum samples is provided in Fig. 10. In the case of the wire screen the area is defined to be external screen area rather than the exact wetted area of all wires which make up the screen. Figure 10, like Figs. 7 and 9, also tends to indicate that the samples were adequately cleaned prior to hydrazine exposure. The screen sample tended to stabilize to a minimum reaction rate after about 400 hr but the tank sample had not fully stabilized after 1000 hr of testing. In the case of the screen material, the fraction of ammonia which dissociates was found to be 0.007. No dissociation was noted with the tank sample.

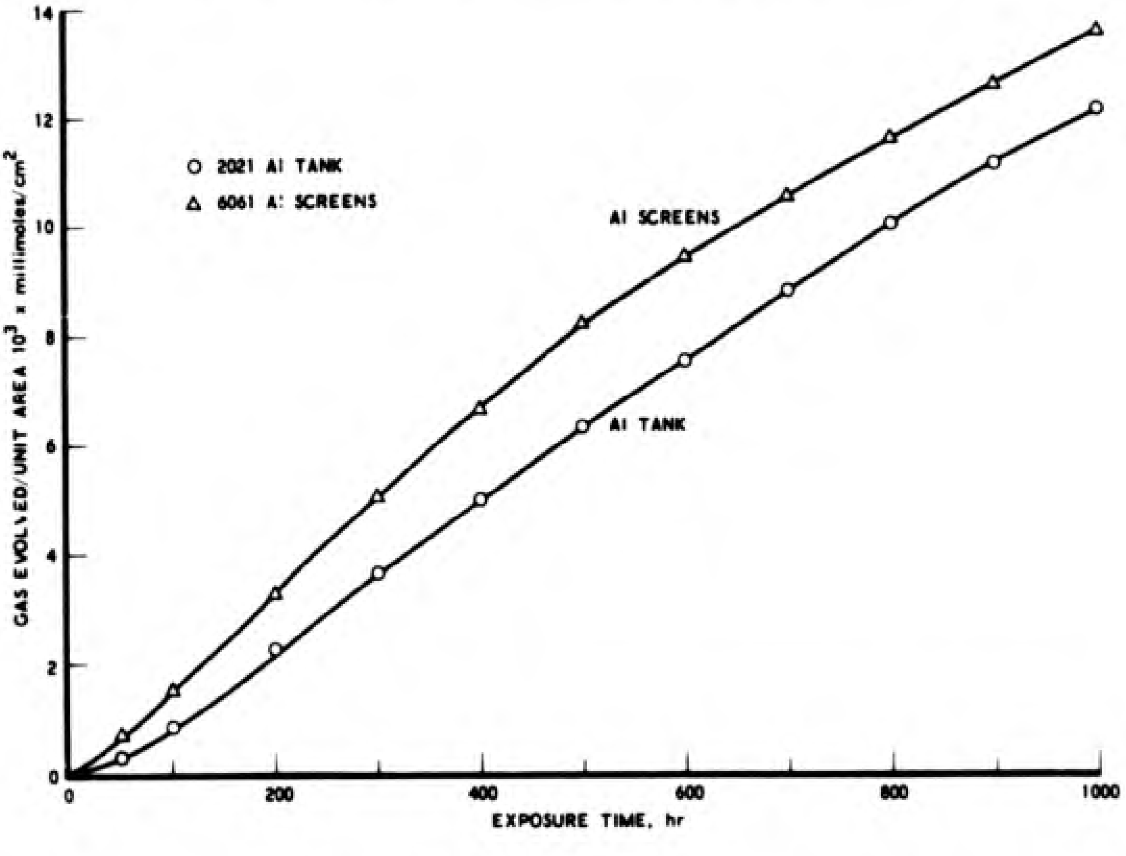

Fig. 10. Gas Evolved per Unit Area, Aluminum Samples

Additional information such as the relative compatibility of various metals with hydrazine at 120°F is readily available from the test data. For example, since the internal tank wall is by far the largest metal surface area wetted by hydrazine in a typical satellite propulsion subsystem, the relative compatibility of tank materials is of significant interest. Figure 11 is simply a replot of previously presented data from the three tank wall materials tested.

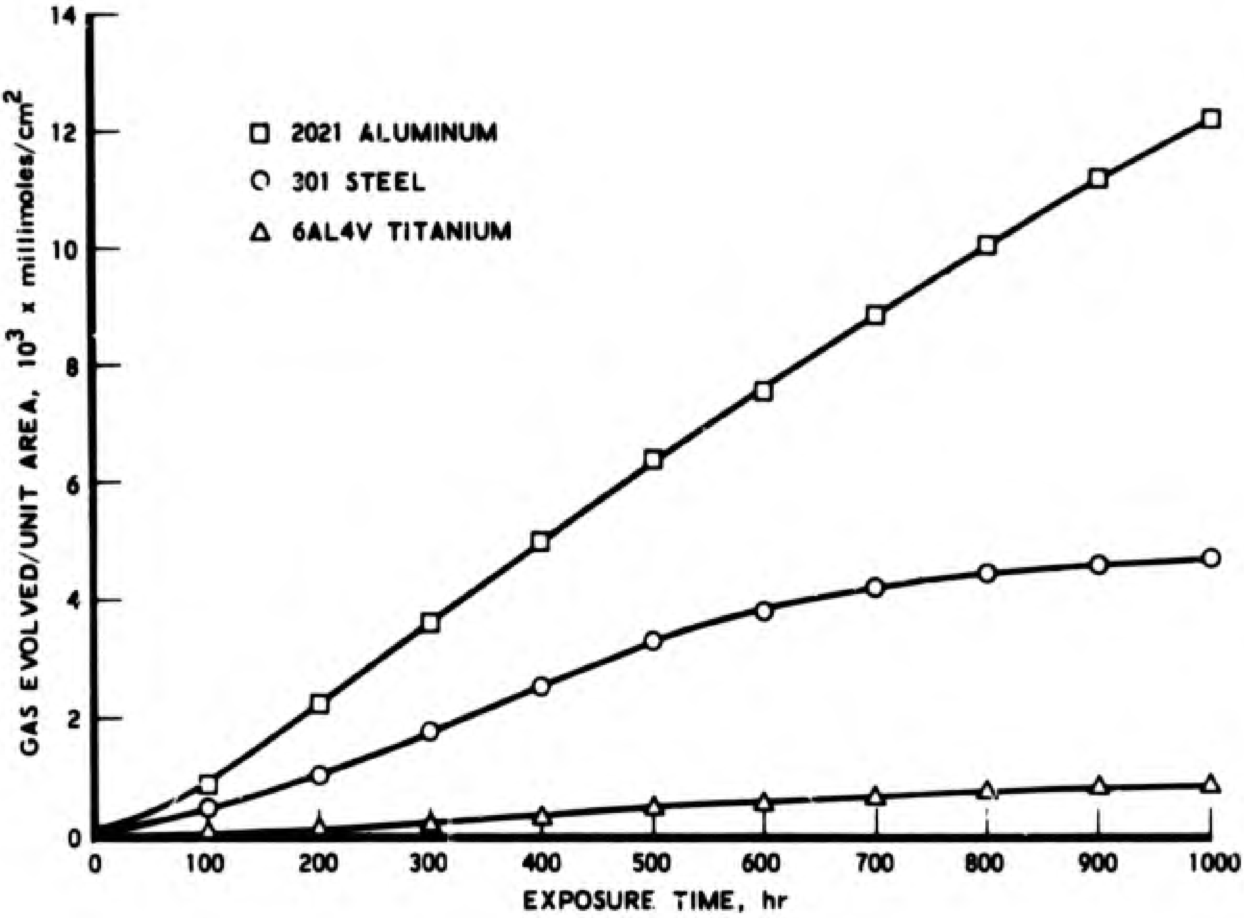

Fig. 11. Gas Evolved per Unit Area, Tank Metals

The tests completed to date are quite limited in scope. In general, only one sample of each material was tested in each original set and only at one temperature. As noted earlier an additional titanium tube sample was tested because of the unexpected initial results with the original sample. Similarly, additional braze joints were tested because of the relative incompatibility of the braze alloy and expected variability in braze alloy flow in the joint. The additional braze joint tests indicated far more variability in results than was even expected and also indicated that the original test sample was the most compatible of the three brazes tested. On the other hand, the results of the second titanium tube test were encouraging for they demonstrated satisfactory repeatability for samples made of a single material.

Still further efforts to verify repeatability of the present test results is needed, and tests at both higher and lower temperatures would be desirable.

G. Extrapolations to a Full Size Subsystem

Extrapolations of experimentally derived data from small scale tests to a full-scale propulsion subsystem were first made for the NATO-III spacecraft. These calculations were made for three purposes. The first and primary purpose was to predict what might occur during the conditioning of the actual subsystem in England as proposed by Marconi. The second purpose was to predict what the long-term pressure rise of the subsystem might be over the desired life of the spacecraft. The third and final purpose was to assist in the establishment of a reasonable success criterion for the first actual conditioning which was to be implemented on the qualification subsystem.

The experimentally derived gas evolution rates utilized for full-scale extrapolation calculations are shown in Table III. To predict what might be expected during the full-scale, 50°C, 10-hr conditioning as originally proposed, pressure rise calculations were made based upon a 95 percent propellant fill, also as proposed, and the initial 10 hr of test data shown in Table III. A similar calculation was made to estimate the volume of gases produced at standard conditions in a full-scale subsystem, but with a 100 percent fill, held at a fixed pressure. The above calculations included the effects of the solubility of ammonia in hydrazine as estimated from data presented in Refs. 2 and 4. It was found that essentially all of the evolved ammonia goes into solution in hydrazine and therefore does not contribute to a pressure rise or volume increase. Table IV provides the results of these calculations. A 95 percent fill (5 percent internal ullage volume), as expected, provides an insignificant pressure rise. Furthermore, it would not allow wetting of the upper portion of the tanks and much of the manifolding and would therefore not condition some of the critical surfaces of the subsystem. However, even with a 100 percent fill, the volume of gases evolved at standard conditions of temperature and pressure was found to be very small.

Table III. NATO-III Experimental Gas Evolution Rates

Temperature 120°F

Time Period	Material	10^3 x millimoles/cm^2
Initial 10 hr of experiment	301 SS	0.019
	304L SS	-----
	308L SS	0.294
	82 % Au, 18% Ni	25.2
Period of 10 hr near the end of the nominal 1000-hr experiment and representative of final gas evolution rates	301 SS	0.014
	304L SS	0.036
	308L SS	0.013
	82% Au, 18% Ni	60.00

Table IV. NATO-III Full-Scale Subsystem Extrapolations

Time Period with Hydrazine at 120°F (48.9°C)	Quantity of Generated Gas	Volume Increase at Standard Conditions	Ullage Pressure Rise at 120°F (48.9°C)
10-hr conditioning 95 percent propellant fill (initial 10 hr of experimental data)	0.240 millimole	1.1 cm^3	0.52 mm Hg
10-hr conditioning 100 percent propellant fill (initial 10 hr of experimental data)	0.265 millimole	1.2 cm^3	10.9 mm Hg
Useful life in orbit 60 percent propellant fill (typical rates near end of experiment)	0.910 mole	4.08 liters	182 mm Hg
Useful life in orbit 60 percent propellant fill (rates required to reach proof pressure)[***]	59 moles	264 liters	11788 mm Hg (228 psi)

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[*] 1.0 psi equals 51.7 mm Hg

[**] 100 cm^3 external ullage volume

[***] not based on experimentally derived rates

In order to predict the long-term pressure rise of the subsystem over the desired life of the spacecraft, calculations were made utilizing a 60 percent propellant fill and the final data shown on Table III. The results of these calculations are also provided on Table IV. This particular extrapolation is very conservative because the subsystem will not remain 60 percent full or at 120°F over the life of the spacecraft.

One final set of calculations was made for Table IV. Again utilizing a 60 percent propellant fill, but assuming the rate of gas evolution was such that the subsystem could reach proof pressure at the end of spacecraft life, estimates were made for the required quantity of generated gas and an equivalent volume increase at standard conditions of temperature and pressure. For the reasons specified above, these calculations are also very conservative. However, it should be noted that for this case only, experimentally developed rates were not utilized for the calculations. In fact, the quantity of gas generated to reach proof pressure would require a gas evolution rate 65 times greater than that found in the experiments with small NATO-III samples.

H. Success Criteria

Several passivations or conditionings implemented to date have been completed without benefit of a success criterion. However, even in those

Table V. NATO-III Conditioning Success Criteria*

PRESSURE RISE

Internal Ullage Volume, cm^3	Maximum Allowable Pressure Rise, mm Hg	External Ullage** Volume, cm^3	Maximum Allowable Pressure Rise, mm Hg
100	106.5	100	108.6
500	20.9	500	21.7
1000	10.0	1000	10.7
2000	4.8	2000	5.4
4000	2.2	4000	2.7

VOLUME

Maximum Allowable Volume Increase at Standard Pressure and Temperature: 12 cm^3

GAS EVOLUTION

Maximum Allowable Quantity of Evolved Gases: 2.70 mmol

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*Subsystem stabilized at 48.9°C (120°F) for 10 hr

**Completely filled subsystem

in Table V. There are several possible reasons for the differences. For example, note on Table III that no value was measured for 304L steel during the first 10 hr of the experiment while in actuality there probably was gas generation during this period. In retrospect, the lack of a measurable pressure rise at this early point in the experiment may have been due to a slight excess of silicone grease in the ball and socket joint on the leg of the compatibility monitor which held the empty container (see Appendix A). Similarly, the full-scale subsystem took many hours to heat up to 50°C; consequently, it would have been more realistic to use data from the second 10-hr period of the experiment for predictions.

A similar correlation was made with a Hughes titanium alloy propulsion subsystem; however, it necessitated extrapolating current experimental data to 175°F. This was accomplished by using additional data at 25°C and 40°C from earlier in-house efforts (Ref. 1) to establish a three-point temperature trend. The predicted pressure rise for the Hughes subsystem was calculated to be 0.5 psi while the actual rise during the 24-hr period at 175°F was reported to be about 0.2 psi.

cases where such a criterion was used, it was found to be so conservative that it would not tend to screen out relatively dirty or incompatible subsystems. Some of the reluctance to utilize a success criterion for the process stems from the practical difficulties inherent in actually making a measurement of pressure rise, volume change or quantity of evolved gases during the conditioning or passivation period. For example, the volume of a metal subsystem is sensitive to temperature; consequently, unless good thermal control is maintained during the stable, high temperature, conditioning period, it may be difficult to distinguish between thermally induced or real evolved gas effects in measuring either a pressure rise or volume increase.

A success criterion such as reaching proof pressure by the end of spacecraft life, while operationally adequate, would allow the acceptance of subsystems more than an order or two in magnitude less compatible or clean than any of the three commonly used metal sets tested. Analyses indicate that the long-term effects of the minimum reaction rates observed experimentally for these materials would be far below levels which would allow typical long-life subsystems to reach proof pressure. Because of this good material compatibility, the primary reason that a high initial reaction rate might be seen during a passivation or conditioning of a subsystem fabricated of these metals would be that the hardware had not been adequately cleaned. Much less activity than that representative of proof pressure levels is therefore highly preferred as an indicator that the metal is both clean and compatible thus minimizing the potential risk of contaminating the fuel which in turn could damage critical hardware such as propellant control valves. With this in mind, calculations were made to assist in the establishment of a reasonable success criterion for the first NATO-III full-scale conditioning attempt which was made on the qualification subsystem. The calculations encompassed several possible ways that evolved gases could be measured including the originally proposed technique of a pressure rise in an internal ullage. The results of the calculations for these options are presented in Table V. The quoted maximum values are based upon gas evolution rates ten times those found in the experimental portion of this effort to account for unknown variabilities in small-scale experimental results, material compatibility, cleaning procedures and implementation of the full-scale conditioning.

I. Correlation with Actual Conditioning Results

The first conditioning implemented on a NATO-III propulsion subsystem was completed on the qualification unit. The configuration at the time of conditioning was similar to Fig. 1 except that thrust chambers and propellant control valves had not been installed. The subsystem was completely filled with military grade hydrazine, heated in a special conditioning enclosure, then stabilized for 10 hr at 50°C (122°F). A special apparatus, developed by Marconi and mounted external to the conditioning enclosure, was used to measure a volume increase due to evolved gas while maintaining the subsystem at ambient pressure. Following the 10-hr hold, the unit was cooled, emptied, decontaminated and dried.

Marconi was able to measure 8 cm^3 of volume change due to evolved gas at the end of the 10-hr time period on the NATO-III qualification unit. This correlated fairly well with the predicted value of about 1.2 cm^3 shown in Table IV and is also within the recommended 12 cm^3 success criterion

III. CONCLUSIONS

The experiments completed on small metal samples, and the subsequent analyses extrapolating the results to full-scale propulsion subsystems, indicate that the process of passivation or conditioning is not of a mandatory nature for hydrazine fueled satellite propulsion subsystems. This was found to be so because (1) samples of commonly employed structural metals tested exhibited a relatively high degree of compatibility with the fuel and (2) contractor component and subsystem cleaning procedures used on these samples proved to be generally adequate. Indeed, if the metal surfaces in flight propulsion subsystems were as compatible as the small samples tested and were cleaned as thoroughly as these samples, then it would be rather obvious that conditioning or passivation would be unnecessary.

On the other hand, while not mandatory, there are at least two potential reasons why the practice of conditioning or passivation would be of significant benefit to hydrazine subsystem hardware; firstly, as a practical means to positively verify that the unit is indeed clean and fuel compatible and secondly, as a thorough final cleaning process. The first reason was found to be valid because the normal hydrazine decomposition reaction which occurs within a subsystem can be highly accelerated and its resulting effects magnified for short-term observation by the proper selection of a conditioning procedure. The second reason was also found to be valid because it is questionable that large components and subsystems can be cleaned as thoroughly as small laboratory samples and yet, almost all samples tested contained some unknown form of a consumable contaminant. It was not within the scope of the present effort, and therefore unknown at this time, whether adverse effects compromise fuel quality if the reaction consuming contaminants takes place within the flight subsystem rather than in the conditioning propellant which is discarded prior to flight.

IV. RECOMMENDATIONS

It is recommended that the process of conditioning or passivation of hydrazine propulsion subsystems be accorded wider consideration in the industry than it now receives; not so much as an absolute necessity (which it is not) or even as a final cleaning process, but rather as a practical subsystem level cleanliness and compatibility verification procedure to minimize potential adverse effects from unknown variabilities in compatibility of selected materials, fabrication techniques and cleaning procedures. A side benefit is some degree of final cleaning.

The process is of most value when employed on flight subsystems; however, if this is judged to be completely unreasonable, possibly because of some unique subsystem design feature, then it is recommended that at least one representative subsystem in a satellite program be so treated to at least improve confidence in the overall design and assembly approach.

It is further recommended that passivation or conditioning be implemented as a single-stage process using full strength military grade hydrazine. The subsystem should be filled to maximum capacity to wet all critical areas with fuel (no internal ullage) and should be configured without thruster propellant control valves in place to facilitate decontamination and drying after the process. Since elevated temperatures and extended time periods amplify the effects of gas evolution, a minimum temperature of 120°F and a time of 24 hr is recommended for the process. A success criterion capable of screening out unclean or incompatible units, rather than one based upon an unrelated event such as reaching proof pressure at end of life, is recommended.

Finally, additional efforts are recommended in several closely related areas. For example, further improvements in component and subsystem cleaning techniques would still be beneficial. Further experimental efforts are needed to verify the repeatability of present test results, to provide similar information at other temperatures such as 70°F and 170°F and to provide similar data for other metallic and non-metallic materials. Similarly, analyses of hydrazine before and after small-scale tests and also before and after full-scale passivations might help clarify any potential adverse effects to the fuel caused by the decomposition reaction in the presence of various materials and contaminants.

APPENDIX A
COMPATIBILITY MONITOR DESCRIPTION

The apparatus for monitoring the compatibility of propellants with materials, shown in Fig. A-1, is of all-Pyrex glass construction with short capillary connecting tubes joined by fusion. The apparatus consists of two detachable sample containers A and B attached to two sides of a small mercury manometer, C; through ball and socket joints D and E. The sample containers are also interconnected and separated by two capillary stopcocks F and G. A third capillary stopcock, H, connects F and G through a tee. Another ball and socket joint I is added for convenience to facilitate evacuation of the sample containers and manometer and for easy attachment to the gas analyzer. The capillary stopcocks and ball and socket joints are sparingly lubricated with silicone grease. The sample containers are of 28 millimeter (mm) outside diameter and 20 mm high with a capacity of about 10 milliliters (ml), and this volume is determined by using water. All the interconnecting capillary volumes below stopcocks F and G, and the volume above the mercury in the manometer, are calibrated by mercury displacement. The apparatus, assembled with the test specimen as shown in the photograph of Fig. 4, is immersed to above stopcocks F and G in a thermostated water bath to provide the desired thermal environment. In this manner, undesirable side effects such as hydrazine vapor pressure, glass wall reactions, mercury reacting with hydrazine vapor, etc., are all cancelled out and only the reaction of interest between the metal sample and liquid hydrazine is isolated for observation and monitoring.

The water bath is temperature controlled by thermostated electric heaters to ± 0.01°C. Two motor-driven stirrers are utilized to maintain a uniform temperature in the bath. A microslide cathetometer is used to read the meniscus level in the mercury manometer to an accuracy of ± 0.01 mm. Figure 4 is a photograph providing an overall view of the compatibility monitors with four samples simultaneously under test, immersed in the water bath.

Prior to implementing a test run, the glass apparatus in Fig. A-1 is thoroughly cleaned, evacuated and leak tested. A clean sample to be tested is placed in container B of Fig. A-1 and evacuated for 20 min to remove any

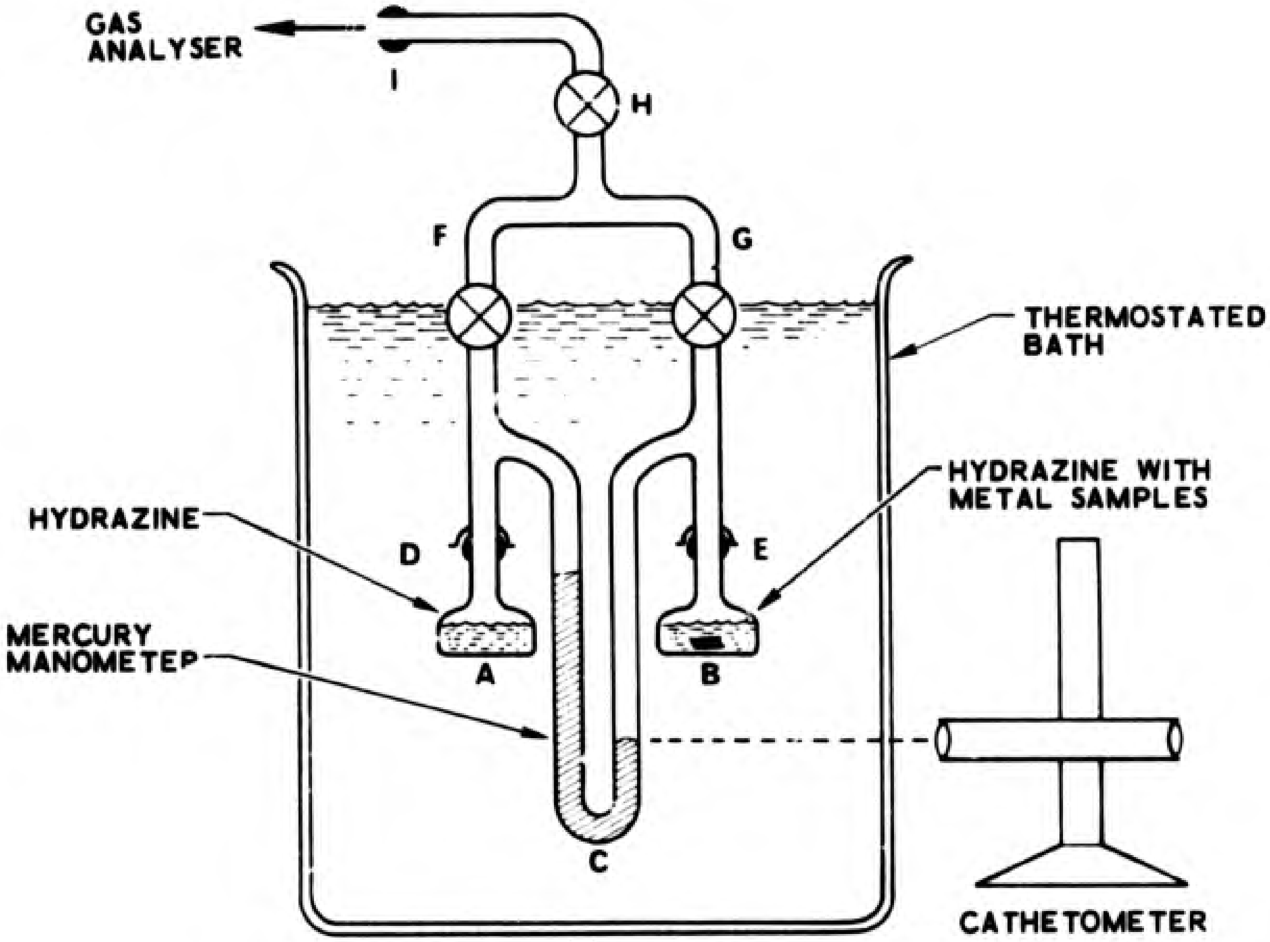

Fig. A-1. Compatibility Monitor

residual solvents. The vacuum is broken with argon and enough military grade hydrazine is loaded to cover the sample. The actual amount of hydrazine in the container is determined by weighing. The container with the sample is then attached to the apparatus at E on Fig. A-1 and a second container with only hydrazine is attached to D. The amount of propellant in each of the two containers is adjusted so that the ullage above the liquid on both sides of the manometer is the same.

The assembled apparatus is attached to a vacuum line through 1 on Fig. A-1, and the hydrazine is degased as follows. First the hydrazine on both sides of the manometer is frozen with liquid nitrogen and the ullage areas evacuated for 5 min to remove air. The hydrazine is then allowed to melt and warm up to room temperature. While the hydrazine is still partially frozen, the apparatus is evacuated occasionally to remove trapped gases. When the hydrazine is completely melted, the apparatus is agitated and again evacuated twice, for about 10 sec each time, to remove all the gas trapped as bubbles in the hydrazine. The apparatus is then removed from the vacuum line and is ready for immersion in the thermostatically controlled water bath.

Initial readings of the manometer and time are recorded following water immersion to establish a base for the long-term test. Mercury levels in the manometer are read frequently during the first hour until a definite trend is established. Readings are then taken at appropriate time intervals as required by the particular sample being investigated. The rate of gas evolution, as indicated by the pressure difference in the manometer, is monitored until a definite rate is established or until the end of a prescribed time period. The apparatus is removed from the thermostat and attached to a gas analyzer where the evolved gases are extracted and analyzed.

APPENDIX B
GAS ANALYZER DESCRIPTION

A sketch of the gas analysis equipment is shown in Fig. B-1. The gas analyzer consists of five parts: a manometer, Q; a series of calibrated volumes, U; a tubular palladium hydrogen diffuser, M; a gas reservoir, Y; and a U-tube ammonia trap, J. All the parts are interconnected by capillary tubing, capillary ball and socket joints, and capillary stopcocks. The volumes of interconnecting tubes and stopcocks have been calibrated. The manometer can be evacuated from both sides through O and N; it is capable of measuring a maximum of one atmosphere of pressure. The series of calibrated volumes below calibration mark W consists of a 10 ml microburette connected to four interconnected bulbs with precisely calibrated volumes of 20, 50, 100 and 200 ml. These bulbs are calibrated by mercury displacement. The 200 ml bulb is connected to a mercury leveling bulb, S. The tubular hydrogen diffuser is 88 mm in diameter and 120 mm long joined to the rest of the apparatus by two Kovar seals. A platinum heating coil is attached to the exterior of the palladium tube. The gas reservoir has a capacity of 600 ml. One end of the reservoir is connected to a mercury leveling bulb, X, and the other to the palladium tube through the capillary stopcock L, and to the trap J through the capillary stopcock K. The trap J is a U-tube cooled with liquid N_2 to freeze out the condensable evolved gases, that is NH_3 and N_2H_4.

The procedure for extracting and analyzing the evolved gases from the compatibility monitoring apparatus is as follows. The apparatus is attached to J and I. The entire apparatus is evacuated by opening stopcocks H, K, L and O to the vacuum pump. The hydrazine in containers A and B is frozen with liquid nitrogen and trap J is cooled with liquid nitrogen. The mercury levels in U and Y are brought up to the calibration marks W and Z. Stopcocks N and L are closed, and stopcock G is opened. The collected gases in B are passed through trap J and expanded into Y by slowly lowering the leveling bulb, X. Stopcocks K and G are closed, and the liquid nitrogen is removed from B. Stopcock L is opened, and the gases are forced from Y into the calibrated volumes U by raising X and lowering S; then, stopcock L is closed and the mercury in Y is again brought up to the mark Z. When the hydrazine in B is almost completely melted, stopcocks G and K are opened and a second extraction is made by repeating the foregoing process. Finally, with L open and K closed and the mercury level in Y and Z, the mercury level in U is brought to W or another appropriate calibrated mark in U. The amount of extracted gas is obtained by measuring P, V and T and by using the ideal gas equation $PV = nRT$ where P is pressure, V is volume, n is number of moles, R is ideal gas constant, and T is temperature in $^{\circ}K$. The heater on M is turned on and the gases are passed twice between

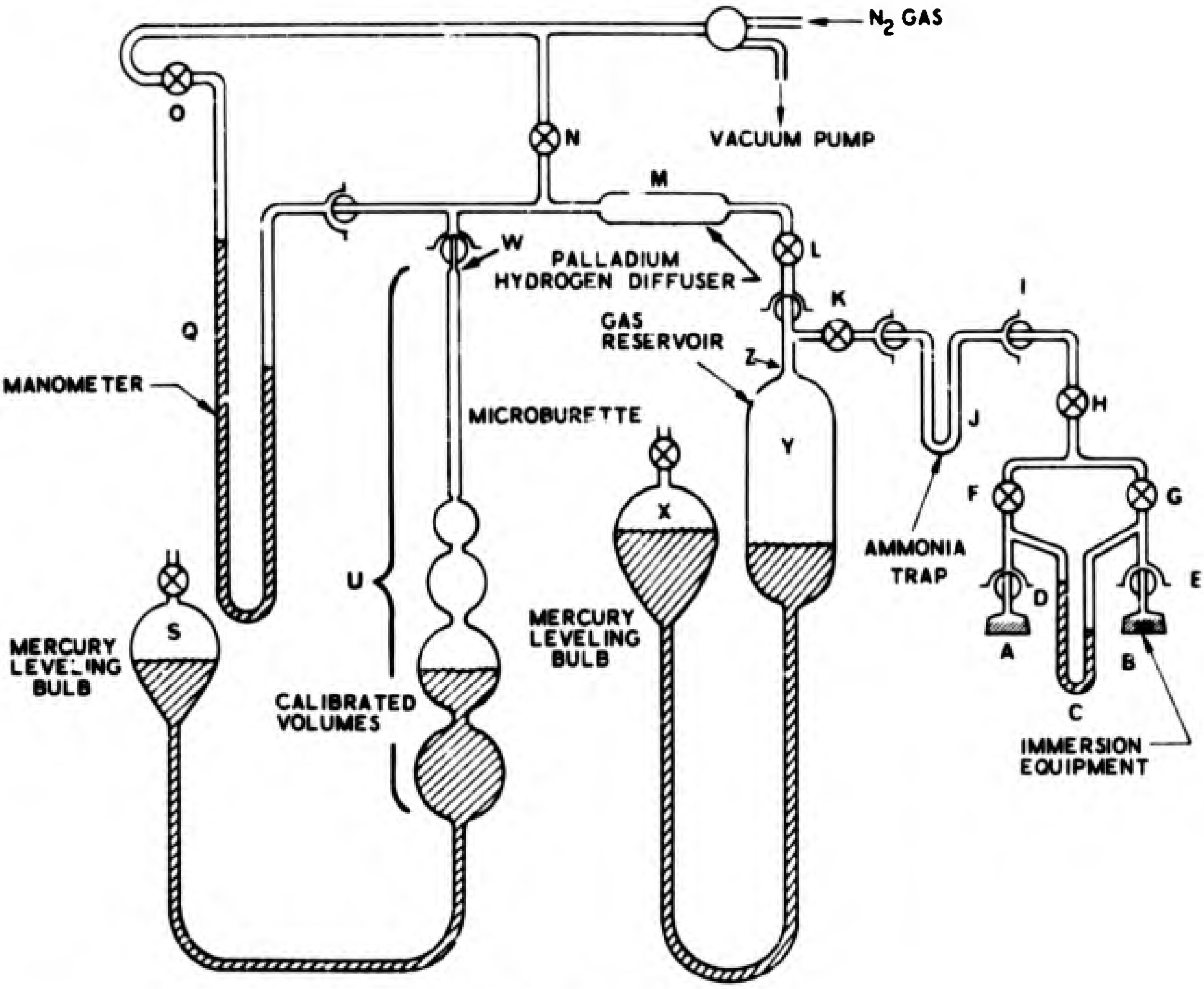

Fig. B-1. Gas Analyzer

U and Y. After the heater is turned off and the remaining gas has returned to thermal equilibrium, P, V and T measurements are made again to determine the number of moles of remaining gas. The difference between the initial and final amounts of gas gives the amount of hydrogen. The remaining number of moles of gas is the amount of nitrogen generated. The entire procedure is repeated for the extraction of gases from container A, the tare side, and the amount of gas generated is subtracted from that of the sample side to obtain the actual amount generated due to the sample alone.

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