Interim Technical Report No. 2 | *August 1964 to May 1965*

SPACE ENVIRONMENT EFFECTS ON POLYMERIC MATERIALS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950324
UNDER NAS7-100

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

*SRI

FACILITY FORM 602

N65-27059 (ACCESSION NUMBER)	(THRU)
74 (PAGES)	1 (CODE)
CR 63529 (NASA CR OR TMX OR AD NUMBER)	18 (CATEGORY)

GPO PRICE $ ______

OTS PRICE(S) $ ______

Hard copy (HC) 3.00

Microfiche (MF) .75

STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

May 30, 1965

Interim Technical Report No. 2 | *August 1964 to May 1965*

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950324
UNDER NAS7-100

JPL Cognizant Engineer: ROBERT HARRINGTON
SRI Project Supervisor: R. F. MURACA

SRI Project No. ASD-4257

Approved: R. F. MURACA, DIRECTOR
ANALYSES AND INSTRUMENTATION

Copy No. 113

FOREWORD

This Interim Report summarizes the work accomplished by Stanford Research Institute during the period August 1964 to May 1965 under Contract No. 950324 for the Jet Propulsion Laboratory of the California Institute of Technology.

Mr. Robert Harrington of the Jet Propulsion Laboratory's Materials and Methods Group was Cognizant Engineer for the project.

The technical effort at Stanford Research Institute was directed by Dr. R. F. Muraca, Director, Analyses and Instrumentation.

As requested by the Cognizant Engineer, the Institute staff members responsible for the various phases of the project are identified in the appropriate Sections of the report.

ABSTRACT

Stanford Research Institute, Menlo Park, California
SPACE ENVIRONMENT EFFECTS ON POLYMERIC MATERIALS
Interim Technical Report No. 2, August 1964 to May 1965
R. F. Muraca *et al.*, May 30, 1965, 66 pp.
(NASA Contract NAS7-100; JPL Contract 950324; SRI Project ASD-4257)

27059

The principles and techniques involved in the determination of weight loss and volatile condensable material are discussed in the light of application to polymeric materials being considered for use in spacecrafts. Results are given for the determinations of volatile condensable material in simulated spacecraft environment and the identifications of volatile materials.

Data are presented concerning measurements made *in situ* of the behavior of mechanical properties of polymeric substances in simulated spacecraft environment.

The commercial elastomers which have been studied include Vitons, Nordels, and Hypalons; of these three, the Vitons appear to be most suitable for spacecraft application.

Discussion is presented of a study of the degradation at elevated temperature *in vacuo* of a laboratory-synthesized polyurethane. Author

CONTENTS

FIGURES

FIGURES (Concluded)

TABLES

I. INTRODUCTION AND SUMMARY

This Interim Report No. 2 summarizes the work done under JPL Contract No. 950324, SRI Project No. ASD-4257, during the period August 18, 1964 to May 30, 1965. Interim Report No. 1, June 8, 1963, described in detail the design of equipment constructed for the various studies, outlined the techniques of operation, and discussed some preliminary results. Final Report for the period October 1, 1962 to November 30, 1963 (published December 8, 1963) summarized the work performed on volatile condensable material and mechanical properties of commercial polymers (Vitons, silicone rubbers, Teflons, and Mylars) and the exploratory studies of the degradation of synthesized polyurethanes and nylon.

The broad objective of this program of work is to provide a definitive study of the effect of simulated spacecraft environment on certain classes of polymeric materials which are considered to be suitable for use in spacecrafts. The work undertaken thus far was designed: (1) to ascertain the extent to which warm polymers release substances in a vacuum which condense at temperatures in the vicinity of 25°C; (2) to determine if polymers undergo gross skeletal degradation in a vacuum at temperatures in the vicinity of 125°C; (3) to determine changes in pertinent physical properties of selected polymers in a vacuum-thermal environment. The commercial polymers selected for study during this period are: Vitons, Nordels, and Hypalons (see Appendix for formulations).

The work performed during this phase of the long-range program permits the following conclusions at this time:

(1) The volatile condensable material released by samples of Nordel and Hypalon in a vacuum-thermal environment has been shown to accumulate in accordance with theoretical calculations for a polymeric substance containing a normal distribution of volatile material (see Section III).

(2) Both loss in weight and accumulation of volatile condensable material indicate the unsuitability of the Nordel and Hypalon samples for spacecraft construction, particularly in comparison with results previously reported for other elastomers such as Viton and silicon rubbers (see Section III).

(3) Mechanical properties measurements made in a vacuum-thermal environment on samples of Viton, Hypalon, and Nordel indicate the comparative superiority of Viton for spacecraft construction, especially under conditions of stress (see Section IV).

(4) Study of a synthesized polyurethane has indicated that no skeletal degradation of this polymeric system takes place at temperatures below about 225°C *in vacuo*.

II. MATERIALS RELEASED BY POLYMERS IN A VACUUM-THERMAL ENVIRONMENT

R. F. Muraca and J. S. Whittick

The loss of matter by outgassing and by evaporation or sublimation is one of the most obvious effects of a vacuum-thermal environment on polymers. Because gross loss of material generally means that the physical properties of polymers are altered or that test chambers will be contaminated by the vaporized substances, the polymers which are considered suitable for use in spacecrafts are those which in laboratory tests exhibit a minimum loss of weight when exposed to the simulated conditions of the vacuum and thermal environment of space. However, it has been found that many polymers which show losses release substances which condense on cooler surfaces and interfere with spacecraft functions.

The object of this part of the program of study was to develop suitable procedures to determine the amounts and to identify the substances released by polymeric materials in a vacuum-thermal environment.

The simplest quantitative value which can be obtained for the behavior of a polymer in a vacuum-thermal environment is the loss of weight. This value obviously does not reveal the nature of the components released by the polymer but, nevertheless, is useful for selecting polymers suitable for spacecraft since, in the majority of instances, it may be safely assumed that mechanical or other useful properties of polymers are degraded when a substantial amount of loss of weight has been incurred. It is customary to assume that polymeric substances which lose less than 1% of their weight in a vacuum-thermal environment are suitable for spacecraft application.

Matter released by polymeric substances in a vacuum-thermal environment may be the ordinary gases (e.g., adsorbed air or dissolved methane), ordinary liquids of relatively high vapor pressure (e.g., water or solvents), liquids or solids of relatively high molecular weight and low vapor pressure (e.g., lubricating oils, plasticizers, etc.), or fragments of high molecular weight which are structurally related to the basic polymeric structures and often originate from skeletal degradation (in contrast with the other volatile materials noted above).

In the early stages of work on the National space program, a great many polymeric substances and systems were examined by direct weight-difference procedures in order to select suitable polymers. Recently, the acceptable polymers have been examined by more refined techniques to determine the rate of the weight loss and to characterize the nature of the volatile substances. In general, these studies have indicated that polymeric materials release the common gases at a rapid rate (especially at some elevated temperature like 100°C) and that the outgassing is relatively complete in a matter of a few hours. On the other hand, these studies have indicated that high molecular weight materials are given off at a much slower rate and that acceptably low incremental weight-loss values are observed when high-molecular-weight materials of very low vapor pressure are still being released at very low rates. These very low rates of evolution of matter from polymers are best detected by use of appropriately designed mass spectrometer inlet systems and it is suggested that, since the selection of polymers for construction of spacecrafts is currently being made with methods which are not capable of detecting very low rates of weight loss, more refined techniques for determining total loss of weight should be employed.

It is to be emphasized that all measured values pertaining to the loss of matter from polymeric substances in a vacuum-thermal environment are functions of time. Thus, for example, the "loss of weight" of a polymeric substance in a vacuum-thermal environment is generally considered to be the total loss of weight suffered by a sample of the material when maintained in the environment for a period of time long enough that the incremental loss of weight suffered during an incremental exposure is acceptably low. Also, the total loss of weight obtained by simple weight-difference procedures gives no information as to the rate at which the weight is lost and the nature of the substances evolved.

Determination of the absolute rates of outgassing or release of materials from polymers is a difficult task. As a first approximation, one may consider that the rate of outgassing or release of material from the surface of a polymer is similar in nature to the rate of evaporation of material from the surface of a liquid or a solid. Accordingly, one might be tempted to use a Knudsen effusion cell to determine the rate of outgassing or loss of weight; an apparatus using a miniature Knudsen-type effusion cell attached to the arm of a recording microbalance has been described by Riehl.[1] The apparatus has been used successfully to determine the rate of evaporation of pure compounds. The Knudsen effusion cell technique for determining the rates of evaporation of materials is based upon the establishment of equilibrium conditions within the cell. The theoretical basis for the Knudsen technique requires that the cell aperture represent a small fraction (less than 1%) of the surface from which evaporation takes place uninhibitedly, that the material within the cell has sufficient surface area for free evaporation so that just as many molecules leave the surface of the material as are deflected back onto the surface from the walls of the cell, and that the number of molecules passing through the aperture is negligible in comparison with the number of molecules in the gaseous state within the cell. Additionally, the diameter of the aperture must be small in comparison to the mean free path of the molecules within the cell and the rate of flow depends on the pressure difference across the aperture, the dimensions of the aperture, and the density of the gas (molecular effusion).

Clearly, when dealing with pure compounds, the loss of material from the Knudsen cell has thermodynamic significance, and the evaporation rate obtained experimentally bears a relationship to all the implications derivable from the principles of statistical equilibrium thermodynamics of the ideal state; thus, the evaporation rate of a pure compound can be related to its vapor pressure by the familiar Langmuir equation (*vide infra*).

---

[1] Riehl, W. A., *Chem. Eng. Prog. Symposium*, **59**, No. 40, 103 (1963).

In contrast, when the Knudsen effusion technique is employed with complex materials, the rates of evaporation of the various molecular species are influenced by many factors and nonequilibrium, nonideal conditions prevail within the cell; since most systems encountered in practice are nonideal, the evaporation rates obtained experimentally are only fortuitously (if at all) related to the vapor pressures of the evaporating molecular species. In particular, when dealing with polymeric substances, the rates of diffusion of the evaporating species within the body of the polymer structure may severely influence the experimental results. For example, if a large, single piece of dense polymer containing a relatively volatile material is enclosed in a Knudsen cell, the rate of arrival of molecules of the volatile material to the surface of the polymer will be much slower than if the same mass of polymer were present in a comminuted form or if the surface of the large mass were finely corruscated. Since the evaporation rates would be different for each of the above cases, it is obvious that a numerical value for the rate of evaporation (or weight loss) of a polymeric substance must be defined in terms of the micro-structural surface area measurement of the polymer specimen and its thickness of section and over-all dimensions. In other words, the specimen size for a given thickness of sample would have to be of such a length and width that evaporation from the sides would be negligible (or accountable); the numerical value for weight loss (evaporation rate) per unit surface area would have to be indicated in terms which also define the rugosity of the surface.

When polymer samples which are heavily laden with plasticizers of low vapor pressure are examined by the Knudsen effusion technique, the rate of diffusion of the plasticizer in the solid polymer matrix will generally be sufficiently great to permit establishment of the equilibrium vapor pressure of the plasticizer. Under these conditions, the apparent evaporation rate of the polymer system as indicated by the results obtained with the Knudsen cell is essentially the evaporation rate of the pure plasticizer itself. In fact, one can show this simply by comparing the results obtained in a Knudsen with a sample of sintered, porous

Teflon containing within its pore structure an oily substance, such as SAE-30 motor oil, with the results obtained on the oil by itself.

If the evaporation of a plasticizer from the surface of a polymer leaves a hard, nearly impermeable skin (as is likely to happen in free space), the evaporation of the plasticizer will be inhibited; in a Knudsen cell, the skin will very likely not form since the vapors of the plasticizer in the cell will tend to prevent the formation of a skin; complications also arise when the accommodation coefficient of the plasticizer molecules on the hard skin is sensibly different from the one on plasticized surface.

It is evident that the Knudsen cell gives only approximate values for rates of evaporation (loss of weight) for polymeric materials and in most instances gives a rate which is governed entirely by a plasticizer; but the values obtained in this way are grossly misleading to the spacecraft engineer, for the Knudsen cell values are for quasi-equilibrium conditions in which the rates of evaporation and condensation of the various molecular species are essentially equal, and these conditions do not prevail in outer space. The rates of evaporation of volatile species from the polymeric surfaces of a spacecraft exposed to the infinite vacuum of space are grossly different than those indicated by a Knudsen cell technique; in space, molecular species can leave the polymer surfaces but they seldom return. Thus, even the simplest loss-of-weight experimental set-up, one in which a bare polymer sample is weighed by a suitable balance, will give rates of evaporation most nearly resembling those encountered in the spacecraft environment.

The quantitative determination of the amount of condensable material which is released by a warm polymeric substance in a vacuum is also influenced by the same factors as the determination of the rate of evaporation (or weight loss). Both determinations require that volatile material be released uninhibitedly from polymer samples under completely nonequilibrium conditions; thus, a Knudsen cell technique is inapplicable. The determination of volatile condensable material requires that the matter given off at an elevated temperature, T_2, by a polymer at a rate W_2 (g/in^2/sec) is condensed on a cooler surface maintained at temperature,

T_1, from which the condensate evaporates at a rate W_1 (g/in^2/sec); the VCM value after a given time is defined as the weight of residue on the collector plate given off from the surface area of the sample. It is evident that the VCM value is actually the weight of condensable matter given off by the sample minus the loss at a rate W_1 of this matter spread out over the collector surface.

Volatile Condensable Material

Volatile condensable material (VCM) has been defined throughout this program of work as the weight of condensate obtainable at 25°C in a given interval of time from a unit area of material of a given thickness maintained at 125°C in a vacuum of at least 5×10^{-6} torr. The temperature of 125°C was selected as the upper limit of temperature encountered in spacecraft operations and to provide comparison with results of mechanical and physical properties measurements and outgassing studies which were performed at this temperature. Space probes and satellites are generally designed to maintain internal temperatures of the order of 25°C, but temperatures as high as 125°C may occur in the vicinity of power-dissipating components. Thus, a suitable polymer for spacecraft application must retain its properties at a temperature of 125°C in a vacuum and must release negligible amounts of material which condense on surfaces at 25°C.

As has been explained before, the determination of VCM depends upon evaporation rate differences. The Langmuir equation permits estimation of the rate of evaporation of a pure compound:

$$W = \frac{P}{17.14}\sqrt{\frac{M}{T}}$$

where

W = rate of evaporation in gm/cm^2/sec
M = molecular weight
T = absolute temperature
P = vapor pressure in mm.

The vapor pressure of pure compounds may be expressed by the equation:

$$\log P_{mm} = A - \frac{B}{T}$$

and this is easily transformed to

$$P_{mm} = 10^{A - \frac{B}{T}} \quad .$$

Now, if it is desired to compare the rate of evaporation of a pure compound at two temperatures, it is obvious that the Langmuir equation can be combined with the exponential form of the vapor pressure expression to yield:

$$\frac{W_1}{W_2} = \frac{10^{A-B/T_1}}{10^{A-B/T_2}} \sqrt{\frac{T_2}{T_1}}$$

where the subscript 2 refers to the higher temperature.

Thus, in the instances of the VCM determination, where the higher temperature is 125°C (398°K), the rates of evaporation at the two temperatures are related by the equation:

$$\frac{W_{398}}{W_{298}} = 0.8653 \left(\frac{10^{A-B/398}}{10^{A-B/398}} \right)$$

Some of the initial work done on VCM determinations was with silicone polymers. It will be instructive to consider the vapor pressures expected from silicone polymers; the work of Wilcox[2] was consulted. Data given in this reference include the vapor pressure equations for compounds of the general form:

$$(CH_3)_3SiO_{1/2}[(CH_3)_2SiO]_x(CH_3)_3SiO_{1/2} \quad .$$

---

[2] Wilcox, D. F., *J. Am. Chem. Soc.*, **68**, 691 (1946).

The coefficients A and B of the vapor pressure equations given in the reference are plotted in Figure II-1 and extrapolated to lower molecular weight values purely for sake of example. Using the data of Figure II-1, the ratios of evaporation rates for various molecular weight compounds were computed; these are summarized below:

RATIO OF EVAPORATION RATES AT 398°K AND 298°K

No. of Si Atoms	M. W.	W_{298}	Ratio $\frac{398^{\circ}K}{298^{\circ}K}$	Ratio $\frac{373^{\circ}K}{298^{\circ}K}$
18	1346	1.5×10^{-9}	578,000	32,400
12	904	3.6×10^{-4}	28,000	3,600
6	458	1.62	430	129

The ratios obviously indicate that in comparison to 298°K the silicone materials evaporate much faster at 398°K than at 373°K (578,000 to 32,400); more importantly, however, the higher molecular weight material is evaporated at an enormous rate at higher temperatures than at lower temperatures, but the rate of evaporation of the lower molecular weight material is (relatively) not influenced very much by an increase in temperature, and the lower molecular weight material evaporates millions of times faster than high molecular weight material at temperatures between 298 and 398°K.

Now, for a polymeric material consisting of a distribution of various molecular weights, it is difficult to make quantitative predictions of evaporation rates at various temperatures; the rates are nearly impossible to compute when various effects such as diffusion of species through a molecular matrix, nonideal vapor pressures, and impermeable surface layers are involved. Nevertheless, qualitative generalizations may be drawn about the results of a VCM determination provided impermeable membranes are not formed and the resin sample is thin enough (or porous) so that diffusion effects are negligible. Referring to Figure II-2, the upper (solid-line) curve in the upper graph indicates the cumulative loss of weight in a vacuum expected from a resin (say at 398°K) which has volatile matter consisting of a more or less uniform distribution

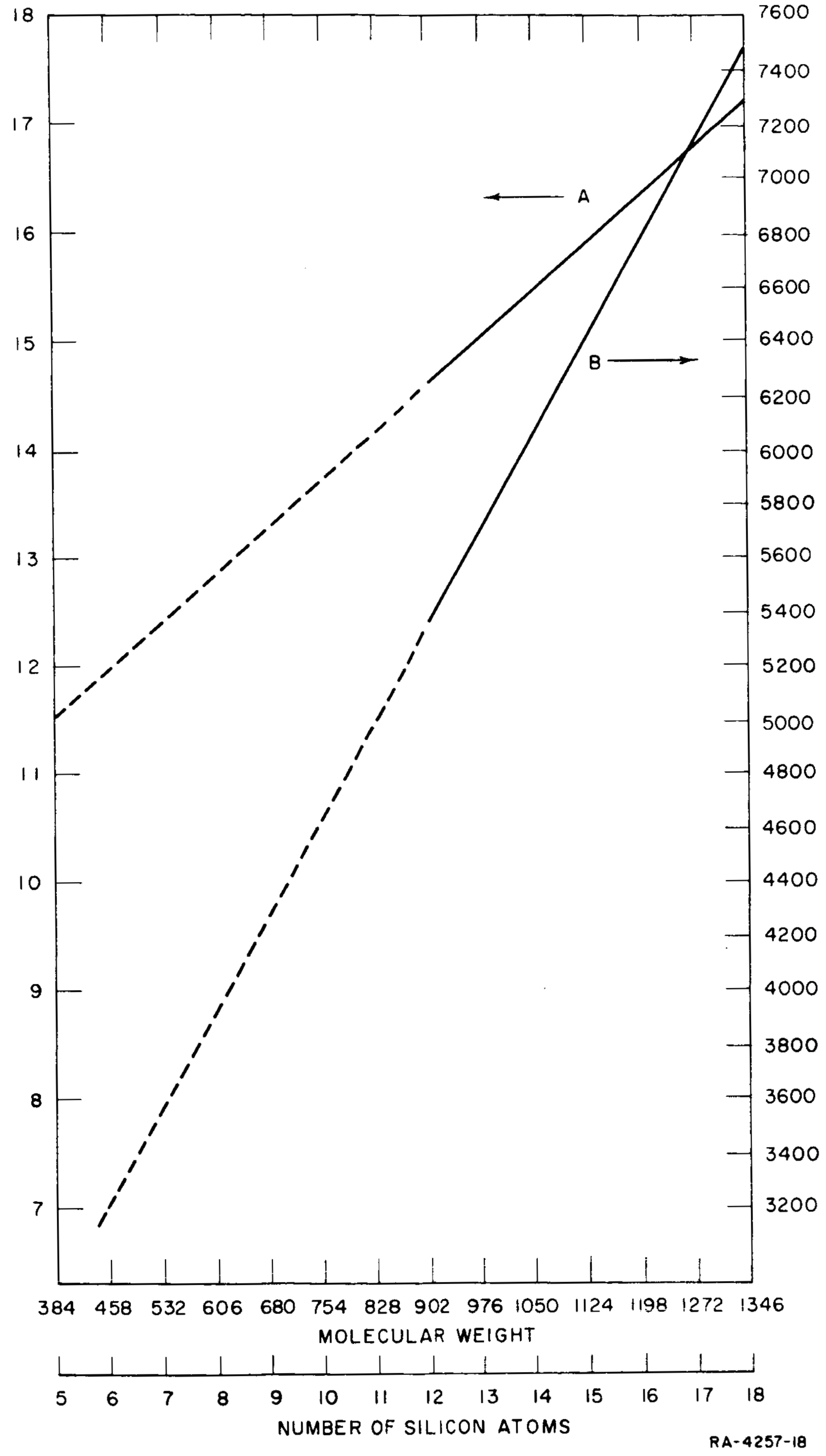


FIG. II-1 COEFFICIENTS IN THE VAPOR PRESSURE EQUATION $\log P = A - B/T$ FOR COMPOUNDS OF THE GENERAL FORMULA: $(CH_3)_3SiO_{1/2}[(CH_3)_2SiO]_4(CH_3)_3SiO_{1/2}$

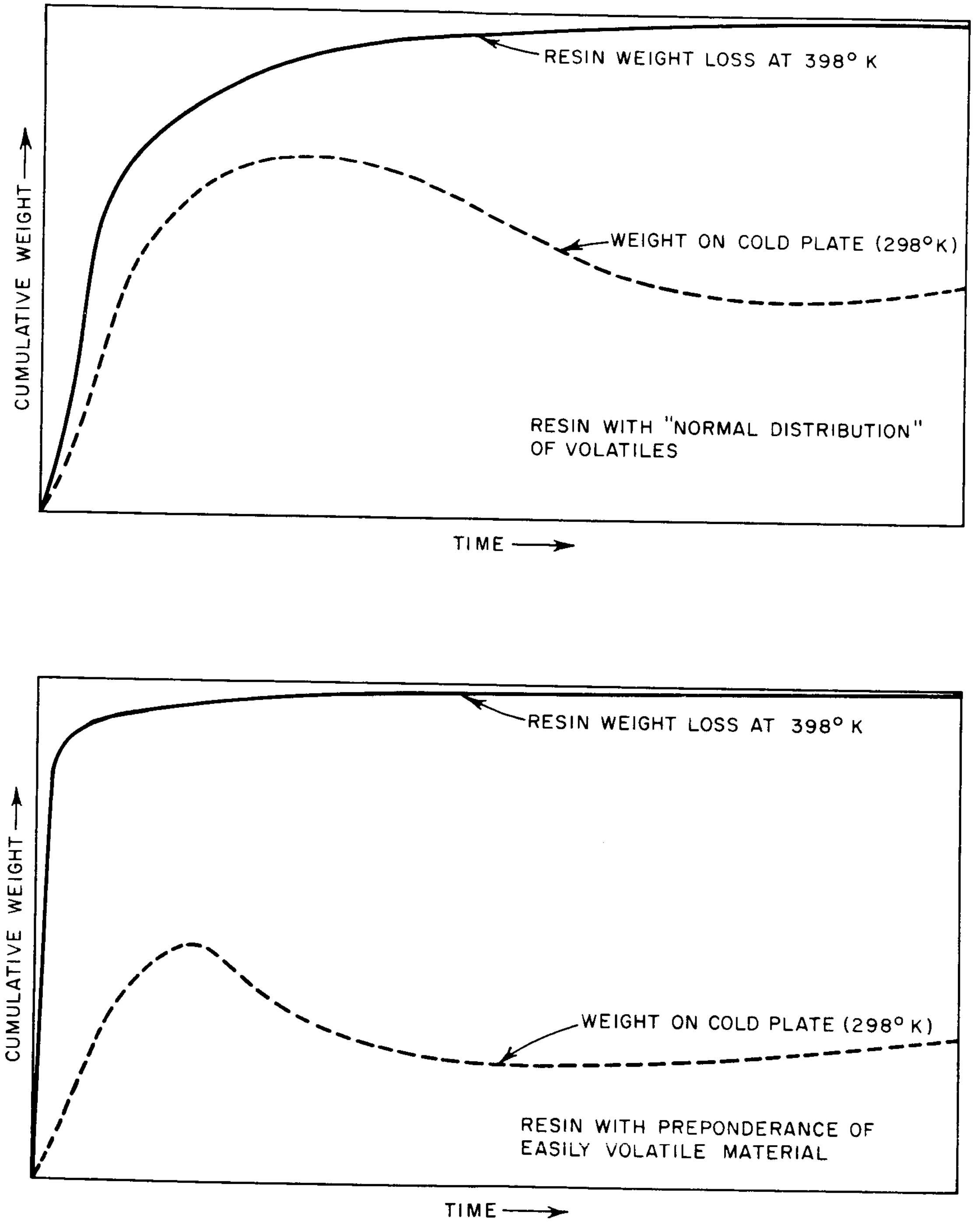


FIG. II-2 DIAGRAMMATIC REPRESENTATION OF THE QUALITATIVE RELATION OF LOSS OF WEIGHT OF RESINS AT 398°K TO VCM RESULTS of molecular weight species. The solid-line curve in the lower graph represents the cumulative loss from a resin which has a preponderance of low molecular weight species in the volatile matter. The dotted-line curve in each graph represents, qualitatively, the cumulative weight on a cold (298°K) collector which receives (straight-line) the material released by the warm resin in a VCM apparatus; an attempt is made, in these graphs, to show that the material collected on the cold collector evaporates slowly and that the weight of material on the cold collector is never stable.

The interesting point brought out by the graphs in Figure II-2 is that the weight of material on the collector plate after a very long time continues to rise slowly if the resin gives off high molecular weight substances, and that the weight on the plate will eventually be zero if the resin ceases to give off material early in the test. The usual Knudsen cell determination cannot reveal this.* Additionally, the graphs do not give any idea of the times involved, but it is important to realize that the relative evaporation rate data tabulated above indicates that considerable time at 298°K will be required to remove thin films of high molecular weight material; for example, for an 18-atom silicone, the weight of material evaporated in one hour at the higher temperature (398°K) will require 578,000 hours for evaporation at 298°K! Moreover, since the evaporation rates of high molecular weight materials are small, an exceptionally long time is required to remove volatile material of this type from resins, and, as indicated in the graphs of Figure II-2, a very long time must be utilized in the determination of VCM to obtain weights of material on the cold collector plates which have "leveled off." Thus, if a VCM determination is performed appropriately, it will be possible to detect a low steady

---

* The usual determinations involve short-time periods of less than 100 hours. If a Knudsen cell contains enough polymer sample to maintain equilibrium vapor pressure, the time required to evaporate each component is prohibitive. On the other hand, if the effusion aperture is made so large that essentially no pressure exists in the cell, then the apparatus and technique is not Knudsen's.

rate of vaporization of matter; this is very important in selecting polymers for use in critical components in a space craft. Figure II-3 shows the actual results obtained from an ethylene-propylene terpolymer with a diene (Nordel A-5411A-113) plasticized heavily with an ordinary hydrocarbon lubricating oil which, obviously, has a "normal distribution" of volatiles (the actual structure distribution was verified by mass spectroscopy). It is to be noted that the shape of the curve in Figure II-3 resembles the curve shown in Figure II-2; however, it is to be emphasized that the curve obtained for the Nordel (Figure II-3) shows clearly that the amount of volatile condensable material is much greater at 340 hours than at 48 hours, showing that the content of the higher molecular weight material slowly vaporizes from the polymer (as predicted from the theoretical considerations indicated above).

A consideration of the results shown in Figure II-3 indicates that the determination of VCM cannot be performed quickly (24-48 hr) and that for most polymeric materials which contain a small amount of volatile substances, the VCM determination may have to be prolonged to thousands of hours. The bump in the curves shown in Figures II-2 and II-3 occurring for time intervals less than about 100 hours bears no relation to the VCM value obtained after thousands of hours; as shown in Figure II-2, the early bump is merely indicative of the easily volatile substances which, incidentally, also volatilize easily after condensation on a cooler surface. The release of easily volatile material and its subsequent condensation on cooler surfaces may be annoying when spacecrafts are tested in environmental chambers, but the deposition of relatively non-volatile matter on the surfaces of spacecrafts after considerable time in space is properly of more concern to the engineer.

The VCM value is not an absolute numerical figure, but rather a relative figure which is derived from an estimation of the total polymer surface area and the total condensing surface area. It is also based on the assumption of a collisionless straight-line path from the warm radiating polymer surface to the cooler condensing surface. Slight differences in construction of various VCM apparatuses and sample handling obviously influence reported numerical values. However, differences in

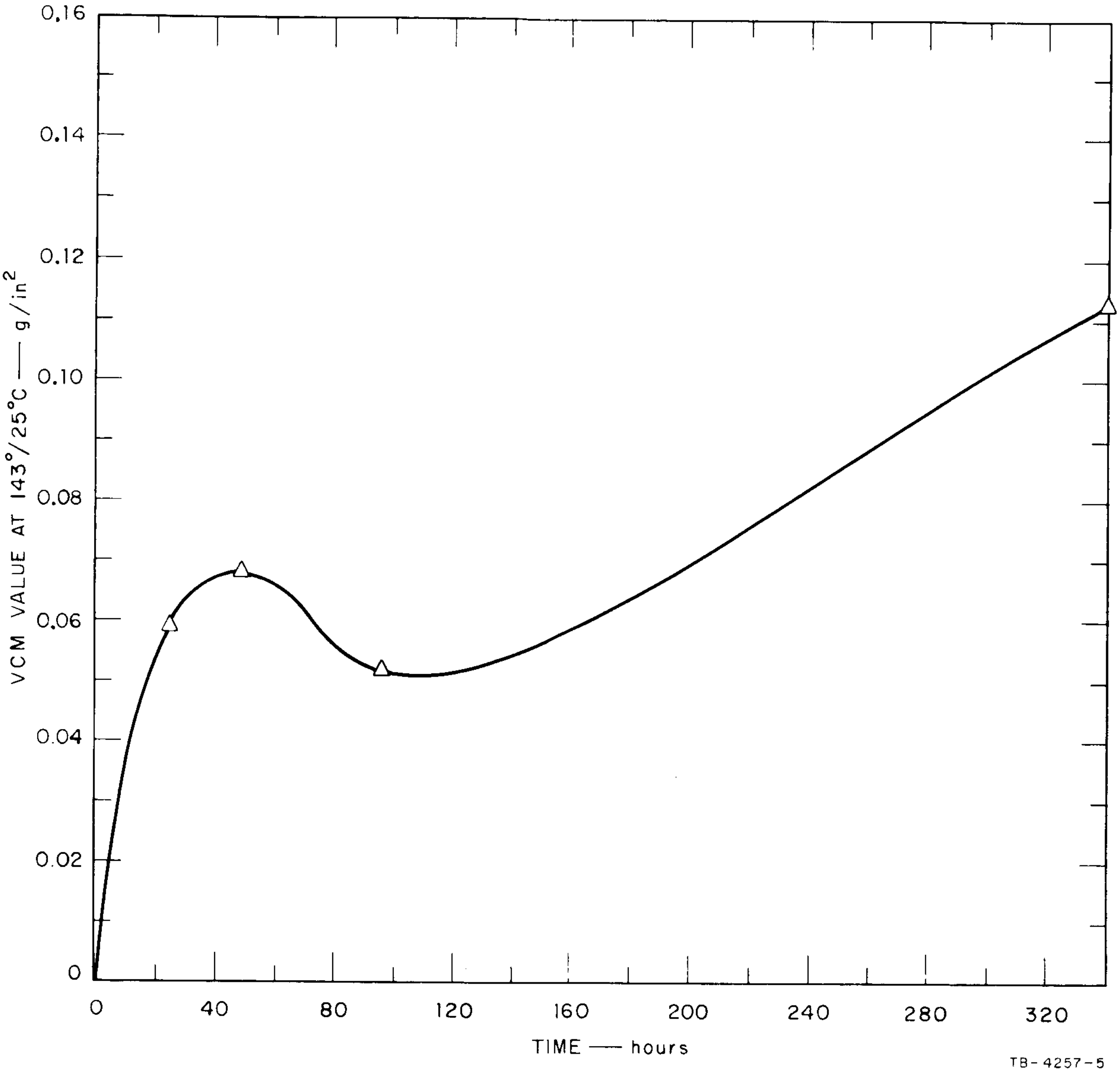


FIG. II-3 VCM VALUE AT 143°/25°C WITH RESPECT TO TIME FOR NORDEL A-5411A-113 values for various materials should be proportional for each laboratory and with the results obtained by other laboratories. The VCM value can provide a realistic screening procedure for polymeric materials, provided the time and temperature selected for the determination lie outside of the conditions for maximum outgassing rate; otherwise, poor reproducibility and misleading values may be expected.

Volatile Condensable Material - Apparatus and Method

Rigid control of temperatures and vacuum conditions are necessary in VCM procedures; simple heating apparatus and vacuum systems will give values for VCM that are not indicative of the behavior of resins in a space environment. Complete design drawings and photographs of the VCM apparatus used at SRI are presented in Interim Report No. 1, Figures III-1 to III-9. The over-all schematic of the VCM unit cluster and an illustrative photograph are included in this report as Figures II-4 and II-5, respectively. Minor changes made in the apparatus can be determined by comparison of Figure II-4 in this report with Figure III-1 of Interim Report No. 1.

Figure II-6 is a detailed view of the heater and sleeve assembly for the VCM unit. The complete vacuum equipment for VCM determinations is indicated in Figure II-7; as can be seen in this Figure, the vacuum chamber is an aluminum box with an 18-inch diameter Lucite window and entry port. The vacuum system is a compact unit comprising a Welch Duo-Seal forepump (No. 13978), a 6-inch oil diffusion pump (CVC Model MCF-700), and a manually-operated valve (CVC Type VT-SB-61). A 6-inch line connects the chamber to a low-loss trap directly connected to the outlet of the valve. Suitable by-passes and ball valves permit "roughing" the vacuum chamber and "holding" the diffusion pump during preliminary evacuation procedures. A Pirani gage and an ionization gage (VG-1A) are used for measuring the pressure in the chamber. The vacuum chamber can easily be evacuated to at least 1×10^{-6} torr and to 5×10^{-7} torr with operating traps.

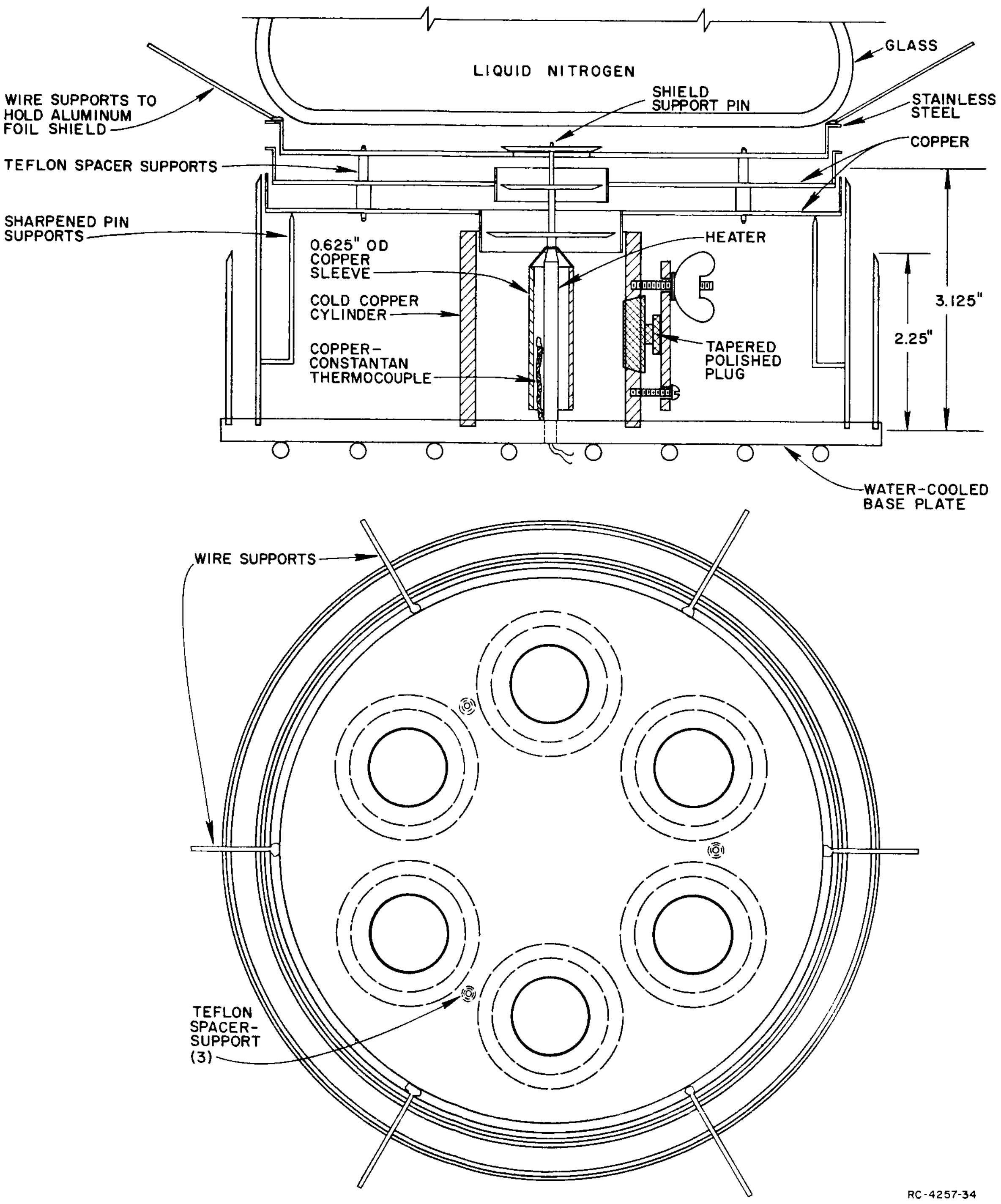


FIG. II-4 SCHEMATIC DIAGRAM OF A SINGLE VCM UNIT AND ARRANGEMENT OF A CLUSTER OF SIX UNITS

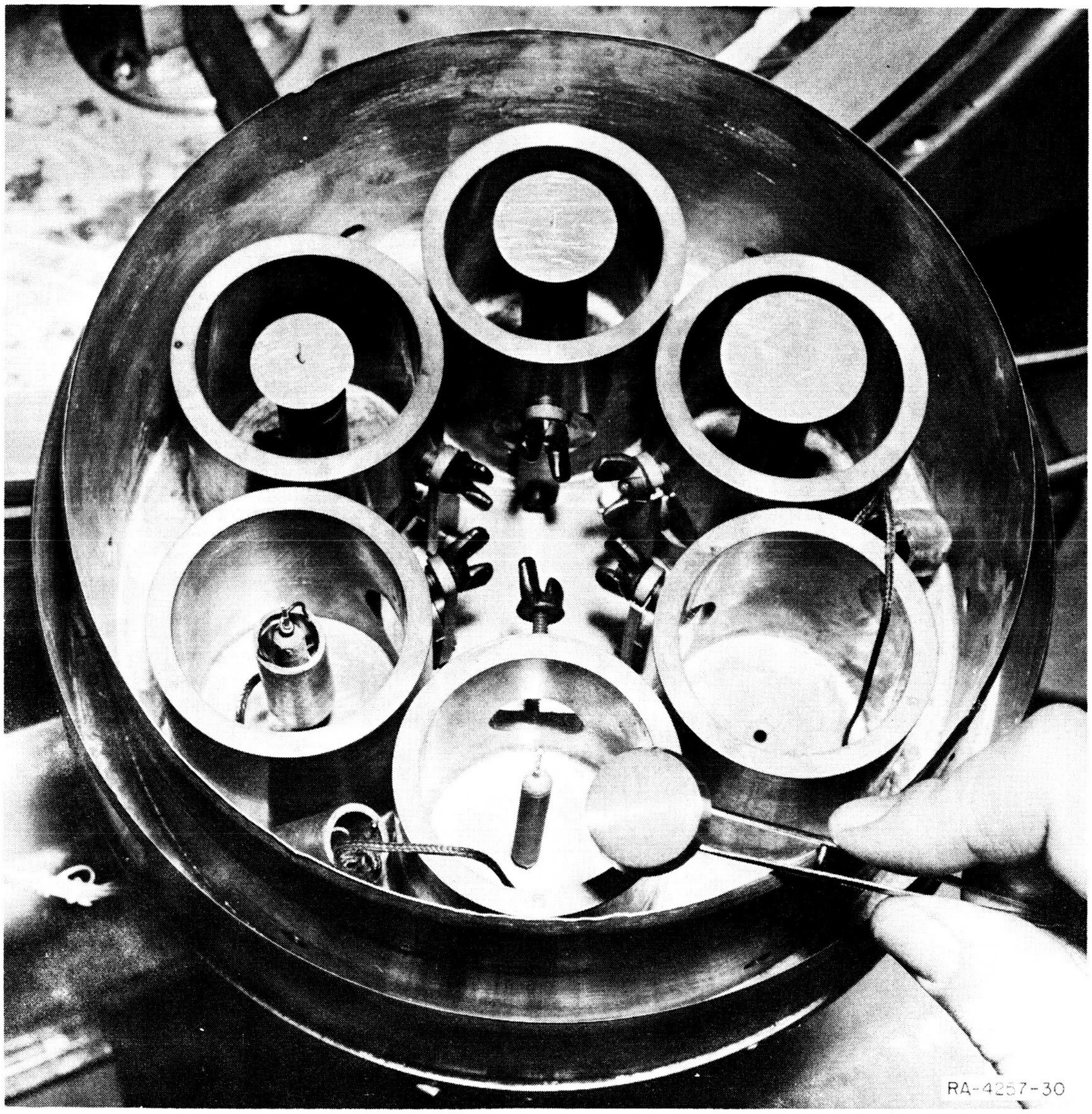
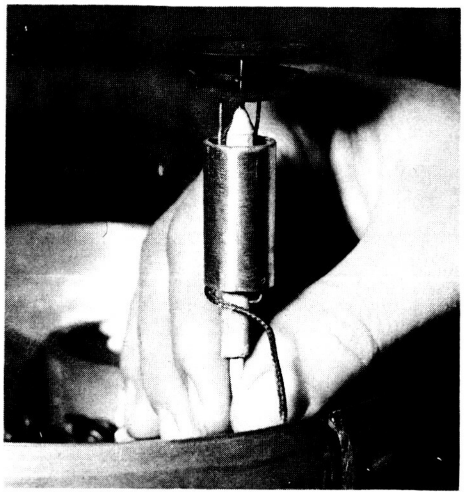
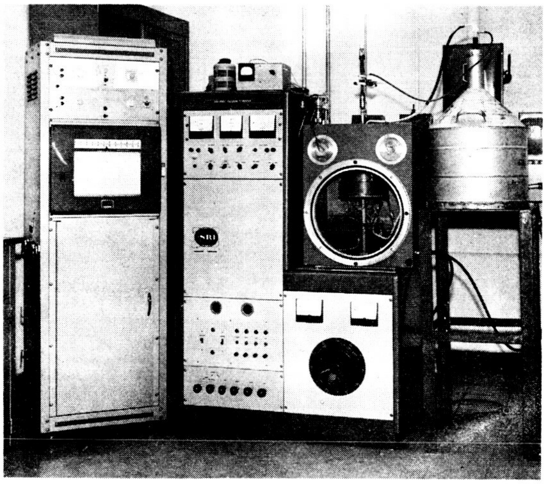


FIG. II-5 INTERNAL VIEW OF VCM APPARATUS SHOWING ARRANGEMENT OF HEATER-COLLECTOR ASSEMBLIES AND SHIELDS



TA-4257-17

FIG. II-6 HEATER AND SHIELD ASSEMBLY FOR VCM



TA-4257-18

FIG. II-7 COMPLETE APPARATUS FOR VCM DETERMINATION

A single determination of VCM, that is, a single run of any duration, has been shown to be of little value except as a screening process for materials which have been previously studied. Since one of the objectives of this program is to study the characteristics of VCM, vacuum-thermal exposures are scheduled to provide values of statistical significance. Previous work has shown that exposure times of 24, 48, 96, and 340 hours will establish the trend of the VCM curve. (Longer runs, of course, will provide more final estimation of the disposition of VCM, but the number of materials which must be studied precludes extremely long exposures.) It is to be emphasized that fresh samples are used for each exposure period; thus, the values represent true interpretations of VCM behavior with time.

Samples are cut to a uniform size which will permit them to be wrapped completely around the heaters (Figure II-5) but without overlap; they are weighed on a microbalance to ±0.005 mgm and then fastened in place with light wires. The clean, polished copper plugs (Figure II-5) are also weighed on the microbalance (about 19 g). When the VCM apparatus is completely assembled and set in place in the vacuum chamber, the system is exhausted at room temperature to a pressure of about 5×10^{-6} torr (cold traps). Then the individual heaters are turned on and cryopumping is initiated. After the prescribed period, the run is terminated and the system is vented with helium. The polymeric samples and the copper plugs are then re-weighed on the microbalance.

Two sets of duplicate samples occupy four of the six VCM units shown in Figure II-5; the other two VCM units, with weighed copper plugs, are run as controls. The control plugs are always found to be entirely devoid of material and to have incurred no weight loss or gain (0.000 ± 0.005 mgm). The absence of matter on the control plugs (cross-contamination) may be taken as an indication of the extreme efficiency of the baffle systems in the VCM units and the adequacy of the cryogenic pumping system. Generally, vacuum systems are so poorly designed that cross-contamination cannot be avoided; this is especially true for the simple-ducted vacuum equipment ordinarily employed for the determination of the loss of weight of multiple samples.

A vivid illustration of the lack of cross-contamination in the SRI apparatus is given by the photograph in Figure II-8; here, the clean surfaces of the control plugs are contrasted with the discolored surfaces resulting from material released from samples of Hypalon and the grossly oil-coated surfaces resulting from the oil released from samples of Nordel.

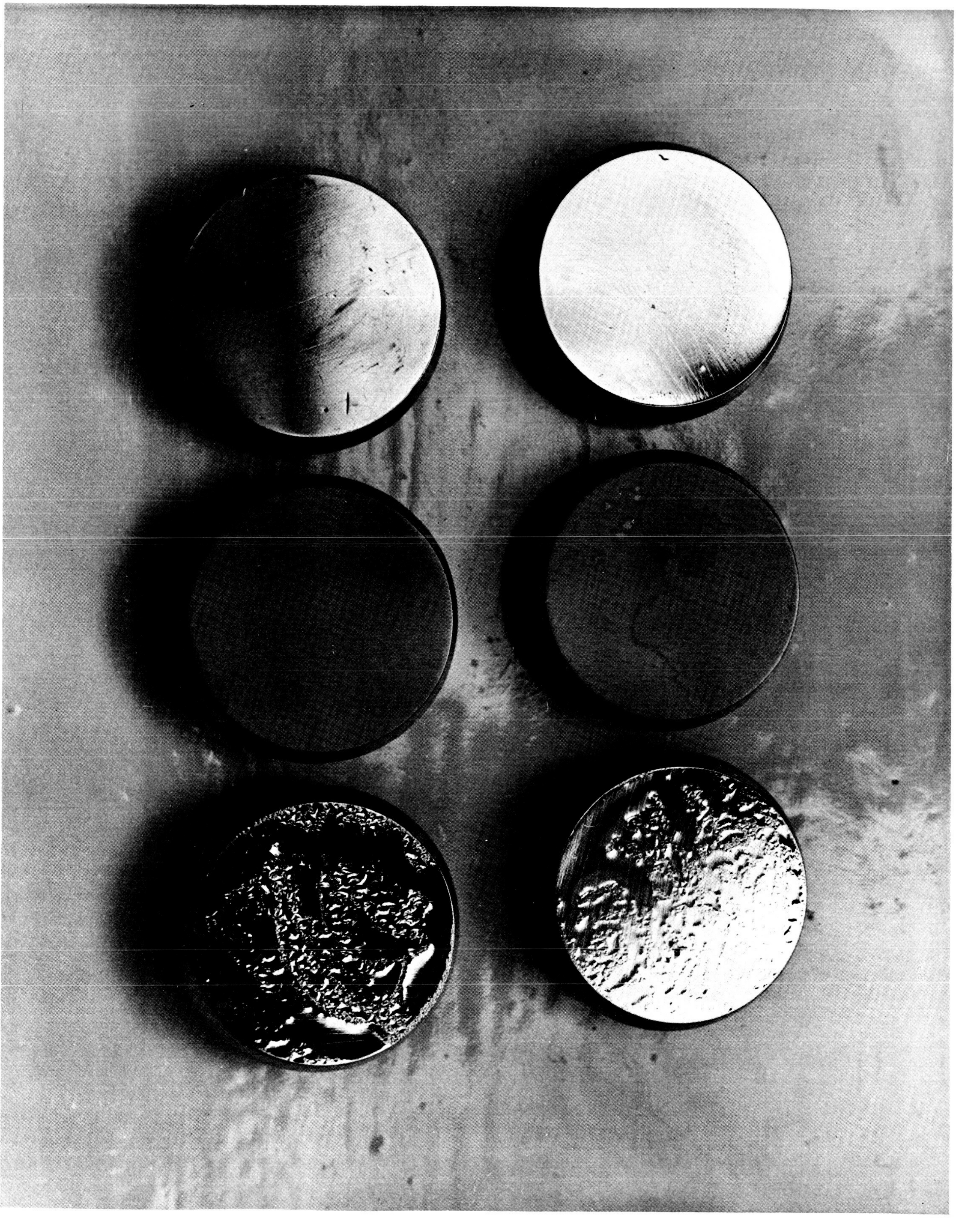
An example of the performance of the SRI apparatus in providing realistic values for VCM is given by the results of a series of determinations on Nordel polymers at 93°C and comparison of the values with those obtained in the same time period at 143°C. At the suggestion of the JPL Cognizant Engineer, Nordel A-2411A-113, -115, and -117 were used for these determinations because of the various quantities of processing oil (see Appendix) and previous analyses which indicated that the VCM consisted primarily of the oil; time and temperature were also specified by the JPL Cognizant Engineer.

The samples were post-cured under the same conditions as those used for the 143°C runs (*vide infra*) and were exposed *in vacuo* at a temperature of 93°C for a period of 22 hours. The table below summarizes the results of these determinations and clearly indicates that the VCM value is a function of the quantity of oil present in each polymer. Were the VCM value a function of the vapor pressure of the oil (such as obtained from Knudsen cells), the value for each polymer at the same temperature would be the same regardless of quantity of oil in it. The VCM values resulting at increased temperature are larger, but the values nevertheless are commensurate with the quantity of oil present. The table below also shows, as expected, that the ratio of 143°C VCM values to 93°C values is essentially constant since the ratio (within experimental error) is a function of the rates of evaporation at these temperatures.

Nordel A-5411A	-113	-115	-117
24-hr VCM Value at 143°C, g/in^2 X 10^4	590	300	120
24-hr VCM Value at 93°C, g/in^2 X 10^4	74	45	17
Ratio of $\frac{\text{VCM-143}^\circ}{\text{VCM-93}^\circ}$	7.9	6.7	7.0

Figure II-8. View of Plugs after 96-hr VCM Run

Top:	Blank plugs.
Middle:	Plugs showing discoloration from Hypalon A-2411A-2717; in actual appearance, the color is a green-yellow.
Bottom:	Plugs showing condensate of oil from Nordel A-5411A-115.



Identification of Volatile Species - Apparatus and Method

The mass spectrometer employed in this work is a CEC Model 21-103C which has been modified to include an additional sampling system between the normal inlet system and the analyzer tube; this system permits facile interchange of various sampling devices, operation with or without the gold (molecular) leak, a line-of-sight path directly into the analyzing region, and a small working volume (about 80 cc compared with the usual 3-liter expansion system). Ion pumping permits attainment of pressures in the mass spectrometer system of less than 10^{-8} torr.

Because the polymers selected for this program of work generally exhibit low vapor pressures and rates of evaporation, the molecular leak between the sampling system and the ionizing region has been removed so as to increase the over-all sensitivity of the ion-gun. In addition, a mass spectrometer sample probe has been constructed during this program to permit observation of the outgassing characteristics of polymers on a micro scale. The probe is easily introduced into the modified inlet system of the spectrometer and permits location of microgram quantities of samples at a position immediately adjacent to the ionizing region (see Figure II-9). Temperature of the sample is controlled by a heater in the probe (see Figure II-10).

The probe system provides for a collisionless path into the ionizing region of the spectrometer for the volatile substances emanating from a heated material; thus, substances of low vapor pressure or low evaporation rates are detectable. It is anticipated that the mass spectra obtained in this fashion will indicate whether subtle degradation is occurring, or whether "tramp" materials evolve steadily for long periods of time. The use of a probe of this type for study of polymeric systems is an innovation developed under NASA-JPL sponsorship and has been reported to the Technology Utilization Officer.

Samples of about 1 mgm weight are used with the probe. When sample and probe are in place in the cold and vented system, the system is evacuated to about 1×10^{-5} torr; then, the ionizing circuit is activated and a mass spectrum is recorded periodically until the characteristic instrument background spectrum is attained--generally

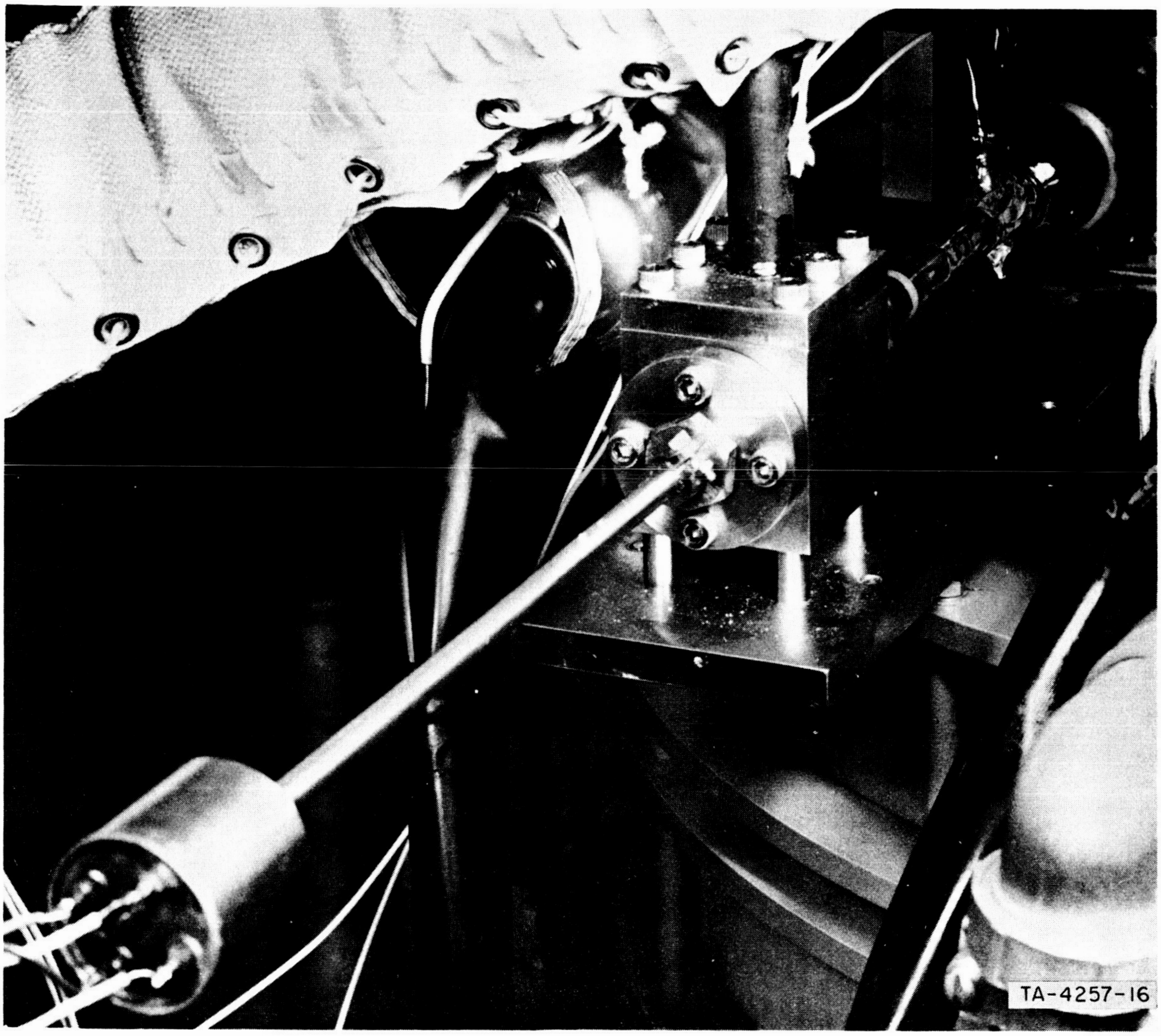


FIG. II-9 MASS SPECTROMETER SAMPLE PROBE FOR POLYMERS SHOWN IN PLACE

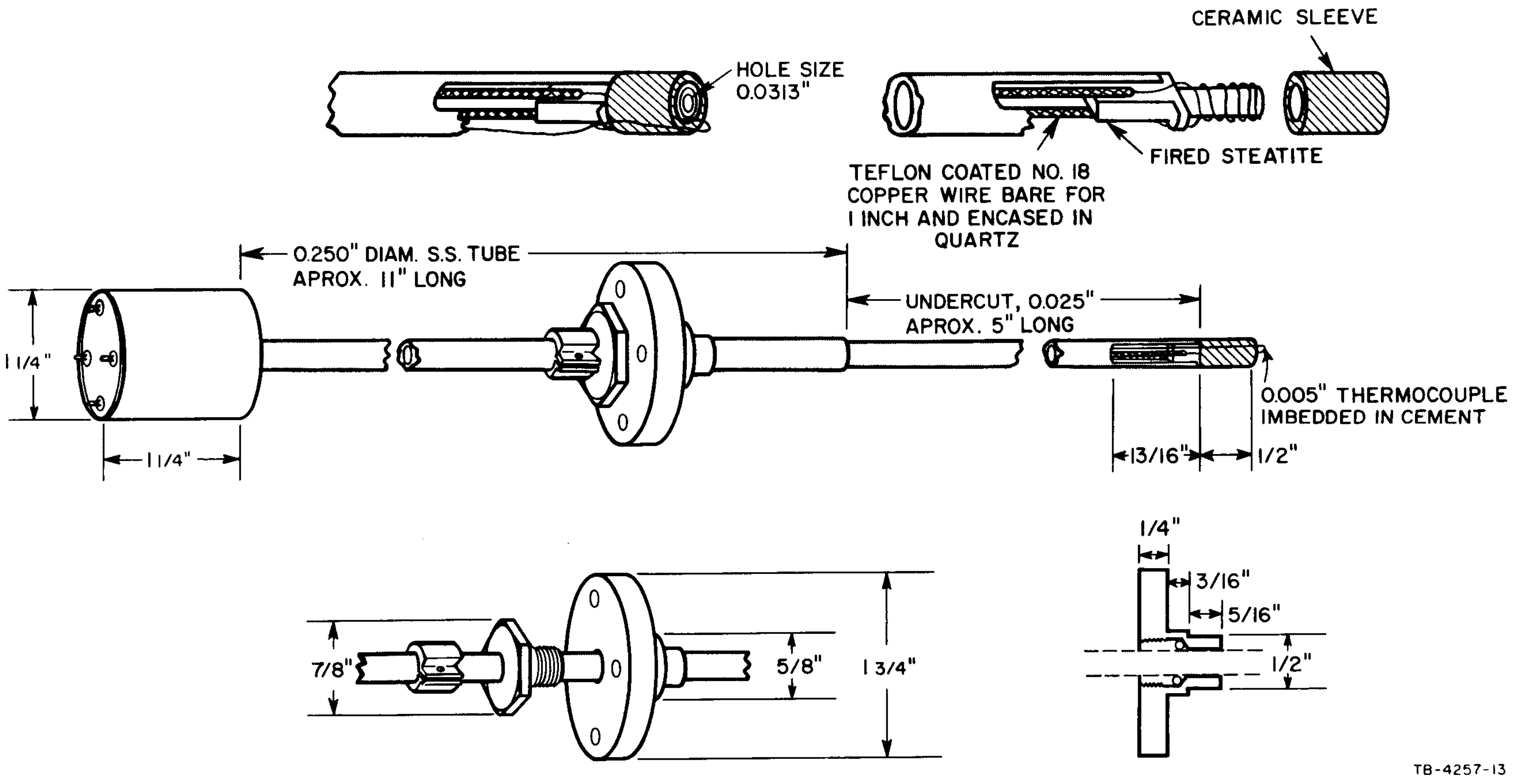


FIG. 11-10 SECTIONED VIEW OF MASS SPECTROMETER SAMPLE PROBE FOR POLYMERS

a period of 24 hours. At this time, the temperature of the sample is raised from about 25°C to the desired temperature within a few minutes and the mass spectrum is recorded immediately. The recording is repeated within a period of 16-24 hours, and every 24 hours thereafter until the spectrum remains essentially unchanged.

Nordel A-5411A-113, -115, -117

Three formulations of Nordel A-5411A elastomers (see Appendix) were studied for outgassing characteristics in vacuum and at a temperature of about 150°C in order to provide an independent check of the VCM determined for these materials in 150°-tests at the Jet Propulsion Laboratory. Since the VCM apparatus used by SRI was designed for operation at 125°C, the determinations were made at 143°C, the maximum achievable temperature. In accordance with instructions, the samples were post-cured at 177°C for 18 hours in air prior to exposure to the vacuum-thermal environment.

Weight loss and VCM data are given in Tables II-1, II-2, and II-3 for Nordel A-5411A-113, -115, and -117. In general, the total weight of VCM is equivalent to or less than the weight loss of the sample depending on the volatility of the material released from the sample. Weight loss and VCM values for Nordel A-5411A-117 are in good agreement, and values for each show good duplication (see Table II-3). On the other hand, the excessive VCM (an oil) released Nordel A-5411A-113 creates difficulties in obtaining equally good VCM values; note particularly the values for the 96-hr run in Table II-1. The oil collected on one plug was pooled and almost heavy enough to drain; the oil pool had apparently drained from the other plug. Additionally, the weight-loss values do not show as good agreement; this, of course, may be due to lack of uniformity of evaporation of the oil in the material. The results and agreements for Nordel A-5411A-115 (5% oil) fall in-between as expected (see Table II-2).

The resilience of the Nordel A-5411A-113 and -115 samples appeared to be little changed after exposure to the vacuum-thermal environment, even after 340-hr exposures. In contrast, the Nordel A-5411A-117 samples exhibited a definite stiffness after the 48-hr and 96-hr exposures, and

Table II-1

VCM AND WEIGHT-LOSS DETERMINATIONS FOR NORDEL A-5411A-113 at 143° C*

(VCM Collector Surface at 25° C)

Time at Temp., Hr.	Sample Weight, g	Weight Loss, %		Total VCM, g		VCM Value at 143°/25° C, g/in.^{2}	
	A- B-	A- B-	Average	A- B-	Average	A- B-	Average
24	3.482072	4.90	4.90†	0.137	0.137	0.059	0.059
	3.311217	-		-		-	
48	3.550925	3.97	3.94	0.126	0.157	0.055	0.068
	3.615450	3.91		0.188		0.081	
96	3.555625	4.70	5.74	0.204	0.120	0.088	0.052
	3.576605	6.78		0.035		0.015	
340	3.478314	5.91	6.36	0.231	0.260	0.100	0.113
	3.399314	6.81		0.291		0.126	

* Samples post-cured at 177° C in air.
Average sample area, 2.31 in.^{2}.

† Single determination (malfunction of duplicate unit).

Table II-2

VCM AND WEIGHT-LOSS DETERMINATIONS FOR NORDEL A-5411A-115 at 143° C*

(VCM Collector Surface at 25° C)

Time at Temp., Hr.	Sample Weight, g	Weight Loss, %		Total VCM, g		VCM Value at 143°/25° C, g/in.^{2}	
	A- B-	A- B-	Average	A- B-	Average	A- B-	Average
48	3.674952	1.93	1.97	0.106	0.091	0.046	0.043
	3.777100	2.00		0.085		0.039	
96	3.292838	2.47	2.53	0.105	0.104	0.046	0.045
	3.432627	2.58		0.103		0.045	
336	3.743790	3.04	3.05	0.124	0.138	0.054	0.057
	3.798033	3.12		0.152		0.060	

* Samples post-cured at 177° C in air.
Average sample area, 2.31 in.^{2}.

Table II-3

VCM AND WEIGHT-LOSS DETERMINATIONS FOR NORDEL A-5411A-117 at 143° C* (VCM Collector Surface at 25° C)

Time at Temp., Hr.	Sample Weight, g	Weight Loss, %		Total VCM, g		VCM Value at 143°/25° C, g/in.^{2}	
	A- B-	A- B-	Average	A- B-	Average	A- B-	Average
24	4.016754 4.444125	0.71 0.78	0.74	0.026 0.029	0.028	0.011 0.013	0.012
48	not run						
96	3.903142 3.968401	1.14 1.11	1.12	0.048 0.038	0.043	0.021 0.012	0.017
340§	4.281712 4.172177	1.14 1.21	1.18	0.052 0.049	0.050	0.024 0.021	0.023

* Samples post-cured at 177° C in air.
Average Sample area, 2.31 in.^{2}.

† Samples quite stiff after this exposure.

§ Sample B was split during the run.

one of the samples (see **Figure II-11**) split at some time during the 340-hr exposure. (Note also the anomalous behavior of Nordel A-5411A-117 reported under Mechanical Properties.)

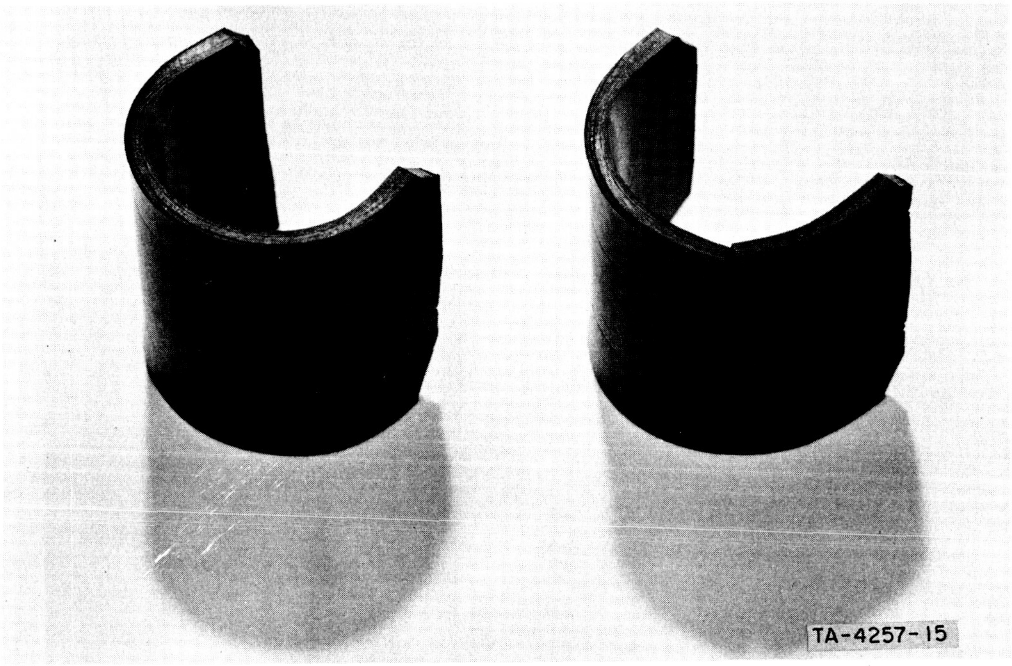

TA-4257-15

FIG. II-11 APPEARANCE OF SAMPLES OF NORDEL AFTER 340-hr VCM RUN

The VCM values for the Nordel samples are plotted in **Figure II-12**). The gradual increase in VCM values from 96 to 340 hours of exposure indicates that the polymers contain a substantial amount of easily volatile materials (primarily an oil of at least C_{27}) and that the Nordel A-5411A-117 contains the least of these materials. (Discussion of this kind of evaporation-condensation behavior is given at the beginning of this Section.)

The outgassing products of Nordel A-5411A-113 were identified by infrared and mass spectroscopy techniques. The VCM from the 96-hr run was sufficiently present to be examined by infrared spectroscopy. The spectra indicated clearly that a hydrocarbon was predominant. For comparison, an infrared spectrum was obtained for an ordinary instrument oil,

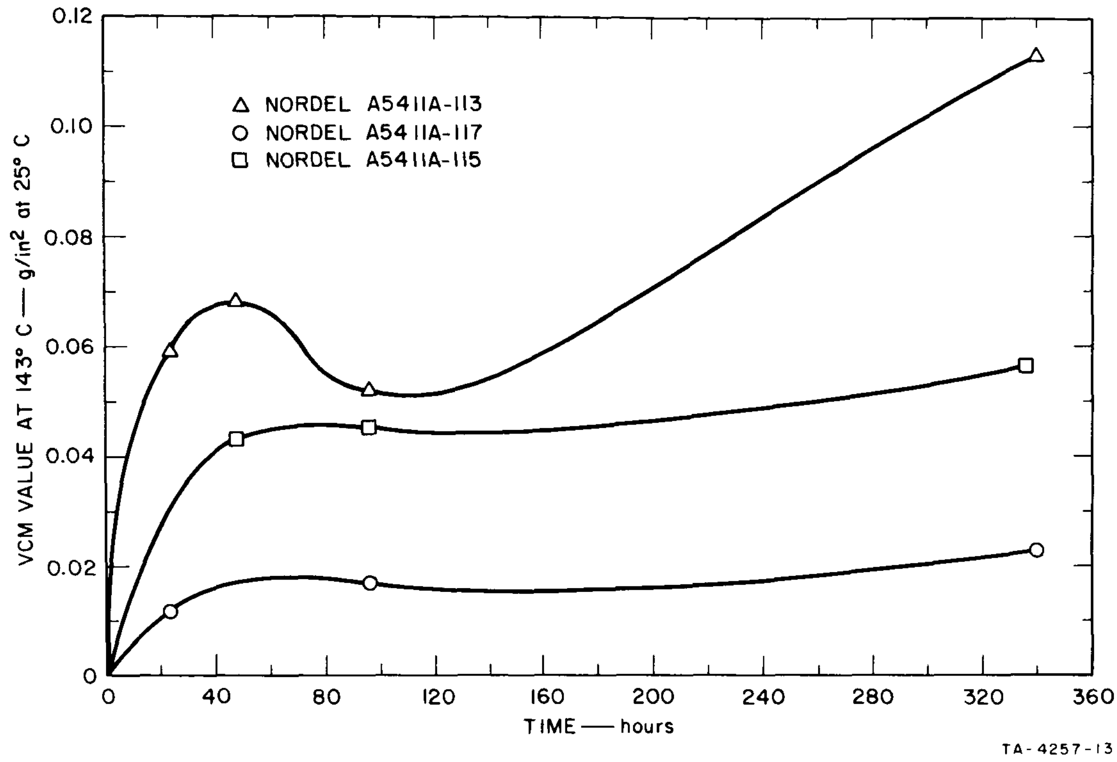
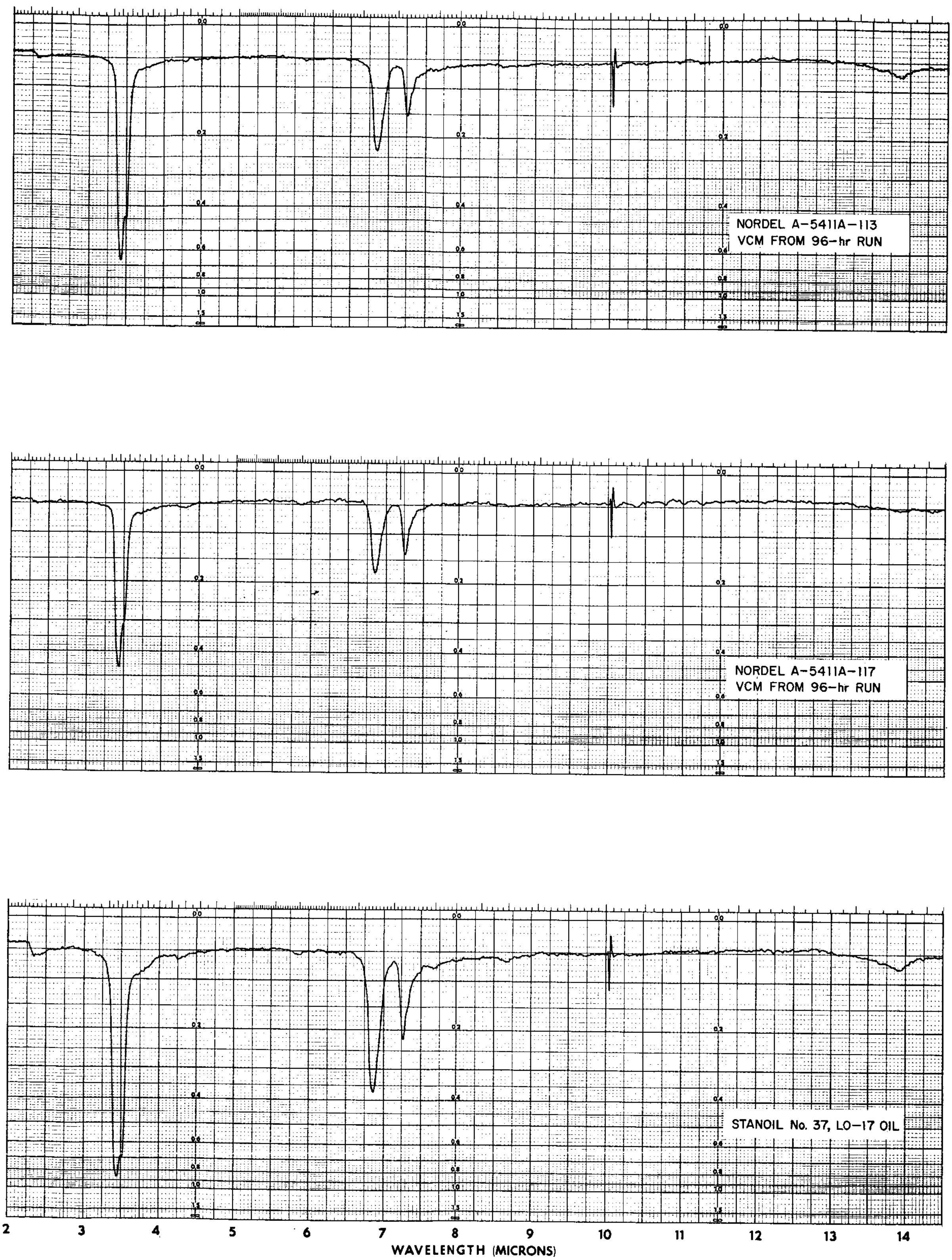


FIG. II-12 VCM VALUES AT 143°/25°C WITH RESPECT TO TIME FOR NORDEL SAMPLES

readily available in the laboratory. Figure II-13 illustrates the infrared patterns for the three materials; hence, the VCM is attributable essentially to the oil (Sun Oil 5150) used in processing the Nordels.

A detailed mass spectrometric analysis of the outgassing characteristics of Nordel A-5411A-113 is given in Table II-4. The long-chain n-alkane hydrocarbon is typical of lubricating oils; the presence of a long-chain aliphatic carboxylic acid is ascribed to the oil itself (such acids are about the only oxygenated compounds thus far isolated from petroleum) since it is doubtful that the origin can be identified with the compounding of Nordel. The terpene, of at least three isoprenoid units, may originate from either the "diene" catalyst used in compounding the Nordel or from incompletely polymerized starting material. A mass spectrometric analysis of Nordel A-5411A-113 in the as-received condition indicated that the presence of CO_2, H_2O, and R-COOH (Table II-4) was not attributable to the post-cure at 177°C in air.



TA-4257-19

FIG. II-13 INFRARED ABSORBANCE OF VCM FROM TWO NORDEL SAMPLES COMPARED WITH AN INSTRUMENT LUBRICATING OIL

Table II-4

MASS SPECTROMETRIC ANALYSIS OF OUTGASSING CHARACTERISTICS OF NORDEL A-5411A-113*

Temp., °C	Time at Temp., Hr	Vacuum, torr	Identification of Products (estimated mol-%)	
150†	0.1	6×10^{-7}	H_2O	50
			saturated hydrocarbons to C_{27}	40
			terpene, to C_{15}	7
			CO_2	2
			aliphatic carboxylic acid to C_{18}	1
150	16	7×10^{-8}	same as above	

* 1.8-mgm sample, post cured at 177°C in air

† Sample was outgassed for 24 hours at 25°C and then raised to 150°C within one hour

Note: Nordel A-5411A-113 in the as-received condition was also analyzed mass spectrometrically; the same products were identified.

Hypalon A-2411A-2717

Duplicate samples of Hypalon A-2411A-2717 (see Appendix) were run concurrently with the Nordel A-5411A-115; hence, this VCM determination also was made at 143°C. In this instance, however, the samples were not subjected to any kind of post-cure.

The Hypalon samples exhibited a definite stiffness after the 336-hr exposure, particularly in contrast to the Nordel A-5411A-115 which was run at the same time.

Weight loss and VCM data are given in Table II-5. The VCM values are plotted in Figure II-14; note the similarity of increase with VCM *versus* time in comparison with the Nordel data (Figure II-12).

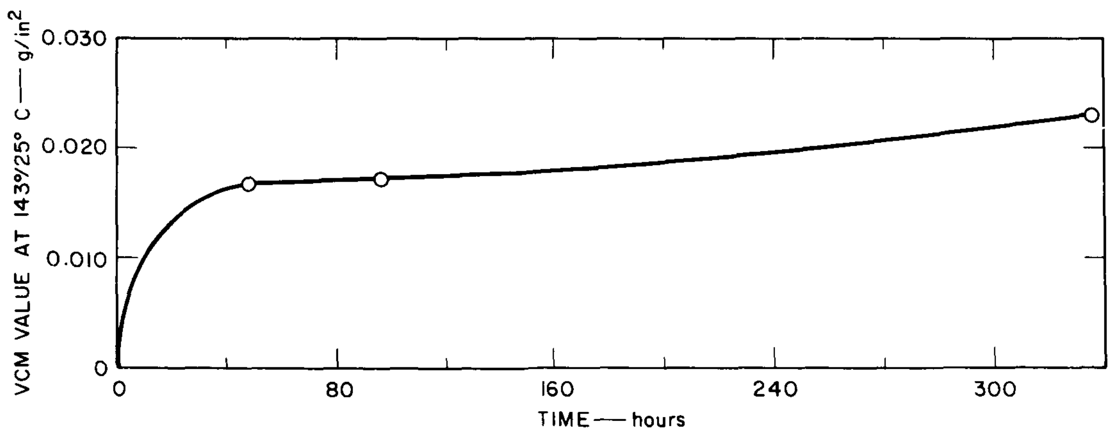
After the 48- and 96-hr exposures, the VCM weight is roughly equivalent to loss in weight. After the 336-hr exposure, however, the VCM

Table II-5

VCM AND WEIGHT-LOSS DETERMINATIONS
FOR HYPALON A-2411A-2717 AT 143°C*
(VCM Collector Surface at 25°C)

Time at Temp., Hr.	Sample Weight, g	Weight Loss, %		Total VCM, g		VCM Value at 143°/25°C, g/in.^{2}	
	A- B-	A- B-	Average	A- B-	Average	A- B-	Average
48	4.572819	0.73	0.76	0.040	0.039	0.017	0.017
	4.414694	0.79		0.037		0.016	
96	4.369907	0.90	0.91	0.042	0.040	0.018	0.017
	4.249205	0.92		0.038		0.016	
336	4.655362	1.23	1.19	0.053	0.053	0.023	0.023
	4.831042	1.15		0.053		0.023	

* As-received
Average sample area, 2.31 in.^{2}



TA-4257-12

FIG. II-14 VCM VALUES AT 143°/25°C WITH RESPECT TO TIME FOR HYPALON A-2411A-2717 weight is about 93% of the weight loss; this would indicate that the polymer is releasing material not condensable at 25°C. This indication is augmented by the results of the mass spectrometric analysis.

The mass spectrometric analysis of the vapor released from the Hypalon is given in Table II-6. The material released immediately at 143°C (other than water) is primarily saturated hydrocarbons but, after 22 hours of exposure at temperature, the predominant species (other than water) is carbon dioxide, with small amounts of hydrocarbons, Cl-containing hydrocarbons, hydrochloric acid, and sulfur compounds. This mixture would indicate either polymeric skeletal breakdown or breakdown of low-molecular-weight polymeric material.

Table II-6

MASS SPECTROMETRIC ANALYSIS OF OUTGASSING CHARACTERISTICS OF HYPALON A-2411A-2717

Temp., °C	Time at Temp., Hr.	Vacuum, torr	Identification of Products (estimated mol-%)	
143	0.1	7×10^{-6}	H_2O	82
			saturated hydrocarbons	14
			CO_2	3
			hydrocarbons containing Cl^-	0.5
			unsaturated hydrocarbons	0.3
143	22	8×10^{-8}	H_2O	62
			CO_2	30
			saturated hydrocarbons	3
			SO_2	2
			hydrocarbons containing Cl^-	1
			CS_2	1
			HCl	1

III. MECHANICAL PROPERTIES OF POLYMERIC MATERIALS

N. Fishman

Continuation of the work reported in the Final Technical Report (December 8, 1963) involved tests on several materials to determine whether changes of mechanical properties occur in a vacuum-thermal environment. The tests may be summarized as follows:

(1) Continuous and intermittent stress-relaxation tests conducted *in situ* in the vacuum-thermal environment.

(2) Constant-strain-rate tests of rings exposed to the vacuum-thermal environments compared with rings stored under ambient conditions.

(3) Continuous and intermittent stress-relaxation tests at elevated temperatures in air.

Before these tests were undertaken, some preliminary investigations were undertaken to resolve some questions which arose during last year's program. These preliminary investigations were concerned primarily with providing assurance that temperatures and pressures measured at the specimen location in the vacuum chamber were valid.

Preliminary Tests

The vacuum chamber previously used for the study of the mechanical properties of polymers in a simulated space environment had been maintained in stand-by operation so that little work was needed to prepare it for extended use. (The vacuum system is described in Interim Report No. 1, June 8, 1963.) The mechanical-property test apparatus, contained in the vacuum chamber, was refurbished in order to assure adequate pumping speed from the heated sample compartments, and sections were rebuilt in order to assure constancy of temperature in the sample region.

The heat-reflecting baffles were reworked and modified; the upper baffle now consists of three copper shields; the upper ones are brightly plated with chromium on all surfaces, and the lowest one is chromium-plated on top and coated with Aquadag on the side facing the sample compartment. This surface thus is a black body and tends to hold the central compartment within the heated space at a constant temperature. Since this shield will be at a lower temperature than the central heating compartment, a polished aluminum cup was interposed between this shield and the sample-holding jaws of the relaxometer; the sides of the cup pick up heat from the sample compartment at a greater rate than heat can be radiated to the lower shield and thus its temperature is essentially that of the sample compartment. The shield in the bottom of the heating compartment is now also chromium-plated and the surface exposed to the sample compartment is covered with Aquadag. This modified construction provides black-body radiating surfaces for the sample compartment. At equilibrium, the temperature of all radiating surfaces should be the same; consequently, a sample mounted in the central region of the cylindrical compartment should achieve the equilibrium temperature very nearly uniformly along its length.

Thermocouples were removed from the lead-in tubes used in the earlier model and reinserted bare through the bottom of each position to minimize the conductive path which had caused erroneously low temperature readings. These changes proved to be effective and temperature gradients were found to be negligible within the relaxometers. It was found necessary to embed each measuring thermocouple junction in a thickness of polymeric material approximately that of the ring specimens to read correct temperatures; the color of the material--white, red, or black--did not appear to have any significant effect. There is confidence that temperature measurement in each position is correct to at least $\pm 1^{\circ}C$.

Previous work had indicated the possibility that tensile properties determined in vacuum may have been different than those determined at atmospheric pressure. Constant-strain-rate tests of Viton B and TFE Teflon, conducted at $125^{\circ}C$ in the vacuum chamber at about 3×10^{-5} torr yielded essentially the same stress-strain curves as those determined at atmospheric pressure. Former discrepancies can be at least partially attributed to erroneous temperature measurement in the vacuum chamber.

Prior to initiating actual testing in the vacuum chamber, load cells and instrumentation were checked and recalibrated and all elements of the system were carefully examined to provide assurance of uninterrupted long-time tests.

Test Results

Continuous and intermittent stress relaxation tests of rings of Viton A-4411A-990 and -991, Nordel A-5411A-113 and -117, and Hypalon A-2411A-2717 and -2718 were conducted in duplicate. Rings of each material were also stored in the relaxed state within the vacuum chamber at the test temperature for later constant strain rate tests. Prior to raising the temperature in the test areas to 125°C, specimens were preconditioned under vacuum at about 50°C for periods ranging from about 200 to 400 hours. Some continuous and intermittent stress relaxation tests were also conducted at 125°C in an air environment.

Results of stress relaxation tests are presented in Figures III-1 to III-8,* inclusive; indicative points are tabulated for comparison in Tables III-1 and III-2.† Rings utilized for stress relaxation tests were weighed before and after each test period; weight losses are shown in Table III-3. The effects of the vacuum-thermal environment on the tensile properties of stored materials are shown in Tables III-4 and III-5.

Time, temperature, and pressure conditions for each test are listed in the footnotes to Table III-3 and also in Table III-5.

Discussion of Results

The results of continuous and intermittent stress relaxation tests can be interpreted to yield information concerning the rates of aggregative and disaggregative reactions occurring upon degradation of rubbery materials. Aggregation includes all those reactions which have the effect of cross-linking or chain lengthening; disaggregation includes chain-scission or cleavage. Cross-linking reactions generally do not

---

* Figures III-1 to III-8 may be found at the end of this Section.

† Tables III-1 to III-5 may be found at the end of this Section.

affect the stress in a continuously stretched sample; thus, the decay of stress at elevated temperatures, occurring in rubbers maintained at constant extension, is a direct measure of the scission reactions alone.

The "net" effect of the cross-linking and scission reactions is measured by allowing the rubber to remain unstrained, as in the intermittent test. In such a test, if the cross-linking reactions are faster than scission, intermittently measured values of stress increase; conversely, if cross-linking is slower than scission, stress decreases. Thus, in Figure III-8 as an example, U is a measure of the fraction of the original network chains uncut after 15 hours of exposure; and X is a measure of the relative concentration of new network links formed by aggregation compared to the original concentration of network chains.

The general configuration of the test results of all the rubber samples tested in the vacuum-thermal environment in this program thus far, as seen in Figures III-1 to III-7, inclusive, consists of the expected decay of stress under continuous strain, and a net increase of stress, after an apparent period of approximately balanced rates of aggregation and disaggregation, in the intermittent test. The slope of the curve of intermittent test data is a qualitative measure of the net rate of aggregation and disaggregation. In general, duplicate results were in close agreement; one exception is noted in the results of tests of Nordel A-5411A-117 (Figure III-2) where erratic data were obtained from one ring of the intermittent test. Such behavior could have resulted from occluded catalyst or other reactant which had a temporizing effect on the cross-linking reactions.

When the rings were removed from the chamber after each test, the appearance of all the materials was about the same. Rings subjected to continuous stress relaxation tests were permanently deformed. The increase in stress shown in the intermittent tests was accompanied by a toughening of the material, although none had yet become brittle.

In examining these data, one should consider how the elastomer is to be used. If the material is normally applied under a tensile strain, results from the continuous test are of greater importance; if the material is relaxed or under slight compression (as in O-rings), the intermittent test provides more directly applicable results. However, as discussed above, the combined results from both tests provide a description of the degradation process of the material.

Specific points from the test data are shown in Table III-1 to provide ready means for comparison of relative stability among the materials. Both batches of Viton appear to be more stable in the vacuum-thermal environment than any of the other materials tested. The net difference between the continuous and intermittent test data is the least for Viton A-4411A-990, with Viton A-4411A-991 being a close second. Continuous test results show the Vitons to be considerably more stable than the other materials. However, if stress decay under strain can be discontinued because of use considerations, Hypalon A-2411A-2718 appears to be the least affected, with Nordel A-2411A-113, Hypalon A-2411A-2717, and Viton A-4411A-990 following in order of decreasing stability. From this point of view, both Viton A-4411A-991 and Nordel A-5411A-17 appear to become too highly cross-linked in this environment.

Figure III-7 is a composite of test results of one batch of each material to illustrate the major differences among the three materials studied. Although the Viton A-4411A-990 appears to show earlier increased cross-linking, the rate is lower than that of the other materials and the net difference between continuous and intermittent curves is seen to be less.

Also included in Figure III-7 are the curves for Viton A-4411A-778 from previous work. The intermittent test was cut short by what appeared to be premature rupture of the ring; stress decay under continuous strain appeared to be considerably more extensive than that of Viton A-4411A-990. This apparent difference should not be too heavily weighted since it is possible that the storage temperature may have been higher than 125°C.

Continuous and intermittent stress relaxation test results for Nordel A-5411A-113 and -117 and Hypalon A-2411A-2717 exposed in air at 125°C are shown in Figure III-8 and in Table III-2. Scission reactions, as indicated by stress decay in the continuous test, appear to be essentially the same, whether in air or in vacuum, except perhaps for the Nordel A-5411A-117 which appeared to experience a somewhat lesser degree of scission in vacuum. Cross-linking proceeded more rapidly in air for both batches of the Nordel, but was substantially reduced in the Hypalon, which showed a net rate of cross-linking less than that of chain scission.

Loss in weight for each of the materials tested is shown in Table III-3. Both batches of Viton again are superior to the other materials from the point of view of outgassing. Nordel A-5411A-113 lost over 10% of weight; if the outgassing products are detrimental to other functions of the spacecraft, only the Vitons appear to be suitable for use.

Results of constant strain-rate tests of rings stored at 125°C in the vacuum chamber are shown in Tables III-4 and III-5. Viton A-4411A-990 again appears to withstand the vacuum-thermal environment better than the others tested, although it is difficult to see much distinction between the two batches of Viton. The exposed rings of Nordel, particularly A-5411A-117, showed considerable increase in modulus and decrease in rupture strain, but the changes observed do not in themselves appear to be so severe as to make these materials unsuitable for use. None of the rings used in the continuous or intermittent stress relaxation tests broke under stress.

The following table summarizes the results discussed above. Apparent suitability for use under the various conditions is indicated by symbols:

"X" = suitable
"O" = unsuitable
"-" = assignment not warranted by test results.

Material	Intermittent Test (use under condition of no strain)	Continuous Stress Relaxation (use under strained condition)	Tensile Properties	Weight Loss
Viton A-4411A-990	X	XX	X	X
Viton A-4411A-991	-	XX	X	X
Nordel A-5411A-113	X	-	-	00
Nordel A-5411A-117	-	-	-	0
Hypalon A-2411A-2717	X	0	not tested	0
Hypalon A-2411A-2718	XX	0	not tested	0

From the above table, it is apparent that of the materials studied in this program, Viton, with a slight edge to A-4411A-990 over A-4411A-991, is the only material which is sufficiently stable for use in a vacuum-thermal environment. However, if the material is to be used in an unstrained condition, and if the outgassing of Hypalon A-2411A-2718 is not disqualifying, then that material might also be suitable for use.

Table III-1

EFFECT OF VACUUM-THERMAL ENVIRONMENT ON STRESS RELAXATION BEHAVIOR OF VITON, NORDEL, AND HYPALON

Material	Intermittent			Continuous		
	Approx. Time to $f(t)/f(o) > 1.0$, hours	$f(t)/f(o)$ at		Approx. Time to $f(t)/f(o) = 0.8$, hours	$f(t)/f(o)$ at	
		20 hrs	500 hrs		20 hrs	500 hrs
Viton A 4411A-990	20	1.01	1.27	20	0.74	0.66
Viton A 4411A-991	3	1.11	1.46	70	0.83	0.76
Nordel A-5411A-113	70	1.0	1.11	1	0.51	0.40
Nordel A-5411A-117	5	1.20	2.48	1	0.65	0.55
Hypalon A-2411A-2717	100	1.0	1.26	0.5	0.48	0.21
Hypalon A-2411A-2717	250	1.0	1.07	0.8	0.52	0.25

Notes:

1. All tests conducted at strains of approximately 0.25.
2. Data obtained from best curves drawn through duplicate test results.
3. Exposure conditions consisted of two stages:

Viton - (a) 325 hours at 50°C and average pressures of from 2×10^{-5} to 7.5×10^{-6} torr (b) up to about 800 hours at 125°C and average pressures of from 2×10^{-5} to 7.5×10^{-6} torr.

Nordel - (a) 425 hours at 50°C and an average pressure of about 7.5×10^{-6} torr (b) up to about 600 hours of 125°C and an average pressure of about 4.5×10^{-6} torr.

Hypalon - (a) 168 hours at 50°C and an average pressure of about 5×10^{-6} torr (b) up to about 800 hours at 125°C and average pressures of from 6×10^{-6} to 3.5×10^{-6} torr.

4. The function $f(t)/f(o)$ is the ratio of the force at time t to the force at time o (the starting time).

Table III-2

EFFECT OF THERMAL ENVIRONMENT ON STRESS RELAXATION BEHAVIOR OF NORDEL AND HYPALON

Material	Intermittent		Continuous	
	Approx. Time to $f(t)/f(o) > 1.0$, hours	$f(t)/f(o)$ at 20 hours	Approx. Time to $f(t)/f(o) = 0.8$, hours	$f(t)/f(o)$ at 20 hours
Nordel A 5411A-113	1	1.2	0.8	0.52
Nordel A 5411A-117	1	1.44	0.8	0.52
Hypalon A-2411A-2717	1 (<1.0)	0.91	0.8	0.44

Notes:

1. All tests conducted at strains of approximately 0.25.
2. Data obtained from tests of single specimens.
3. Environment consisted of one atmosphere of air at 125°C.

Table III-3

WEIGHT LOSS OF RINGS USED FOR STRESS RELAXATION TESTS

Material	50°C Exposure		125°C Exposure		Weight Loss, %, Average of four rings
	Time, hours	Ave. Pressure, torr	Time, hours	Ave. Pressure, torr	
Viton A-4411A-990	325	2×10^{-5} to 7.5×10^{-6}	800	2×10^{-5} to 7.5×10^{-6}	0.075
Viton A-4411A-991	325	2×10^{-5} to 7.5×10^{-6}	800	2×10^{-5} to 7.5×10^{-6}	0.12
Nordel A-5411A-113	425	7.5×10^{-6}	600	4.5×10^{-6}	10.5
Nordel A-5411A-117	425	7.5×10^{-6}	600	4.5×10^{-6}	3.0
Hypalon A-2411A-2717	168	5×10^{-6}	800	6×10^{-6} to 3.5×10^{-6}	3.5
Hypalon A-2411A-2718	168	5×10^{-6}	800	6×10^{-6} to 3.5×10^{-6}	2.5
Nordel A-5411A-113	0		54	760 (air)	1.1*
Nordel A-5411A-117	0		30	760 (air)	0.95*

* Average of two rings

Table III-4

EFFECT OF VACUUM-THERMAL ENVIRONMENT ON TENSILE PROPERTIES OF VITON

Batch No.	History	Test Temp., °C	Stress at Strain of 0.25, psi	Stress at Rupture, psi	Strain at Rupture, in./in.
A-4411A-990	Control	25	127	1495	4.65
	Exposed	25	130	1940	4.85
	Control	125	79	338	2.10
	Exposed	125	102	402	1.64
A-4411A-991	Control	25	116	2180	4.32
	Exposed	25	118	2025	3.92
	Control	125	88	453	1.78
	Exposed	125	115	449	1.37

Notes:
1. All data points are averages of measurements on duplicate specimens.
2. Tests were conducted at an extension rate of 0.1 in./min.
3. Control specimens were stored at normal room conditions for the entire period from specimen preparation to final testing.
4. Exposure conditions consisted of two stages: (a) 325 hours at 50°C and average pressures of from 2×10^{-5} to 7.5×10^{-6} torr, (b) 820 hours at 125°C and average pressures of from 2×10^{-5} to 7.5×10^{-6} torr.

Table III-5

EFFECT OF VACUUM-THERMAL ENVIRONMENT ON TENSILE PROPERTIES OF NORDEL

Batch No.	History	Test Temp., °C	Stress at Strain of 0.25, psi	Stress at Rupture, psi	Strain at Rupture, in./in.
A-5411A-113	Control	25	63	1395	9.31
	Exposed	25	90	1630	7.39
	Control	125	60	305	2.77
	Exposed	125	79	477	2.77
A-5411A-117	Control	25	142	1425	5.09
	Exposed	25	382	1468	3.37
	Control	125	110	632	2.73
	Exposed	125	258	619	1.48

Notes:
1. All data points are averages of measurements on duplicate specimens.
2. Tests were conducted at an extension rate of 0.1 in./min.
3. Control specimens were stored at normal room conditions for the entire period from specimen preparation to final testing.
4. Exposure conditions consisted of two stages: (a) 405 hours at 50°C and an average pressure of about 7.5×10^{-6} torr, (b) 605 hours at 125°C and an average pressure of about 4.5×10^{-6} torr.

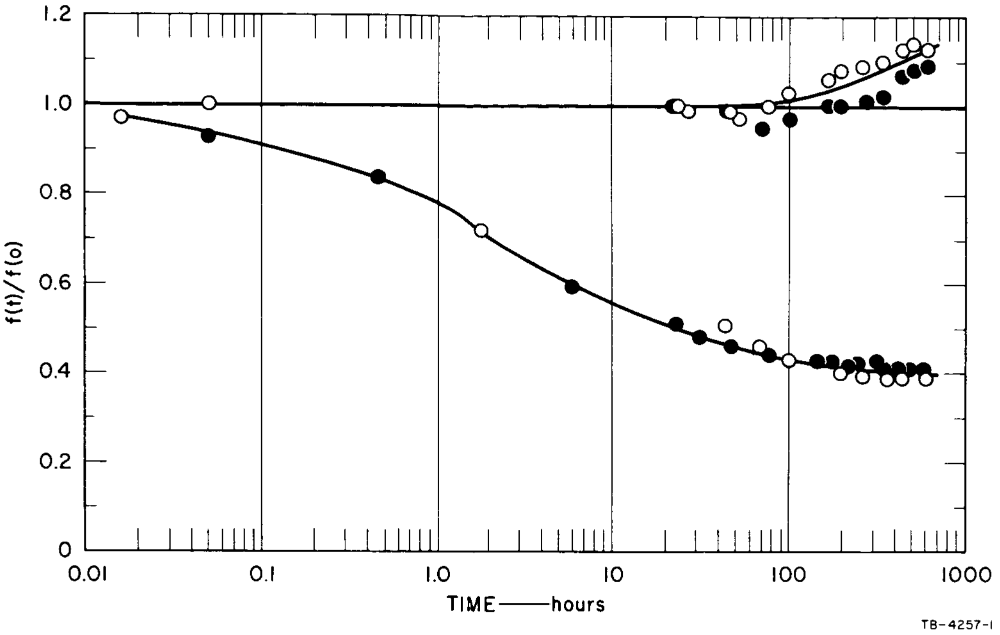


FIG. III-1 CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR NORDEL A-5411A-113 IN VACUUM AT 125°C

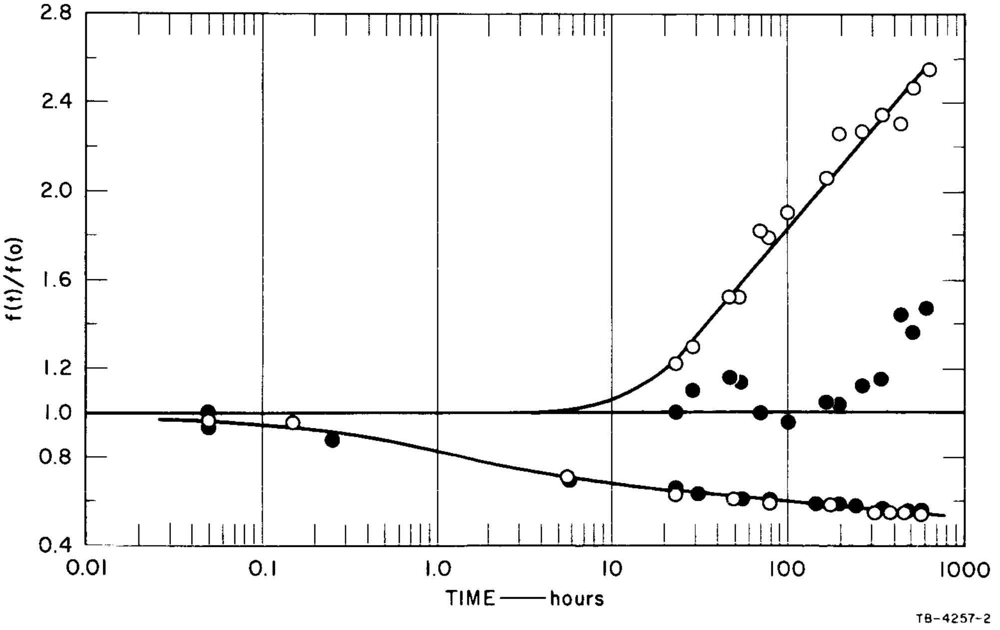


FIG. III-2 CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR NORDEL A-5411A-117 IN VACUUM AT 125°C

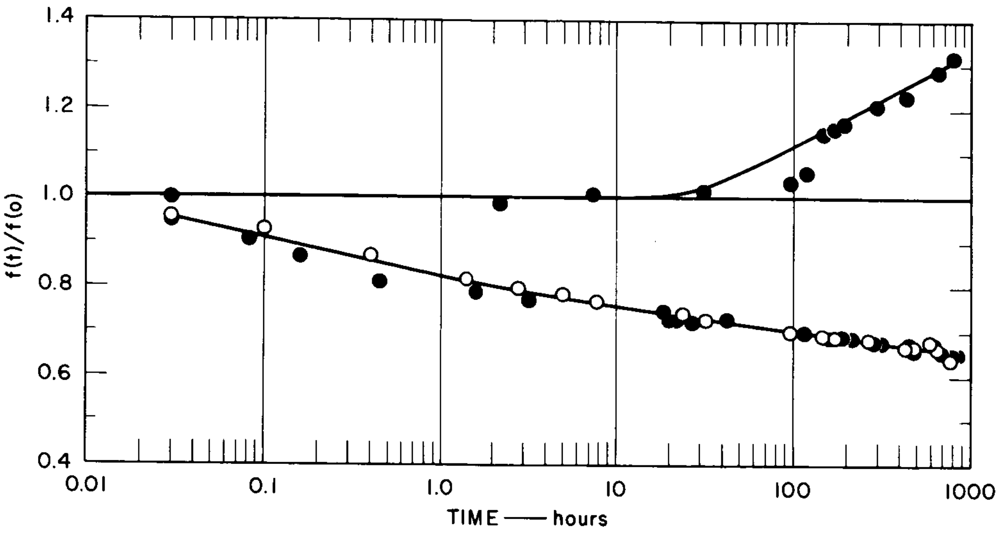


FIG. III-3 CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR VITON A-4411A-990 IN VACUUM AT 125°C

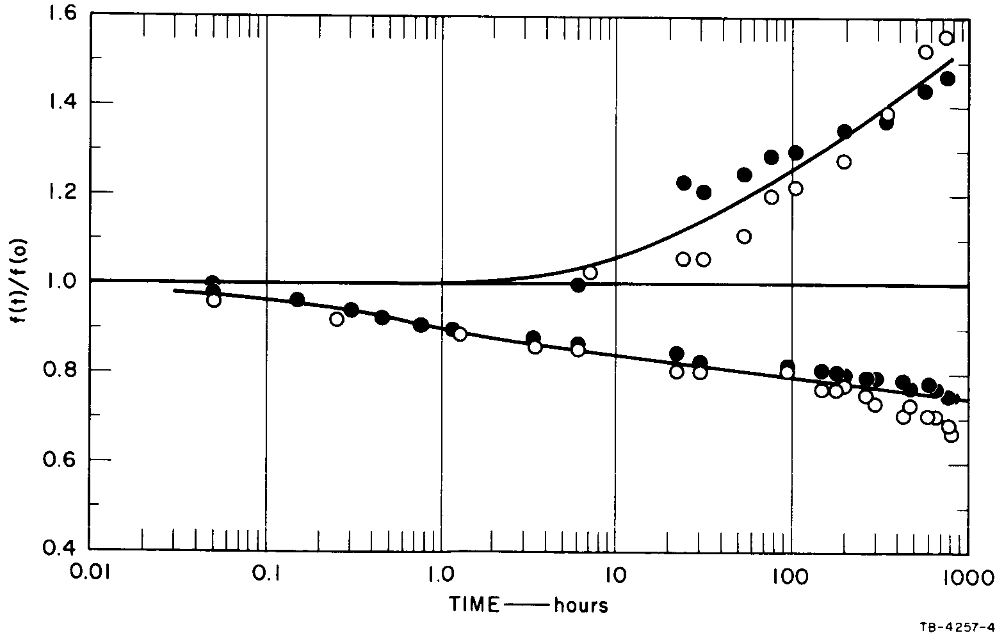
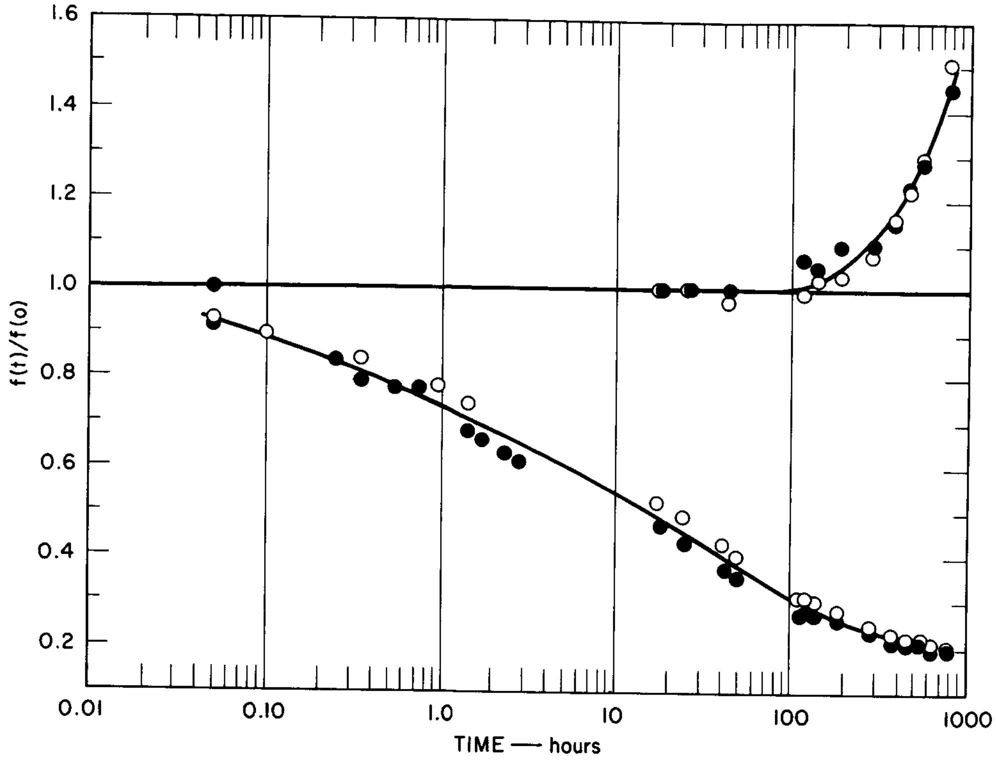
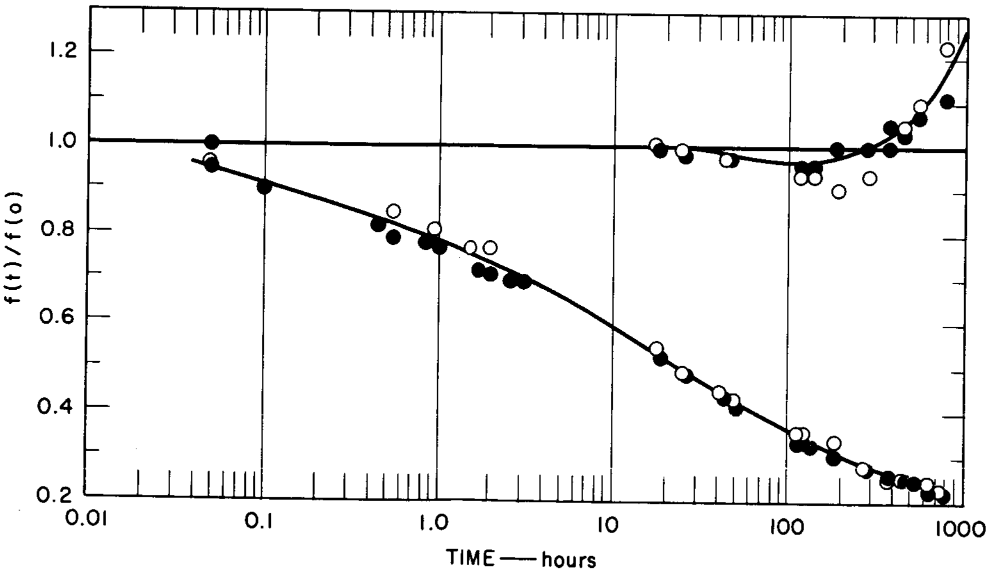


FIG. III-4 CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR VITON A-4411A-991 IN VACUUM AT 125°C



TB-4257-9

FIG. III-5 CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR HYPALON A-2411A-2717 IN VACUUM AT 125°C



TB-4257-10

FIG. III-6 CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR HYPALON A-2411A-2718 IN VACUUM AT 125°C

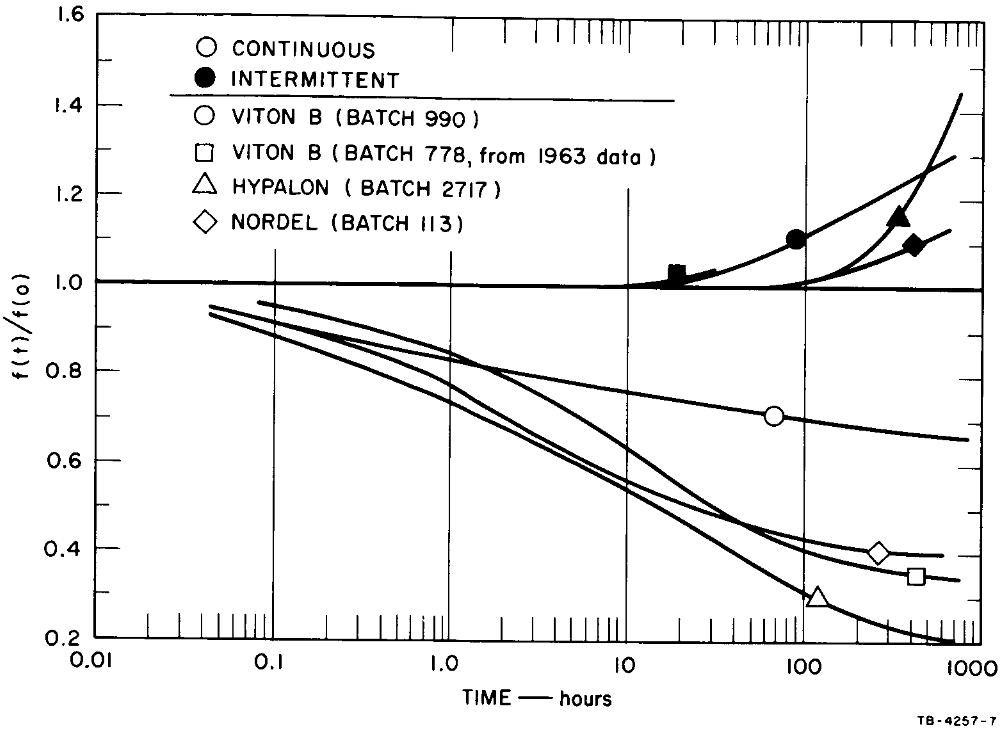


FIG. III-7 COMPARISON AMONG CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR SELECTED BATCHES OF HYPALON, NORDEL, AND VITON IN VACUUM AT 125°C

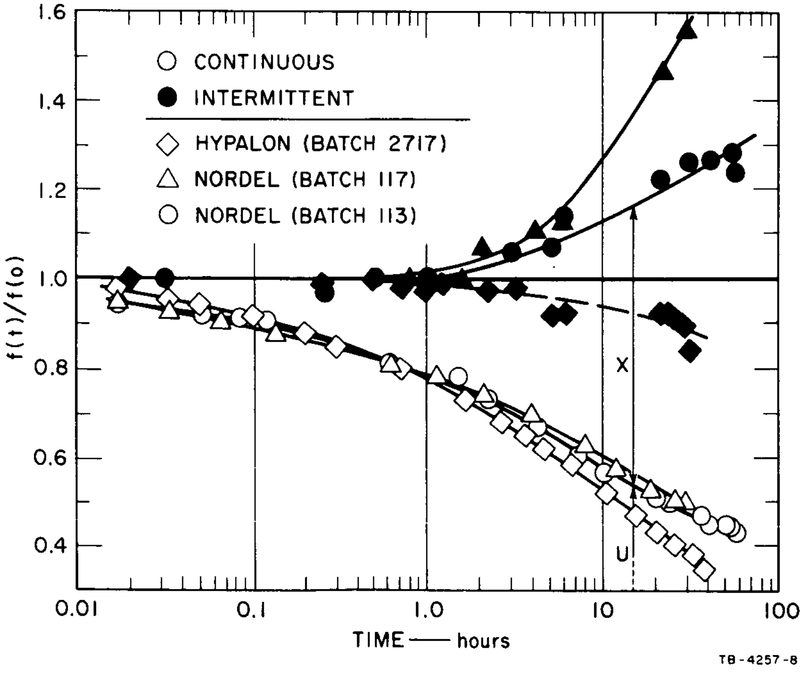


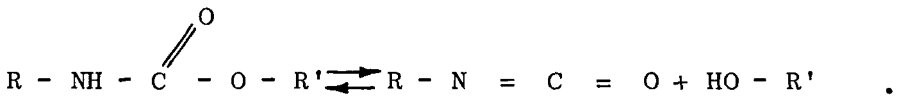
FIG. III-8 CONTINUOUS AND INTERMITTENT STRESS RELAXATION RESULTS FOR HYPALON A-2411A-2717, NORDEL A-5411A-113, AND NORDEL A-5411A-117 IN AIR AT 125°C

IV POLYURETHANE DEGRADATION

J. Heller

Vacuum-thermal degradation of certain selected polyurethanes carried out during the first phase of this program and described in detail in the Final Report of December 8, 1963 has shown that the structure of the polyurethane has a profound effect on both the nature and extent of degradation.

For example, it was found that polymers based on primary amines decomposed at considerably lower temperatures than those prepared from secondary amines. This, of course, is due to the thermal dissociation of the urethane linkage at elevated temperatures, i.e.,



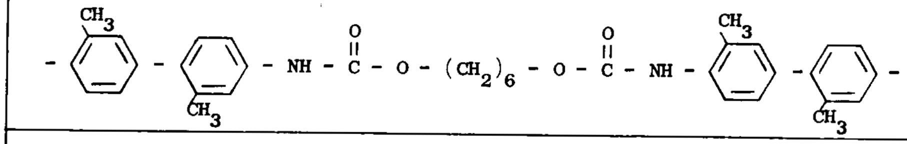
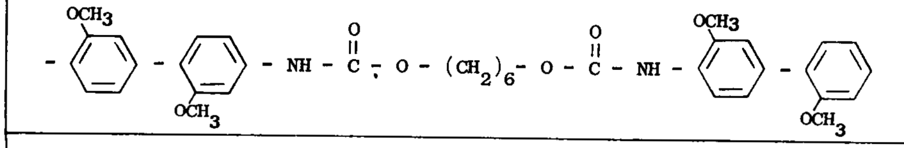
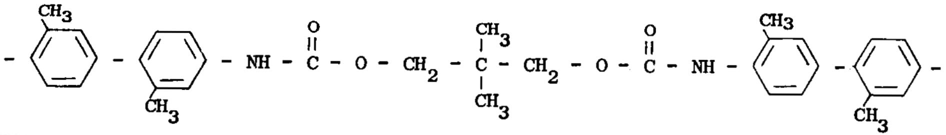
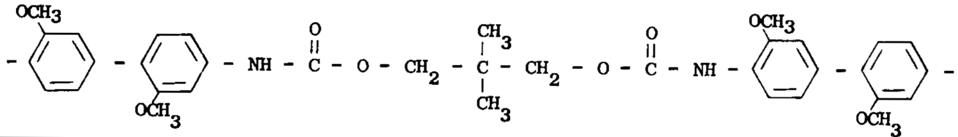
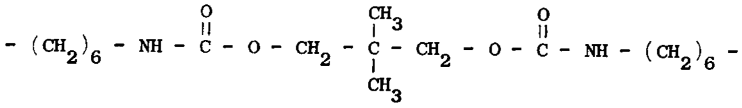
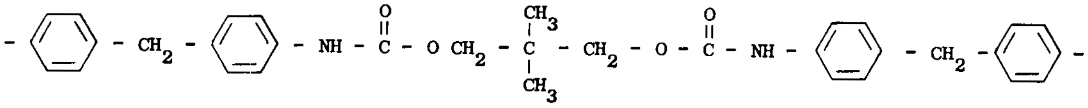
$$R-NH-\overset{O}{\overset{\|}{C}}-O-R' \rightleftharpoons R-N=C=O+HO-R' \quad .$$

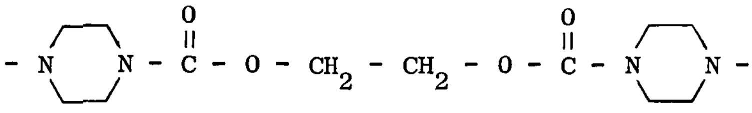
Thus, when this project was resumed, it was decided (1) to synthesize a series of polyurethanes based on primary amines in an effort to ascertain the relative effects of various structural parameters on the stability of the urethane linkage; and (2) to expand the piperazine urethane series. In Table IV-1 are shown the polymers that have been synthesized.

At a later date in the course of the contract, it became necessary to limit the amount of time to be spent on this portion of the program; hence, it was not possible to study the vacuum-thermal degradation of all these compounds. Therefore, it was planned to restrict the studies to the degradation of polymers based on the secondary diamine, piperazine. The following polymer systems were prepared and investigated:

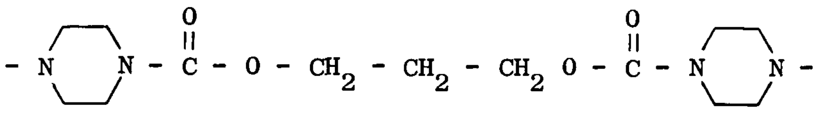
Table IV-1

SYNTHESIZED URETHANE POLYMERS

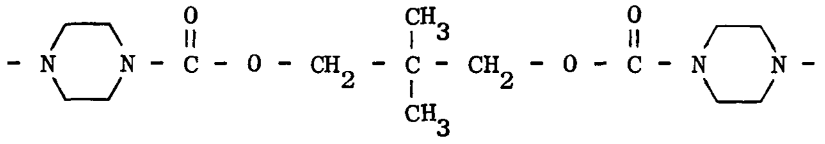
Polyurethane Structure	Film Thickness, microinch	Polymerization Method	Code Designation
	0.40	Solution	DMePP-6U
	0.37	Solution	DMeOPP-6U
	0.21	Solution	DMePP-DMe3U
	0.28	Solution	DMeOPP-DMe3U
 $-(CH_2)_6-NH-\overset{O}{\overset{\parallel}{C}}-O-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-O-\overset{O}{\overset{\parallel}{C}}-NH-(CH_2)_6-$	0.20	Interfacial Polymerization	6 - DMe3U
	0.58	Solution	DDM - DMe3U



I



II



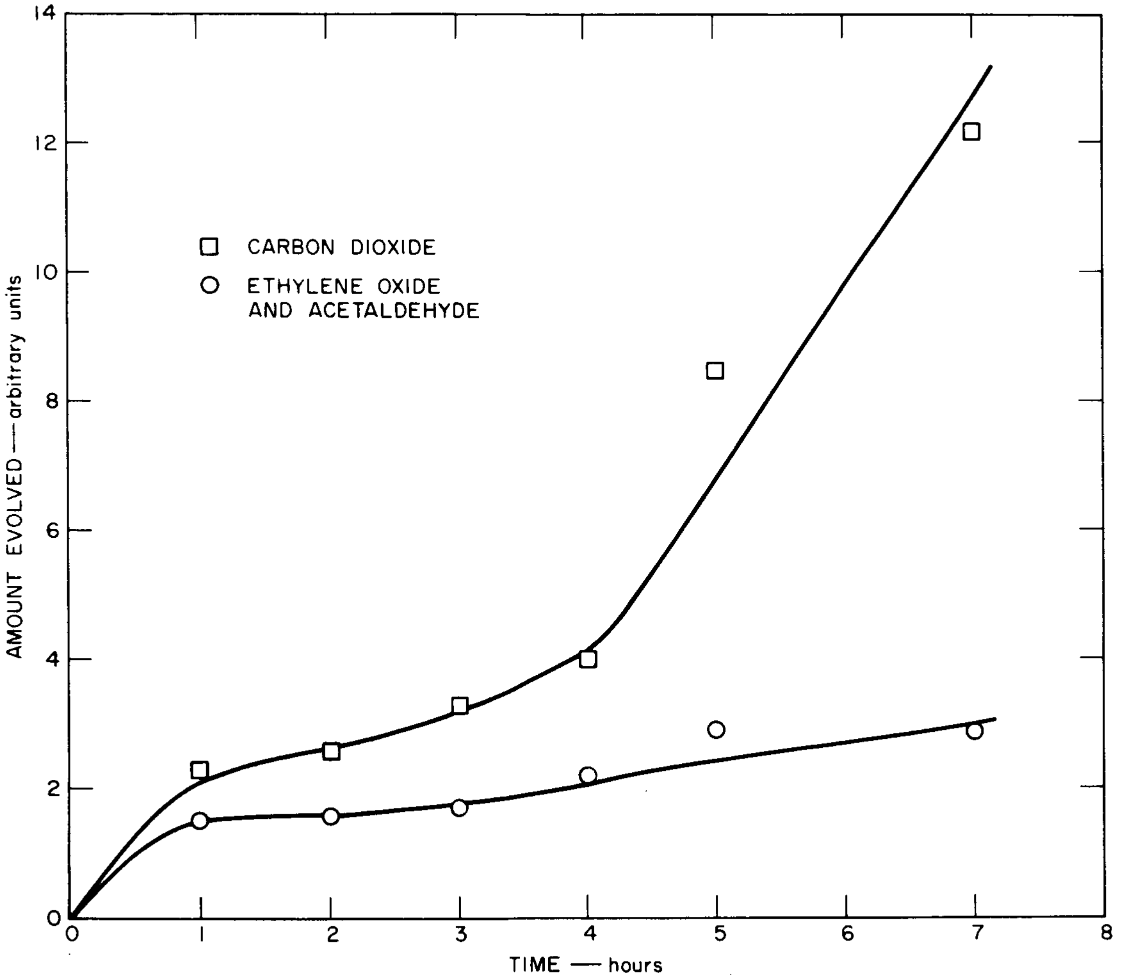
III

Code designations used for these polymers are as follows:
I = pip-2U; II = pip-3U; and III = pip-DMe3U.

The most extensively investigated polymer was pip-2U. Figure IV-1 shows the formation of carbon dioxide and other volatile degradation products (in arbitrary units from identical amounts of starting material) as a function of time when heated to 255°C.

It is interesting to note that the production of volatile products other than carbon dioxide, identified as ethylene oxide and acetaldehyde, reach a more or less steady value early in the reaction while the production of carbon dioxide is relatively slow at first, but then begins to increase rapidly.

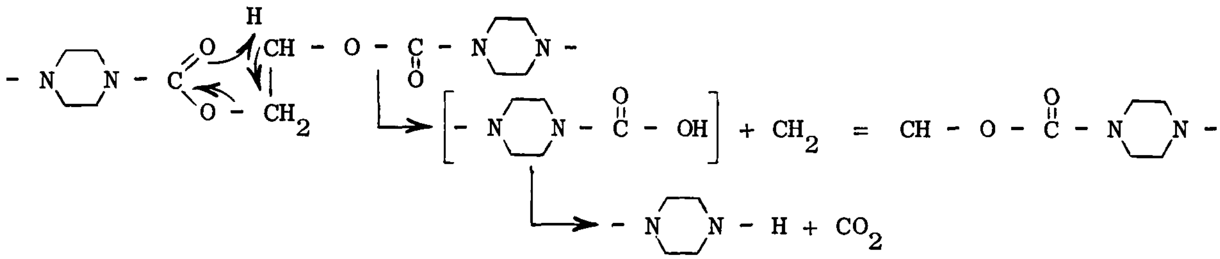
The pip-2U data thus suggest that two different degradation modes may be operative and while a number of hypotheses can, of course, be advanced, it is felt that the data are still too fragmentary to justify any valid conclusions. As mentioned previously, the residues from these degradations remain soluble and are being examined by nuclear magnetic resonance spectroscopy. Unfortunately, at the time this report is written the NMR analysis has not been completed and serious consideration of reaction mechanisms is deferred.



TA-4257-11

FIG. IV-1 EVOLUTION OF GASEOUS PRODUCTS AS A FUNCTION OF TIME FROM THE DEGRADATION AT 255°C OF Pip-2U IN A VACUUM

One of the degradation mechanisms postulated previously involved an elimination reaction similar to an ester pyrolysis, i.e.,



Therefore, an abvious polymer system to be investigated is the pip-DMe3U, where the β-hydrogens necessary for this elimination have been blocked by methyl groups.

A study of the degradation of this system has shown that at 255°C there is indeed very little degradation and that no serious gas evolution takes place before 325°C. At 325°C, significant gas evolution does take place and half of the polymer is converted to volatile products in six hours. The principal gaseous products thus far identified by gas-liquid chromatography and infrared spectroscopy were carbon dioxide and isobutylene. Again, as with the pip-2U polymer, the solid residue remains soluble and mechanistic discussions will have to be deferred until the nuclear magnetic resonance spectrum of the residue is analyzed.

For the sake of completeness, the pip-3U polymer system was also investigated to assure that a three-carbon segment between the urethane linkages has no significant stabilizing effect. Limited degradation data thus far available show this to be true, and, indeed, the pip-3U system seems to degrade at 255°C at a considerably more rapid rate than the pip-2U system.

Work on all three systems is continuing and nearing completion. When this study is completed, the results will be assembled into a manuscript for submittal to the Journal of Polymer Science.

Experimental

1. Polymer Degradation

Standard vacuum techniques were used. The polymer, contained in a glass tube sealed to the vacuum system, was degassed at room temperature until a pressure of 5×10^{-7} torr was attained. At this point (usually 24-48 hours) it was heated by means of a vapor bath around the tube at the desired temperature for a certain length of time.

Gaseous products were collected in a calibrated trap (cooled in liquid nitrogen) which was connected to a manometer so that the total amount of volatile products could be ascertained. The contents of the trap could also be fractionated by warming to dry ice-acetone temperature and allowing products volatile at that temperature, such as carbon dioxide, to condense into another calibrated trap cooled with liquid nitrogen. Analysis of the volatile products could be achieved by condensing them into a small bulb which was then connected to a gas-sampling valve of a gas-liquid chromatograph or to a mass spectrometer. The volatile products could also be transferred to a 10-cm gas cell and analyzed by infrared spectroscopy.

2. Polymer Synthesis

Polymers were synthesized by solution polymerization or interfacial polymerization techniques, as described in past reports.

V. SPECIAL BIBLIOGRAPHY

J. S. Whittick

The Special Bibliography, entitled "Effects of Spacecraft Environments on Polymeric Materials," was issued as a separate publication on January 15, 1965. The content of the bibliography is indicated by citation of the Abstract:

> "Literature on the behavior of polymeric materials under service conditions within a spacecraft has been collected and reviewed. The restricting parameters for selection of citations were environmental conditions of pressure of 10^{-5} mm of Hg or less and temperatures of 25 to 125 °C; 40 references are given. The references are annotated with regard to general disclosure, experimental procedures, and conclusions. An Analytical and Subject Index is also provided."

As a means of analyzing the state-of-the-art in the field of testing polymeric materials under simulated spacecraft environment, the experimental conditions utilized and the tests employed by various workers were summarized and tabulated (see Table V-I and References). A discussion of the results of this analysis is given.

Table V-1

EVALUATION OF POLYMERS FOR SPACECRAFTS; SUMMARY OF ENVIRONMENTAL PARAMETERS AND PHYSICAL TESTS USED BY VARIOUS WORKERS

Pressure mm of Hg	Temperature °C	Exposure Hours	Weight Loss		Mech. Prop.		Phys. Prop.		Gas Analysis		Residue Analysis	Reference
			Ext.*	in situ	Ext.*	in situ	Ext.*	in situ	Ext.*	in situ		
10^{-6}	20-30	2000					x		x		x	2
10^{-6}	120	250					x		x		x	2
10^{-6}	35-100	20-30					x		x		x	3
10^{-6}	25-100	50+								x		6
10^{-7}	80	100			x			x				7
10^{-6}	70-95	30-100		x			x			x		8
10^{-10}	35-300	~						x				9
10^{-6}	to 140	168	x									10
10^{-7}	140	~		x		x						11
10^{-6}	25	12		x						x		12
10^{-7}	to 400	168-300			x				x			13
10^{-5}	120	~			x			x				13
10^{-2} to 10^{-5}	93-225	1-1/2-6	x		x		x		x			14
10^{-6}	25	~						x				16
10^{-6}	50-100	25-170	x									17
10^{-6}	26-260	48		x								18
10^{-3} to 10^{-7}	25-180	~					x					22
10^{-7}	100	100	x							x		23
10^{-5}	25-325	96	x									24
10^{-5}	25-325	24	x				x					25
10^{-5} to 10^{-7}	125	50-1000	x			x	x			x		26
10^{-5} to 10^{-6}	70-150	120-168			x							27
to 10^{-7}	to 225	100		x		x						29
10^{-6}	to 140	24	x				x		x		x	30
10^{-9}	25	1000		x								31
10^{-6}	100	~		x								32
10^{-5}	27	24-770	x		x							33
10^{-5}	100-400	4									x	34
10^{-3}	95-375	300	x		x		x					35
10^{-6}	21-185	3-24	x		x							36
10^{-6}	150	24	x		x		x					37
10^{-6}	125	24	x			x						38
10^{-6}	25-200	24-100		x			x					40

* Ext. = external, measurement made before and after exposure.

REFERENCES

1. Achhammer, B. G., "Polymer Degradation Studies by Absorption and Mass Spectrometry," Anal. Chem., 24, 1925 (1952).
2. Achhammer, B. G., Reiney, M. J., Wall, L. A., and Reinhart, F. W., "Study of Degradation of Polystyrene by Means of Mass Spectrometry," J. Polymer Sci., 8, 555 (1952).
3. Achhammer, B. G., Reinhart, F. W., and Kline, G. M., "Mechanism of the Degradation of Polyamides," J. Res. of Natl. Bur. Stds., 46, 391 (1951).
4. Achhammer, B. G., Tryon, M., and Kline, G. M., "Chemical Structure and Stability Relationships in Polymers," Modern Plastics, 37, 131 (1959).
5. Anonymous, "Ultrahigh Vacuum Made to Order Can Pretest and Qualify Materials for Space Flights," Western Aerospace, March 1963.
6. Barton, R. S., and Govier, R. P., "A Mass Spectrometric Study of the Outgassing of some Elastomers and Plastics," United Kingdom A.E.A.R. Group Report, No. CLM-R16, 1962.
7. Blackmon, P. H., Clauss, F. J., Ledger, G. E., and Mauri, R. E., "Materials Evaluation Under High Vacuum and Other Satellite Environmental Conditions," Lockheed Report No. 3-77-61-23, January 1962.
8. Boebel, C., Mackie, N., and Quaintance, C., "Materials for Space Vehicle Use," Transactions of the Tenth Vacuum Symposium, The MacMillan Co., New York, 1963, p. 59.
9. Bonis, L. J. and Ansell, G. S., "Materials Selection and Development for Application in Inter-Planetary Vehicles," Transactions of the Ninth Vacuum Symposium, the MacMillan Co., New York, 1962, p. 286.
10. Boundy, R. A., "Selection of Plymeric Materials for Spacecraft Application," JPL Section Report No. 353-1, October 15, 1962.
11. Cardarelli, N. F., "Space Suit Materials Testing Program," Institute of Environmental Sciences Proceedings, April 11, 12, and 13, 1962, p. 363.
12. Caruso, S. V., and Looney, W. C., "A Study of the Outgassing and Evaporation Products of Some Materials Upon Exposure to Reduced Pressure," Marshall Space Flight Center, MTP-P&VE-M-62-7, April 2, 1962.
13. Colner, W. H., "Space--a New Environment for Materials," Materials Research and Standards, 2, 656 (1962).

14. DeWitt, E. A., Podlaseck, S., and Suhorsky, "Effect of Low Pressure at Elevated Temperatures on Space Vehicle Materials," The Martin Co., Report RM-29, March 1959.

15. Forsyth, P. F., "Vacuum Considerations of Space Environment," Bell Aerosystems Co., Report No. 8500-920002, 15 January 1962.

16. Frisco, L. J., "Dielectrics for Satellites and Space Vehicles," Johns Hopkins University, Report No. 3, DA Project 3A-99-15-001, March 30, 1962.

17. Fulk, M. M., and Horr, K. S., "Sublimation of Some Polymeric Materials in Vacuum," Transactions of the Ninth Symposium, The MacMillan Co., New York, 1962, p. 324.

18. Gloria, H. R., Stewart, W. J., and Savin, R. C., "Initial Weight Loss of Plastics in a Vacuum at Temperatures from 80° F to 500° F," NASA TN D-1329, December 1962.

19. Goetzel, C. G., and Singletary, J. B., Editors, "Space Materials Handbook," (AF 04(647)-673), Lockheed Missiles and Space Company, Sunnyvale, California, 1962.

20. Happe, R. A., in: "Mechanical Design of Spacecraft," Seminar Proceedings, Jet Propulsion Laboratory, August 1, 1962, p. 55.

21. Jaffe, L. D., and Rittenhouse, J. B., "Behavior of Materials in Space Environments," Jet Propulsion Laboratory Technical Report No. 32-150, November 1, 1961.

22. Jensen, Niels, "Vapor Pressure of Plastic Materials," J. Appl. Phys., 27, 1460 (1956).

23. Jolley, C. E., and Reed, J. C., "The Effects of Space Environments on Insulation of Teflon TFE and FEP Resins," presented at Eleventh Annual Signal Corps Wire & Cable Symposium, Asbury Park, New Jersey, November 28-30, 1962.

24. Matacek, G. F., "Vacuum Volatility of Organic Coatings," First Symposium, Surface Effects on Spacecraft Materials, John Wiley & Sons, New York, 1960, p. 263.

25. Mattice, J. J., "The Decomposition of Organic Resins at High Temperature in a Vacuum Environments," Coating for the Aerospace Environment, WADD TR 60-773, July 1961, p. 107.

26. Muraca, R. F., et al., "Space Environment Effects on Polymeric Materials," Final Report, Stanford Research Institute Project 4257, December 8, 1963.

27. Ossefort, Z. T., and Ruby, J. D., "The Effects of a Simulated Space Environment on the Properties of Elastomers," Proceedings of Fifth National Meeting, Institute of Environmental Sciences, April 6-7, 1961.

28. Podlasek, S. E., and Kramer, I. R., "Effects of Vacuum Environment on the Mechanical Behavior of Materials," The Martin Company, Report No. RM-102, October 1961.

29. Podlasek, S. E., Suhorsky, J., and Kramer, I. R., "The Behavior of Organic Materials under Simulated Space Environment Conditions," The Martin Co., Report No. RM-130, December 1962.

30. Ringwood, A. F., "The Behavior of Plastic Materials in the Space Environment," GE Tech. Info. Series, No. 63SD243, March 11, 1963.

31. Rivera, M., Fassell, W. M., Jr., and Jensen, J., "The Low-Pressure Gas Desorption of Some Polymeric Materials," Transactions of the Ninth Vacuum Symposium, The MacMillan Co., New York, 1962, p. 342.

32. Robens, E.,Robens, G., and Sandstede, G., "Measurement of Sorption, Vaporization, and Decomposition of Materials Used in Vacuum Technology by Means of an Electromagnetic Microbalance," Vacuum, 13, 303 (1963).

33. Snyder, C. E., and Cross, W. B., "Theoretical and Experimental Evaluation of Polymeric Materials for Use in a Space Environment," Coatings for the Aerospace Environment, WADD TR 60-773, July 1961, p. 75.

34. Stromberg, R. R., Strauss, S., and Achhammer, B. G., "Infrared Spectra of Thermally Degraded Poly (Vinyl Chloride)," J. Res. Natl. Bur. Stds., 60, 147 (1958).

35. Thomas, J. P., and Stout, R. J., "Effects of Elevated Temperature and Reduced Atmospheric Pressure on Adhesives, Potting Compounds, and Sealants," General Dynamics/Fort Worth, Report No. ERR-FW-129, 30 December 1961.

36. Vanderschmidt, G. F., and Simons, J. C., Jr., "Material Sublimation and Surface Effects in High Vacuum," First Symposium, Surface Effects on Spacecraft Materials, John Wiley & Sons, New York, 1960, p. 247.

37. Wahl, N. E., and Lapp, R. R., "The Effects of High Vacuum and Ultra-violet Radiation on Plastic Materials," WADD TR 60-125, July 1960.

38. Wahl, N. E., Lapp, R. R., and Haas, F. C., "The Effects of High Vacuum and Ultraviolet Radiation on Nonmetallic Materials," WADD TR 60-125, Part II, June 1962.

39. Wall, L. A., and Flynn, J. H., "Degradation of Polymers," Rubber Reviews, 35, 1157 (1962).

40. Whipple, C. L., and Curtindale, E. G., "Performance of Silicone Materials in Thermal-Vacuum Environment," Transactions of the Tenth Vacuum Symposium, The MacMillan Co., New York, 1963, p. 63.

VI. FUTURE WORK

The program of work to provide engineering information on the behavior of polymeric materials in simulated spacecraft environment (VCM and mechanical properties) will be continued under a new contract.

VCM values for Hypalon A-2411A-2718 and Viton A-4411A-778 will be obtained in order to attempt correlation of these values with the date obtained from studies of the mechanical properties of the polymers. Subsequently, Vitons A-4411A-990 and -991, as well as Silicones SE-555 and -3604 will be studied for correlation with mechanical properties measurements.

Continuation of the work on mechanical properties will include:

(1) Completion of vacuum-thermal studies of Silicone elastomers SE-555 and SE-3604, currently in progress.

(2) Constant strain rate tests of Hypalon A-2411A-2717 and -2718 and Silicone SE-555 and -3604 rings, both controls and those exposed to the vacuum-thermal environment.

(3) Continuous and intermittent stress relaxation tests of Viton A-4411A-990 and -991 and Silicone SE-555 and -3604 elastomers in air at 125°C.

Studies of the mechanisms of polymer degradation at elevated temperatures will not be continued at this time in view of the findings that none of the polymers studied during the course of this program have indicated skeletal breakdown at the temperatures expected within a spacecraft.

Appendix

COMMERCIAL POLYMER FORMULATIONS

NORDEL (Du Pont)

General Composition: Ethylene propylene terpolymer with a diene

A5411A-	113	115	117
Nordel 1070	100	-	-
Nordel 1040	-	100	100
Zinc Oxide	20	20	20
SRF Black	70	70	70
Sun Oil 5150	30	10	1
Thionex	1.5	1	1
MBT	2	2	2
Sulfur	0.8	0.8	0.8
Hypalon-40	-	5	5
Cure:	30'/307° F	30'/307° F	30'/307° F

VITON (Du Pont)

General Composition: Vinylidene fluoride
and hexafluoropropylene

A4411A-	778	990	991
Viton B	100	100	100
Maglite Y	15	20	15
Mt Black	20	20	20
Diak #4	-	2	-
Diak #3	3	-	2
Cure:	30'/320° F	30'/310° F	30'/300° F
Post-cure:	24 hr/450° F	24 hr/400° F	

HYPALON (Du Pont)

General Composition: Chlorosulfonated polyethylene

A2411A-	2717	2718
Hypalon-40	100	100
Sublimed litharge	20	20
Maglite D	-	20
MBTS	0.5	0.5
Tetrone A	0.75	0.75
NBC	3	3
SRF Black	25	25