[redacted]

SPACE ENVIRONMENTAL EFFECTS ON SEVERAL POLYMERIC AND METALLIC MATERIALS

by

John P. Mugler, Jr.

NASA Langley Research Center
Langley Station, Hampton, Va.

To be presented at the 11th National Symposium of the
Society of Aerospace Material and Process Engineers

[redacted]

St. Louis, Missouri
April 19-21, 1967

SPACE ENVIRONMENTAL EFFECTS ON SEVERAL POLYMERIC AND METALLIC MATERIALS

by

John P. Mugler, Jr.

NASA Langley Research Center
Langley Station, Hampton, Va.

ABSTRACT

The NASA Langley Research Center is engaged in continuing research on space environmental effects on materials. In this paper several current programs are reviewed. The programs involve space environmental effects on some polymeric materials and the adhesion of metals in ultrahigh vacuum.

1. INTRODUCTION

The NASA Langley Research Center is engaged in continuing research on space environmental effects on materials. Experimental and theoretical programs are being conducted on the effects of both natural and induced space environments on a variety of spacecraft materials. It is the purpose of this paper to review several current experimental programs which involve space environmental effects on some polymeric materials and the adhesion of metals in the ultrahigh vacuum of space.

2. SPACE ENVIRONMENTAL EFFECTS ON POLYMERIC MATERIALS

Polymers find widespread use in space and there is continuing practical interest in defining the behavior of these materials in the space environment. Therefore a wide variety of polymeric materials are being studied in Langley Research Center space environmental effects programs. In this section of the paper a current program will be reviewed in which several filled elastomers are being investigated and some exploratory tests on nylon parachute material will be reported.

2.1 Filled Elastomers

Frequently elastomers are filled with other materials to improve their performance in a given application, and there is concern that exposure of filled elastomers to the space environment, particularly for long periods of time, will cause degradation in critical materials properties. Solid-propellant fuels and heat-shield materials are two types of filled elastomers that are often used in space systems, and a program is underway to study the space environmental effects on these two types of materials.

As a first step in this program the rate at which gas is given off, or outgassed, in vacuum from the materials was determined. Outgassing rates for several solid-propellant fuels and for one heat-shield material were measured at vacuum levels from 10^{-5} to 10^{-9} torr and at vacuum exposure times to about 500 hours. This portion of the program is essentially complete and the results are currently being published (e.g., NASA TN D-3790). Therefore, the data will not be duplicated here. The results from these measurements show that solid-propellant fuels and heat-shield material continue to outgas at relatively high rates even after extended vacuum exposure.

Next, vacuum weight loss measurements were made to determine what the outgassing rates represented in terms of actual mass lost. Representative results from these measurements for two materials are presented herein. The first material is a composite solid-propellant fuel which has PBAA (polybutadiene acrylic acid) as the binder and ammonium perchlorate as the oxidizer. The second material was a silicone elastomer heat-shield material (Langley Research Center #E4A1). It consists of an elastomeric resin with silicon echospheres, phenolic microballons, and microquartz fibers added.

[redacted]

The weight loss measurements were made by placing a sample on the pan of a vacuum microbalance exposing five-sixths of the sample surface area to the vacuum. For the solid-propellant fuel the sample was a 2-cm cube and had an initial weight of 13.27 grams; for the heat-shield material it was a 2.54-cm cube and had an initial weight of 10.32 grams. The trapped diffusion pumped system was evacuated to a pressure of 10^{-5} to 10^{-6} torr and the weight of the sample was recorded continuously. The test duration was 270 hours for the propellant and 348 hours for the heat-shield material. The temperature of the glass bell jar enclosing the vacuum balance and sample was measured during the tests and varied from about 71° F to 78° F. The minimum weight change the balance can record is about 0.5 milligram, thus the precision of the sample weight measurements is about 0.005% of the original weight. The measured data are corrected for buoyancy effects.

The measured weight loss data for these two materials are presented in figure 1 as the weight change in percent of original weight as a function of vacuum exposure time. Also shown for reference on figure 1 are data for silicone rubber (Dow-Corning Silastic silicone rubber #916-4-480, reference 1) which is similar to the unfilled elastomer used in the other two materials. The percent of original weight lost during vacuum exposure was small for all of the materials, ranging from about 0.17 percent for the solid-propellant fuel at 270 hours to 1.03 percent for the heat-shield material at 348 hours. For both the solid-propellant fuel and the heat-shield material the weight loss rate was higher initially than after 25 or 50 hours of exposure; however, both materials continued to lose weight throughout the vacuum exposure. After several hundred hours the heat-shield material tended to seek a loss rate of about 0.1 percent per hundred hours and the solid-propellant fuel a rate of about 0.05 percent per hundred hours. Reference 1 indicated that the silicone rubber lost all of its weight during the first 10 hours of vacuum exposure. However, the small sample used in that study may have precluded the detection of small weight loss rates.

Mass spectrometric measurements were also made to identify the types of gases being evolved from these two materials during vacuum exposure. These measurements were made by placing the analyzer of a time-of-flight mass spectrometer and a sample in the vacuum chamber and evacuating the chamber to about 10^{-8} to 10^{-9} torr with a trapped diffusion pumped system. Mass spectrograms were then taken periodically for vacuum exposure times to about 500 hours. The samples used were slabs about 10 cm square and 1 cm thick and all measurements were made at ambient temperature.

Mass spectrograms are presented in figure 2 for the two materials as the ion current from the analyzer for each of the peaks at different mass-to-charge ratios. In figure 2(a) for the solid-propellant fuel after 180 hours in vacuum the mass spectrogram shows a variety of outgassing products. The peaks at a mass-to-charge ratio of 18 and 28 indicate that water and nitrogen are being released; however, they constitute only a small percentage of the outgassed products. These two peaks are probably from atmospheric air which was either trapped in the propellant during mixing or absorbed during storage. The other peaks at mass-to-charge ratios up to 126 are characteristic of hydrocarbons from principal material constituents and are probably coming from the cracking pattern of some parent hydrocarbon. Analysis of the mass spectrograms over the entire exposure time shows that the 18 and 28 peaks from the atmospheric gases predominate during the first 15 hours of vacuum exposure. However, as the vacuum exposure increases the 18 and 28 peaks continually diminish and the hydrocarbon peaks become and remain predominant for the remainder of the vacuum exposure. In figure 2(b) for the heat-shield material after 173 hours in vacuum the mass spectrogram indicates a picture similar to that for the propellant, i.e., the 18 and 28 peaks (again probably from atmospheric gases) appear but the other peaks predominate. The lower level of peaks above the background in figure 2(b) is because the total pressure in the chamber was about a factor of 10 less than for figure 2(a).

The mass spectrometric measurements showing continuous evolution of a variety of gases coupled with the measured losses in weight raise a question about the vacuum stability of these two materials. In these tests the source of the evolved gas could not be determined. But that may not be pertinent since loss from any source can change materials properties, and it appears likely that continued loss during extended exposure would cause changes.

As the next step in the program it was decided to measure directly any changes in key materials properties due to environmental exposure. For the solid-propellant fuels, apparatus has been constructed to measure the tensile strength of samples in vacuum subsequent to vacuum exposures of varying duration. In situ tensile testing will eliminate uncertainties associated with the effects of readsorption of gases on the samples if they are reexposed to the atmosphere for tensile testing. Tests using this apparatus are currently in progress. For the heat-shield materials, apparatus is being constructed so that samples can be removed from the vacuum chamber after exposures of varying duration and transferred to an arc jet while still under vacuum, can be repressurized with gases representative of various planetary atmospheres, and can then be injected into the high-enthalpy stream to determine the thermal performance.

2.2 Nylon Parachute Material

Many spacecraft use parachutes as the deceleration and landing system for the reentry capsule. Thus a question is raised as to the effects of the vacuum soak and subsequent atmospheric reexposure on the tensile strength of the parachute material. We have conducted some exploratory tests for nylon parachute material to determine these effects. Nylon parachute material samples were exposed to vacuum below 1×10^{-6} torr for approximately 1 month. After removal from vacuum the samples were exposed to air with 60-percent relative humidity. Samples were then tensile tested to their ultimate strength as a function of time after removal from vacuum. These results were compared to results from a group of control samples to determine the magnitude of the effects.

The samples were cut from a standard nylon personnel parachute canopy. The material conforms to Mil. Spec. MIL-C-7020, type 1, and was manufactured on September 18, 1963. It weighed approximately 1.1 ounces per square yard and had an ultimate tensile strength rating by the manufacturer of 40 pounds per inch of width. The samples were made by cutting rectangular strips 9 inches long and approximately $1\frac{1}{4}$ inches wide and then raveling to 1-inch width by removing approximately the same number of threads from each side. This procedure is in accordance with Fed. Spec. CCC-T-1911, method 5104. All samples were cut from the same sheet of cloth.

The samples were hung inside a stainless steel bell jar vacuum chamber and the system was evacuated with a trapped diffusion pump system to below 1×10^{-6} torr. After 10 days of vacuum exposure a malfunction caused the system to be shutdown. During this shutdown the chamber returned to ambient pressure for about 5 minutes and the samples were exposed to ambient air at 75° F and 60-percent relative humidity. The pumping was then resumed and the vacuum was maintained for 27 consecutive days below 1×10^{-6} torr. The temperature of the bell jar during tests was about 75° F.

Upon completion of the vacuum exposure the samples were stored in air at atmospheric pressure and at 75° F and 60-percent relative humidity. Tensile testing was begun shortly after completion of the vacuum exposure. A standard tensile testing machine was used at a cross head speed of 12 inches per minute. The sample gauge length was 5 inches. Samples were tested at intervals of a few minutes for the first 40 minutes after vacuum exposure. Then 5 additional samples were tested starting at about 60 minutes after vacuum exposure and the last 5 samples were tested starting at about 24 hours. All tests were conducted at ambient conditions of 75° F and 60-percent relative humidity.

Control samples, from the sheet of cloth from which the vacuum samples were cut, were prepared as previously described. A group of 5 control samples were tested at ambient conditions on the day the vacuum test was started. The average ultimate strength of these samples was 48.6 pounds per inch. A second group of 5 control samples was placed on the shelf, was stored at ambient conditions until the day that the vacuum tests were completed, and was then tested. The average ultimate strength of these samples was 47.6 pounds per inch. The average ultimate strength of all 10 control samples, 48.1 pounds per inch, was used as the reference in computing the percent change in ultimate strength of the vacuum exposed samples.

The results from these tests are presented in figure 3 as the ultimate strength change in percent of original strength versus time out of vacuum. The data at 24 hours after removal from vacuum have not been included because they did not vary significantly from the data taken at about 60 minutes. Figure 3 indicates that long-term vacuum soak followed by subsequent exposure to humid air causes increasing degradation to occur reaching a value of about 10 percent about 30 minutes after removal from vacuum. With further increases in time to about 40 minutes the material appeared to regain a substantial amount of the strength lost. However, at 60 minutes and at 24 hours after removal from vacuum the material still suffered about an 8-percent reduction in ultimate strength. It is noteworthy that although the degradation due to vacuum exposure at first appeared to be very small, the vacuum had rendered the nylon material susceptible to substantially greater degradation at a later time.

3. ADHESION OF METALS

It has been demonstrated in laboratory ultrahigh vacuum systems that clean metal surfaces will adhere. When it is recognized then that in the ultrahigh vacuum of deep space several mechanisms act to clean exposed surfaces (i.e., evaporation, erosion by energetic particles, and abrasion), it becomes apparent that the adhesion of clean metal surfaces may present a critical problem in the performance of space systems. A program on the adhesion of materials is underway at the Langley Research Center in which the adhesion of spacecraft metals is being defined and adhesion phenomena are being elucidated. Since surface cleanliness is an important parameter in adhesion phenomena, also included in this program is the development of techniques for measuring the degree of surface cleanliness of materials and a study of surface cleaning techniques. In this paper we will present selected results from a recent contract study performed by the National Research Corporation (ref. 2) which is a part of the overall program.

One of the objectives of this study was to determine if abrasion between mating metal parts, such as might be experienced during service in space, would disrupt the contaminating films and cause adhesion. In the atmosphere when metals are abraded and then separated, the disrupted oxide and contaminated films are reconstituted almost instantaneously because the impingement rate of the atmospheric gas is very high. In the ultrahigh vacuum of space, however, this is not the case. The gas impingement rate is very low and it would take days or even months before the oxide and contaminant films could re-form. In the meantime the clean metal surfaces are exposed and, if brought into contact, may adhere. In order to simulate possible space service conditions in this study the samples were subjected to an abrasion treatment in vacuum followed by adhesion tests in vacuum.

A sketch of the experimental apparatus is shown in figure 4. The chamber was a 16-inch-diameter stainless-steel cylindrical vessel enclosed at both ends with seal plates supporting the loading stages. Optical and instrumentation ports were provided around the chamber wall. The chamber was evacuated with a trapped diffusion pumping system. After bake-out to 400° C, the system attained a pressure of 3×10^{-10} torr with the full experimental assembly. For tests with the samples at elevated temperatures a resistance wound platinum wire furnace was installed surrounding the samples.

Rotary and vertical forces were imparted to the samples by the upper and lower loading assemblies. In the upper assembly the rotatable shaft vertically penetrated through a low conductance bearing seal in the upper flange plate. Exterior to the chamber the shaft was enclosed in a diffusion pumped cylindrical housing to minimize gas leakage into the test volume through the bearing seal. The free end of the shaft was coupled to an electric motor which could drive the shaft at about 20 rpm under compressive loads up to 100 pounds. For compressive loads greater than 100 pounds the shaft was manually rotated at about the same speed. In the lower assembly a manual screw ram drive permitted vertical shaft translation into the test volume through a bellows seal. The maximum ram force was 1000 pounds. The force imposed on the samples was monitored by a load cell attached to the lower shaft. The upper and lower loading shafts were rigidly aligned in the vacuum chamber by a guide fixture (not shown).

Sample couples were fabricated of copper, titanium, and tungsten. The upper sample was a hemisphere-cylinder with a nose radius of 13/16 inch. The lower sample was a $1\frac{3}{8}$-inch-diameter cylinder with the mating surface an inverted cone with a half-angle of 71.5°. Thus, when the samples were brought into contact the area of contact was a narrow radial band. After machining, the sample test surfaces were ground and polished, heat treated, and then given a final diamond polish. The samples were then ultrasonically cleaned. After cleaning the samples were stored in a dessicator until used. When the samples were being installed in the test volume special care was taken to keep them clean.

Tests were conducted by evacuating the system, with a pair of like samples installed, to a pressure of about 5×10^{-10} torr at room temperature. The samples were then subjected to an abrasion treatment. The abrasion method used was to rotate the upper sample at about 20 rpm while in contact with the stationary lower sample for a fixed period of time under load. For the results presented here the loads and times, respectively, were 500 pounds and 3 minutes for titanium; 500 pounds and 1 minute for tungsten; and 20 pounds and 10 minutes for copper. The effects of variations in load during abrasion and length of time of abrasion were also studied and the results showed that significant adhesion took place for loads as low as 20 pounds and times of about a minute. Immediately following the abrasion treatment adhesion tests were conducted according to the following procedure: (1) With the samples stationary, a compressive load of 1000 pounds was applied for 5 minutes at room temperature. (2) Upon release of the compressive force, the residual shear torque required to rotate the upper hemispherical sample relative to the lower sample was measured with a torqueometer attached to the upper shaft. (3) The test was repeated with the samples at temperatures up to 500° C.

The results from these tests are presented in figure 5 as residual shear torque versus sample temperature. For titanium essentially no adhesion was detected until about 150° C. With further increases in temperature the adhesion increased substantially, as indicated by the large increase in residual shear torque. For both tungsten and copper significant adhesion was detected at room temperature. For tungsten, however, increases in temperature to 500° C caused only slight increases in adhesion. In contrast, for copper the adhesion was extremely sensitive to temperature, so much so that the residual shear torque exceeded the limit of measurement of 300 in-lb above about 200° C.

These results indicate that substantial adhesion forces may be generated in engineering metals in deep space during normal service. The results also suggest that the adhesion of metals is related to properties of the oxide film as well as the mechanical properties of the bulk material. The titanium samples were the softest of the three materials tested. However, the copper and tungsten, which have lower oxide bond energies, showed a much greater tendency to adhere at ambient temperature than titanium which has a tenacious oxide that is difficult to remove. On the other hand for copper and tungsten the softer copper gave higher adhesion forces than the harder tungsten. At elevated temperatures reduction in the yield strength for copper and titanium caused increased plastic flow in this load-temperature range, and thus the adhesion increased. For tungsten, which has a very high melting point, very little plastic flow was induced and thus the adhesion was rather insensitive to temperature in this load-temperature range.

4. CONCLUDING REMARKS

Several current space environmental effects programs at the Langley Research Center have been reviewed. Selected results from a program on the space environmental effects on polymeric materials indicate that: (1) several filled elastomers evolve gases continuously during vacuum exposures of hundreds of hours, further, this gas evolution results in weight losses of about 1 percent or less; and (2) long-term vacuum soak of nylon parachute material causes reductions in tensile strength as high as 10 percent on reexposure to the atmosphere. Selected results from a program on the adhesion of metals in ultrahigh vacuum indicates that copper, titanium, and tungsten may adhere in space during service as a result of abrasion between mating parts.

REFERENCES

1. Rivera, Michael, et al.: The Low-Pressure Gas Desorption of Some Polymeric Materials. 1962 Transactions of the Ninth National Vacuum Symposium of the American Vacuum Society.

2. Hordon, M. J., and Roehrig, J. R.: Investigation of the Adhesion of Metals in Ultra-High Vacuum. Summary Technical Report under NASA Contract NAS1-2691, Task #7, by National Research Corporation, December 1966.

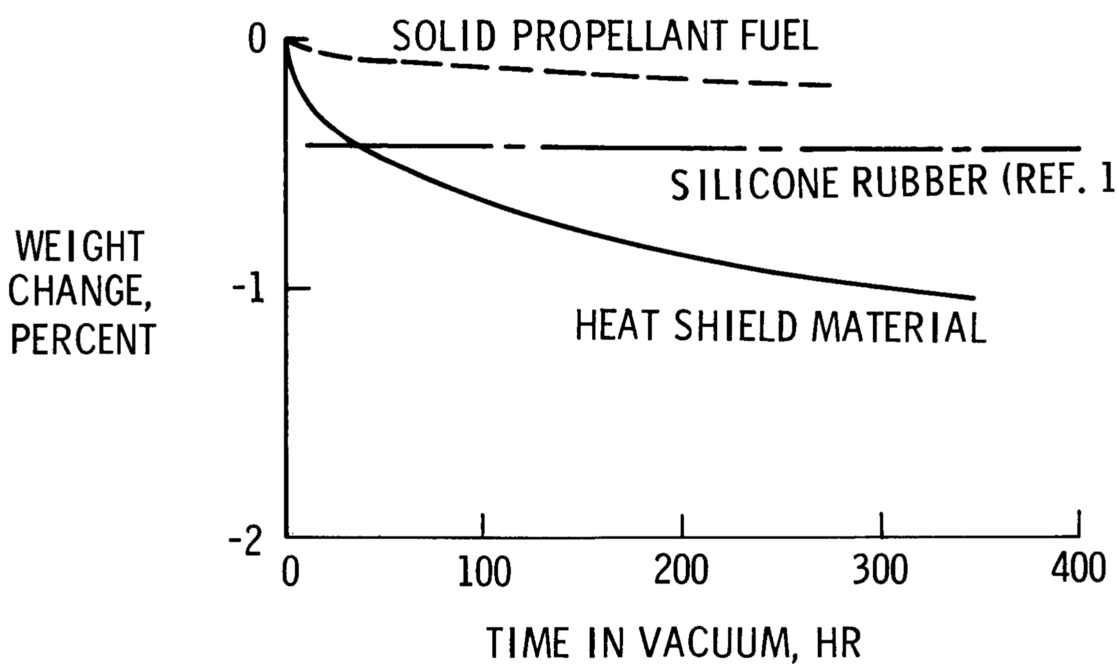

Figure 1.- Weight loss as a function of vacuum exposure time.

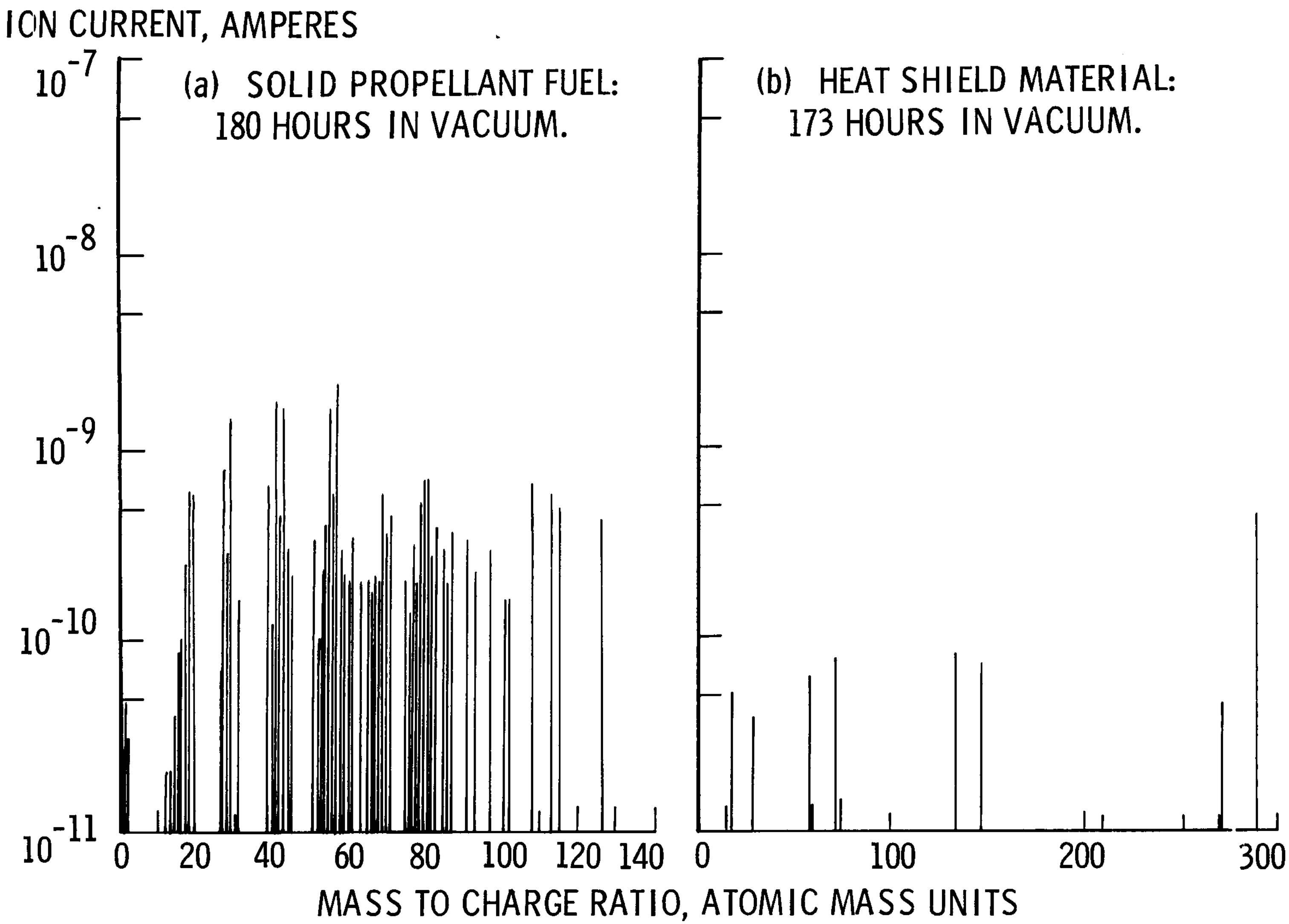

Figure 2.- Mass spectrogram of outgassing products.

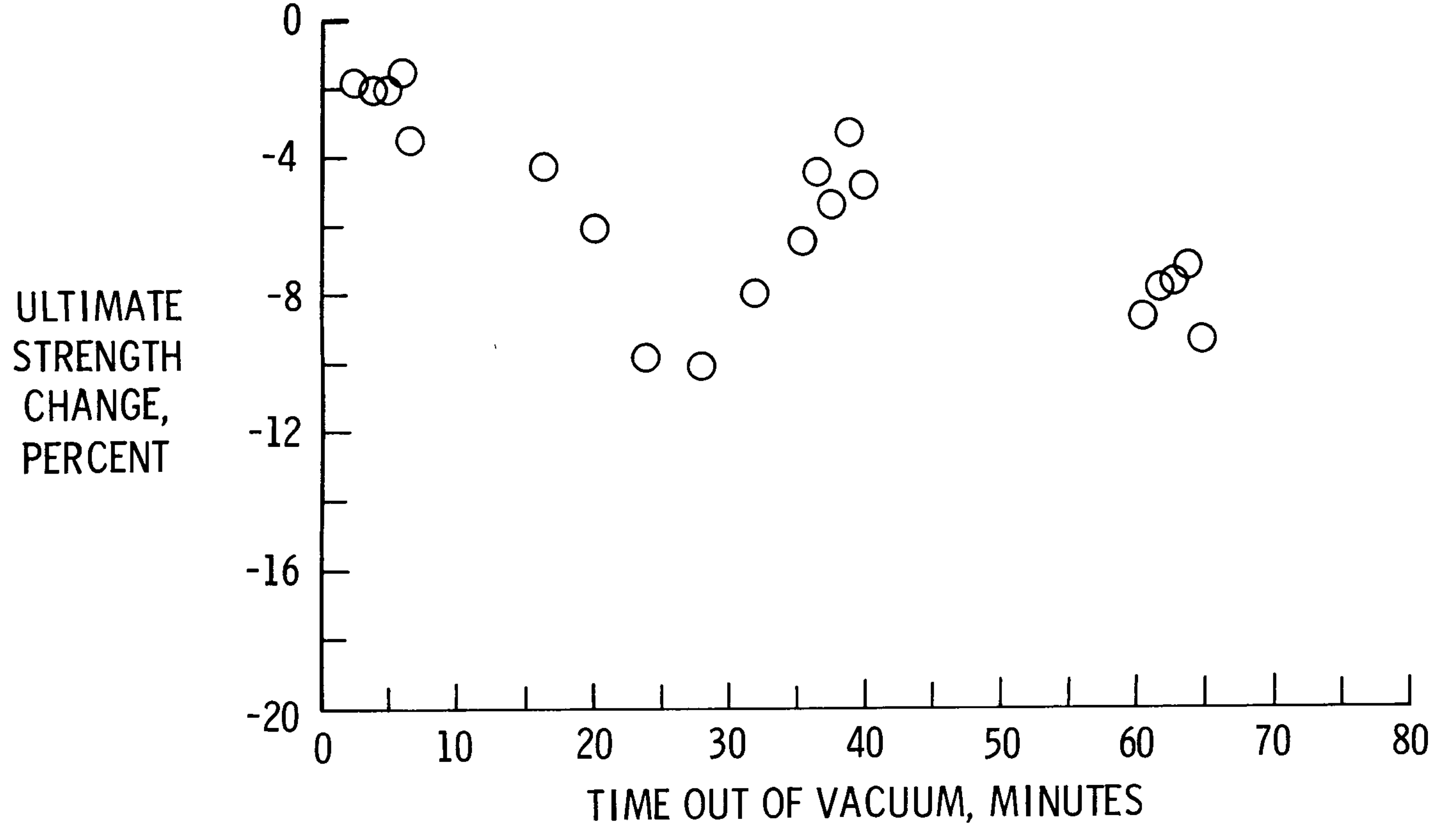

Figure 3.- Strength of nylon parachute material as a function of time after removal from vacuum.

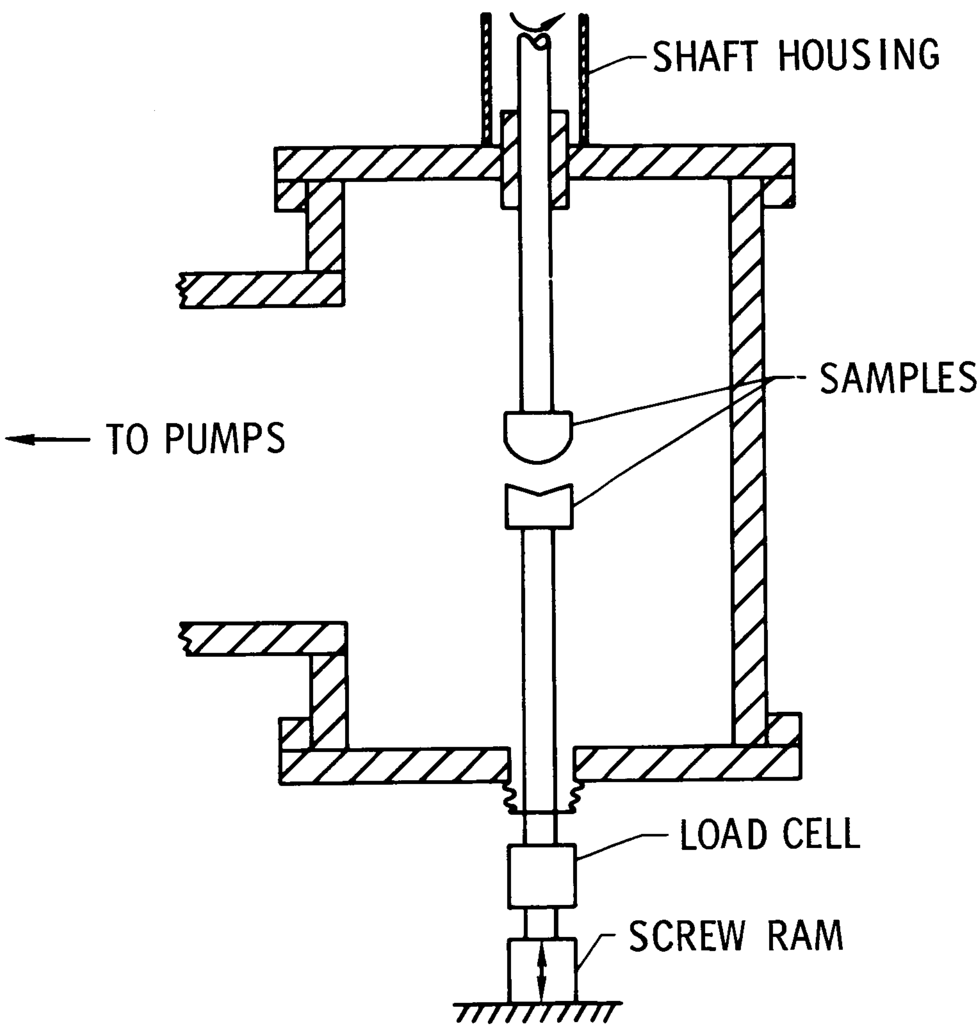

Figure 4.- Schematic of vacuum adhesion apparatus.

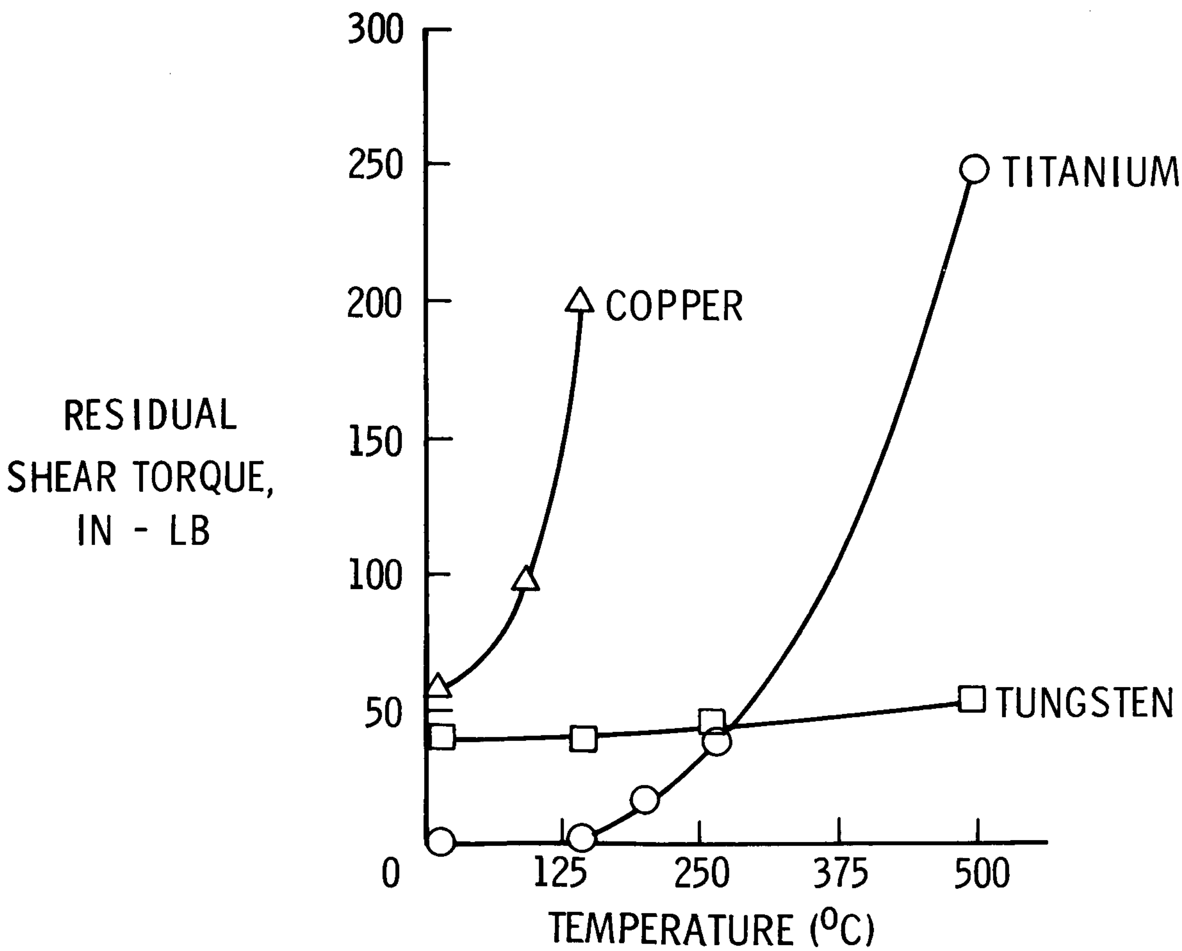

Figure 5.- Variation of residual shear torque with temperature.

NASA-Langley, 1967