POLYMERIC FILMS FOR SEMICONDUCTOR PASSIVATION

By
S.M. Lee

March 1969

Prepared Under Contract No. NAS 12-2011 By

AUTONETICS DIVISION
NORTH AMERICAN ROCKWELL
Anaheim, California

Electronics Research Center
National Aeronautics and Space Administration

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POLYMERIC FILMS FOR SEMICONDUCTOR PASSIVATION

By S. M. Lee

Autonetics Division of North American Rockwell Corporation
Anaheim, California

SUMMARY

Test results demonstrate that Parylene functions as an excellent barrier coating material for semiconductor devices. Extended electrical stressing at 175 C indicated that no failures occurred when any of the three Parylenes were used as coatings on "Rel-chips."

The Reliability chip (Rel-chip) designed and developed at Autonetics enables an investigator to determine immediate and magnified changes in critical electrical parameters of MOS and IC devices. This was used to study the effects of Parylene on semiconductor surfaces.

The performances of Parylene-coated MOS FET's on the Rel-chip were compared to those made by the standard "canned" process under the following stress conditions: (1) increasing temperature storage; (2) -25 volts on the P-regions; (3) -20 volts on the P-regions and +20 volts on the gate; and (4) no stress (control). All stressed devices were exposed for 16 hours consecutively at 100, 125, 150, 175 C, and finally 128 hours at 175 C. The most sensitive electrical parameters (V_{GST}, I_{DSS}, BV_{DSS}, BV_{SDS}) of the MOS FET's were measured after each of the above thermal and electrical stresses.

The results indicate that changes in the electrical parameters were negligible on most of the devices after they were subjected to the various stress conditions. The average threshold voltage shifted less than 0.1 volt, the breakdown voltage changed less than one volt and the leakage currents drifted within a few picoamperes for all groups. The only noticeable change resulted with the severest stress on the Parylene N coating group.

Vacuum deposition equipment for Parylene was designed and fabricated. Then a series of experiments using Parylene C, D, and N were conducted to optimize coating process variables on several different types of substrates.

Thickness measurements were made after coating at various locations throughout the chamber. By using a baffle and extending the preheat zone, very clear films were prepared of uniform thickness and free from unreacted dimer.

A satisfactory technique for the application of pinhole-free coatings of Parylene has been achieved. This technique involves pretreatment of the surface with A-174 silane adhesion promoter, followed by vacuum deposition of Parylene. Coatings have been applied to Rel-chips, stainless steel disks, platinum disks, matrix

and "Y" connector boards, and glass slides. Pinholes have been determined utilizing a simple, nondestructive, electrographic procedure.

An analysis of the results obtained from the moisture insulation studies indicated that the insulation resistance of connector boards coated with Parylene C appears to reach a maximum value of 40 x 10^8 Ω with coatings of about 10 microns. Connector boards treated with A-174 silane promoter prior to coating with 1 and 2 microns thick Parylene D films exhibited insulation resistance that was an order of magnitude difference greater than the untreated boards. Insulation resistance changes of a Parylene C and polyurethane coating were compared during exposure to a ten-day period of humidity.

Physical properties of thin Parylene films were measured; these include: thermal conductivity, moisture vapor permeability, water extract resistivity, and outgassing.

INTRODUCTION

Polymers have been developed and made available that are capable of being deposited as ultrathin, chemically inert, and pinhole-free, barrier layers. The introduction of these improved, high-purity, polymeric films made it important to assess the feasibility of employing this coating as either a replacement or an adjunct to inorganic passivation layers or as a barrier coating capable of maintaining the semiconductor surface free of moisture, ions, and other contaminants. The polymeric coating in direct contact with the semiconductor device plays a more critical role than the conventional hermetic package where the gas ambient serves as a buffer and protective agent. It was the purpose of this investigation to evaluate the suitability of using Parylene coatings (poly-para-xylylenes) as insulation and barrier coatings to be applied over inorganic passivation layers.

Acknowledgments

This report was prepared by the Autonetics Division of North American Rockwell in fulfillment of National Aeronautics and Space Administration-Electronics Research Center, Contract NAS 12-2011.

Dr. Stuart M. Lee was the Project Supervisor, and this report covers work accomplished during the period of 1 July 1968 to 30 April 1969.

The author wishes to thank Mr. Irving Litant, the cognizant NASA-ERC Program Monitor, Union Carbide personnel, for their many contributions and assistance and Mr. Charles Chitjian for assistance in performing the laboratory studies contained herein.

MICROELECTRONIC DEVICE TESTING

To study the effects of temperature and electrical stress on semiconductor devices coated with various Parylenes, the Rel-chip designed and developed at

Autonetics was chosen. This enables an investigator to determine immediate and magnified changes in critical electrical device parameters for MOS and IC devices. The Rel-chip is a 44-mil-square pattern (Figure 1) containing chosen electrical parameters that are not obscured by the usual electrical background measurements and that become apparent after subjection to stress or environmental exposure. The devices on the Rel-chip which can be measured electrically are listed in Table I and include four MOS transistors (two different types), four diodes (three different types), a diffused resistor metal test strip, and a MOS capacitor. Pin numbers are listed in Table II.

The proposed methods for evaluating the stability of the Rel-chip based on leakage currents and threshold voltages are discussed as follows.

MOS Transistor Drift

The V_T of the MOS may drift due to contamination of various types. Measurements of V_T are accomplished by an Autonetics-developed technique involving a computer program. Variations or drift in V_T of more than 500 millivolts as compared with a controlled standard package are unacceptable. Temperature stressing is accompanied with a bias stress to accentuate the drift. Temperatures of 125 to 175 C and bias of +10 to +20 volts were utilized. Any of the four MOS transistors may be stressed, although the inverter (pins 18, 19, 20) is the easiest to measure. C-V plots were taken between pins 14 and 15 to see large changes in V_T.

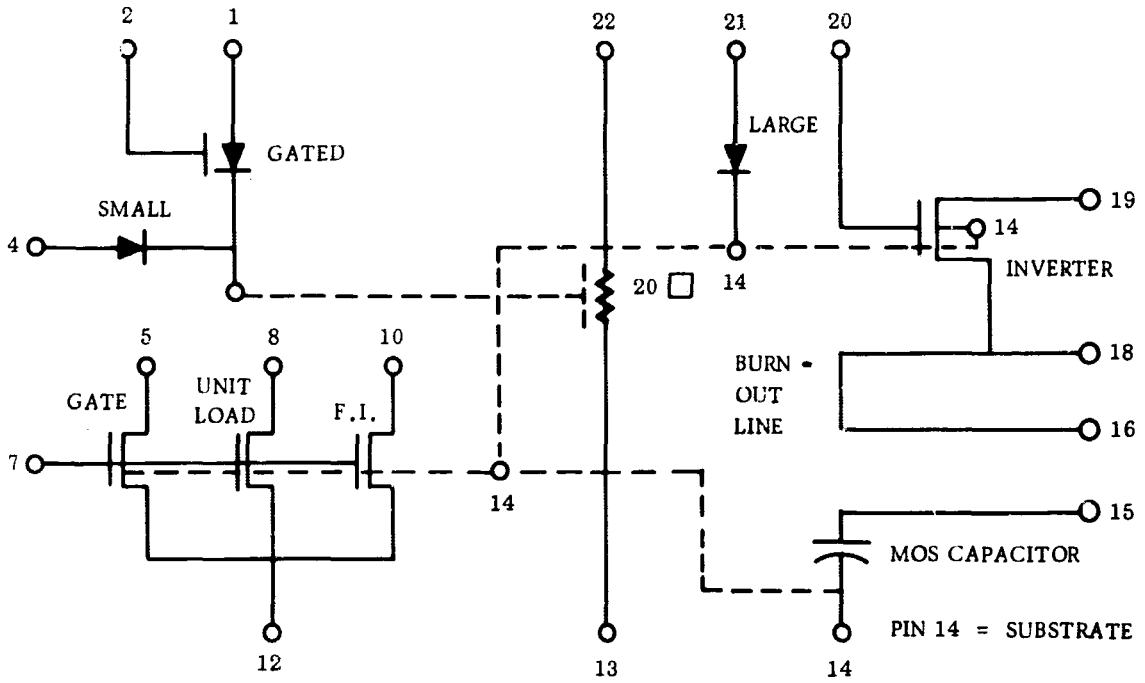


Figure 1. Rel-Chip Diagram

TABLE I
ELECTRICAL TEST FUNCTIONS - REL-CHIP

Devices	Parameter
Gated Diode	Field Controlled Breakdown $BV_{DB\ (Gate)}$
Large Diode, Small Diode	I_o, I_{o_S}, I_{o_B}, BV_{DB}
2 x 2 Mil Device	K', $BV_{DB\ (Gate)}$
	BV_{OX}, BV_{DSS}, V_T
Unit Load	K, $BV_{DB\ (Gate)}$, V_{GST}, BV_{DSS},
	V_T, R_{on}, $\frac{W}{\ell}$
Field Inversion	V_{TF}
Inverter MOS	K, V_T, R_{on}
MOS Capacitor	V_T (Drift), $C_{o\ (Gate)}$
Diffused Resistor	R_p
Metal Pattern	I_{MAX}, R_{MET}

TABLE II
PIN ASSIGNMENTS 81956 REL-CHIP

Pin No.	Function
1	Large Gated Diode Anode
2	Large Gated Diode Gate
3	N/C
4	Small Diode Anode
5	2 x 2 MOS Drain
6	N/C
7	Test MOS Gates, 2 x 2 Unit Load, Field Inversion
8	Unit Load MOS Drain

TABLE II. (Concluded)

Pin No.	Function
9	N/C
10	Field Inversion Drain
11	N/C
12	Test MOS Sources, 2 x 2 Unit Load, Field Inversion
13	Sheet Resistance
14	Substrate (Body)
15	MOS Capacitor
16	Metal Test (-V)
17	N/C
18	Metal Test (GND), Inverter MOS Source
19	Inverter MOS Drain
20	Inverter MOS Gate
21	Large Diode Anode
22	Sheet Resistance

Leakage Currents

Reverse currents of p-n junctions may be affected by surface treatment. Two regular diodes were used to determine surface and bulk leakage current components while a drain of an MOS (pin 19) was used to monitor gate-affected leakage. Gate-affected leakage was measured with the gate grounded (connected to the cathode). Typical leakages of the diodes are in the order of a few hundred pico-amperes (10^{-12} amperes). Coefficients of bulk and surface leakages may be found by the following theoretical equations:

$$B = \text{bulk leakage coefficient} = \frac{I_{bulk}}{Area}$$

$$= 4.96 \times 10^{-5} I_{o_{22}} - 9.80 \times 10^{-5} I_{o_4} \text{ pa/micron}^2$$

$$S = \text{Surface leakage coefficient} = \frac{I_{surface}}{Perimeter}$$

$$= 4.97 \times 10^{-3} I_{o_4} - 1.30 \times 10^{-3} I_{o_{22}} \text{ pa/micron}$$

where

I_{o_4} = leakage of small diode (pin 4) in pa.

$I_{o_{22}}$ = leakage of large diode (pin 22) in pa.

Coating of Reliability Chips with Parylenes. - Sixty Rel-chips (Figure 2) were used for evaluating the Parylenes as barrier coatings for semiconductor devices. It was originally planned to divide this group of 60 into four groups of 15 each. Three groups containing 15 unlidded devices (Figures 3 and 4) were to be coated with three different Parylenes, i.e., Parylene C, D, and N, while 15 of the "lidded" devices were to function as controls. The devices, after fabrication, were stored in a dry nitrogen environment until being placed in the vacuum coating chamber. They were held in place in the coating chamber utilizing magnets to hold the Kovar case (Figure 5). After coating the first batch of 15 with Parylene C (Table III, Run 45), four additional tested Rel-chips were made available. An additional two devices were used (total 17) for each of the remaining two experimental runs. Fifteen of the devices were treated with the Union Carbide A-174 adhesion promoter and two were left untreated for comparison of the effects of electrical stress on the untreated vs the treated ones.

Seventeen of these devices were coated with Parylene D (Table III, Run 1) and an additional batch of 17 were coated with Parylene N (Run 2). Immediately after coating, all the devices were removed, stored, and transported in a desiccator to the testing facility. They underwent electrical/temperature stressing to evaluate the stability of Parylene coatings on the "Rel-Chip" based on measurement of leakage currents and threshold voltages.

The four groups of devices, plus the extras described above, received initial measurements on V_{GST}, I_{DSS}, I_{SDS}, BV_{DSS} and VB_{SDS}. The four groups (hermetically sealed can and the three plastics) of 15 units each were subdivided for three types of electrical stress. This test plan matrix is presented in Figure 6. The coated extras did not receive the thermal and electrical stresses, so that they could be used as control checks at every measuring period. During measurements, the coated devices without lids were protected against light to eliminate possible photocurrents.

Figure 7 shows the stability of the threshold voltage V_{GST} for the four groups. It is readily seen that the threshold voltage shift is negligible, except on the N-type Parylene devices at the severest thermal stress (128 hours at 175 C), as indicated on the plots in Figure 7(d). Each line plot represents a single device.

Figure 8 shows similar plots for the leakage current (I_{DSS}) changes for devices subjected to the four processes. The first thermal stress (i.e., 16 hours at 100 C) appeared to lower the leakage currents slightly for most of the devices. This indicates that these units needed more bakeout than was given to them. In general, no significant difference in the leakage current change can be seen for devices subjected to the four different processes.

In Figure 9, the threshold voltage shift is shown for the three different stress conditions. Devices prepared by the four processes are grouped together, so that a

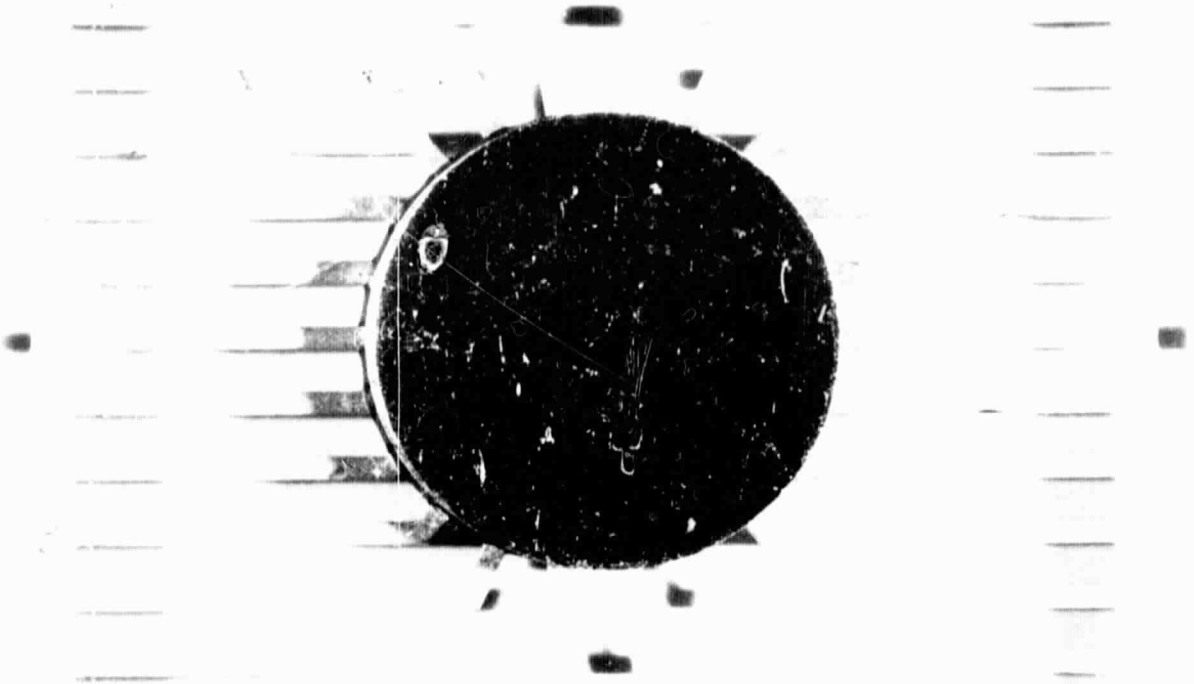


Figure 2. Rel-Chip Package (With Lid)

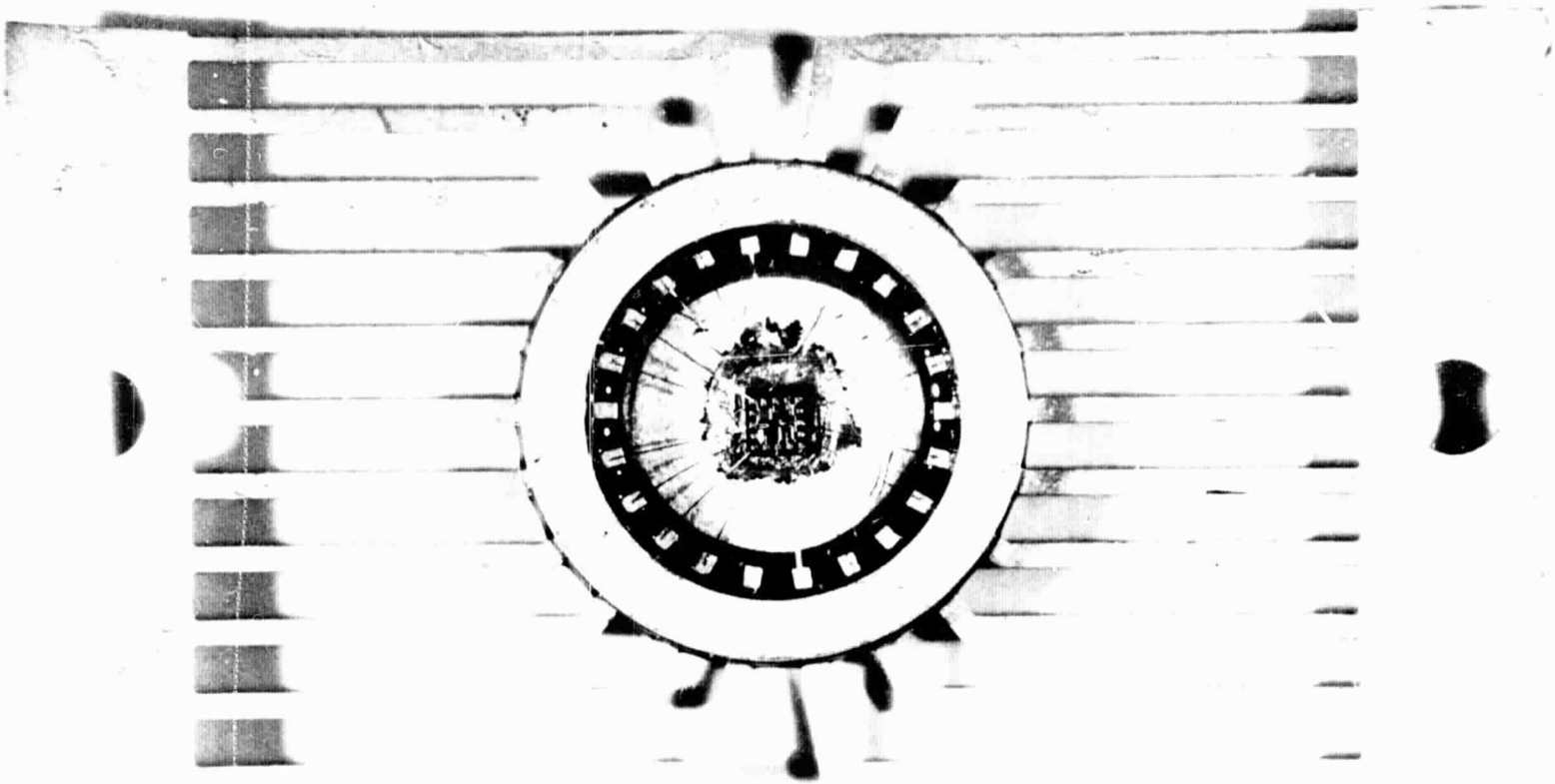


Figure 3. "Delidded" Package

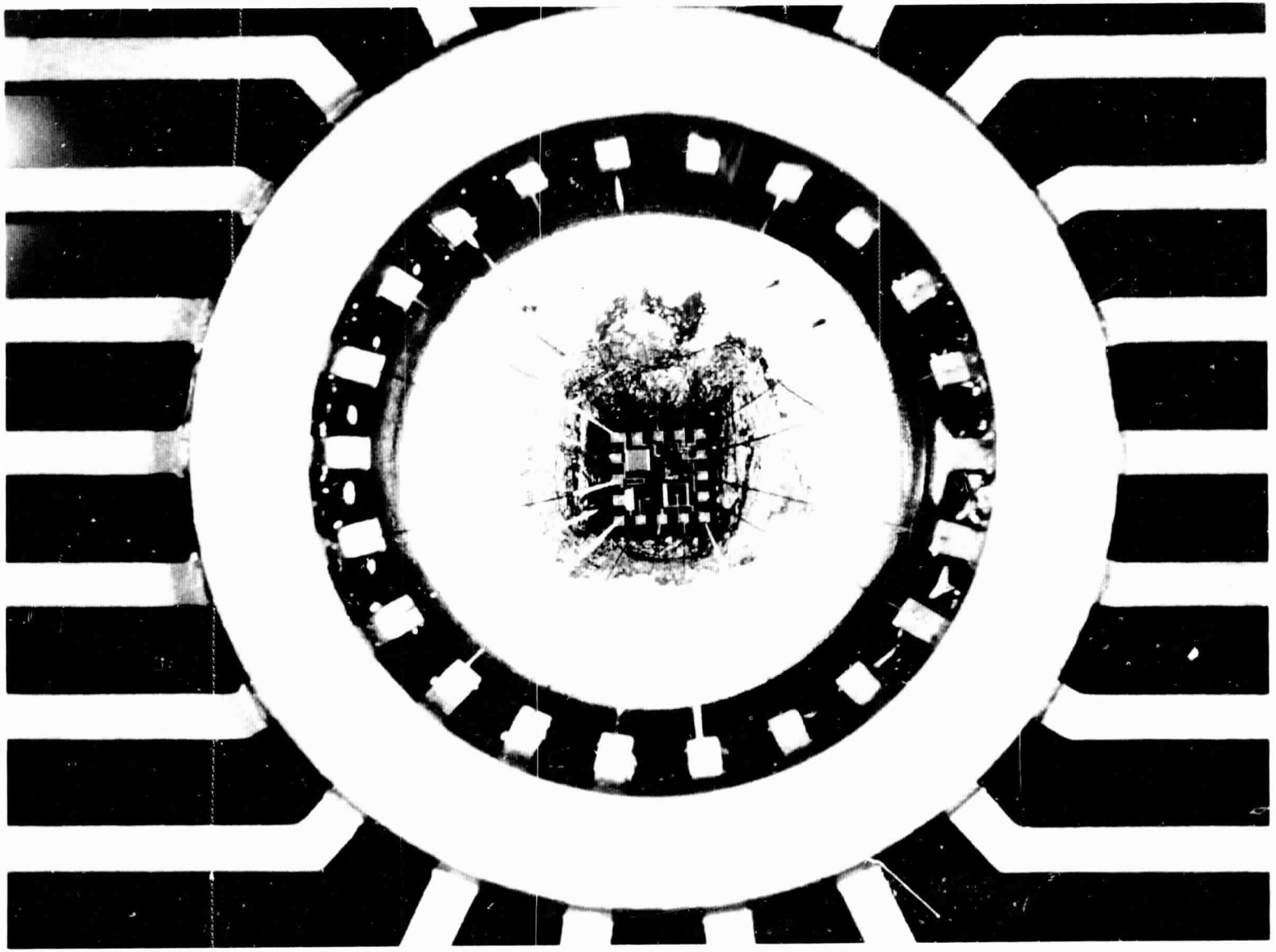


Figure 4. Closeup of "Delidded" Package

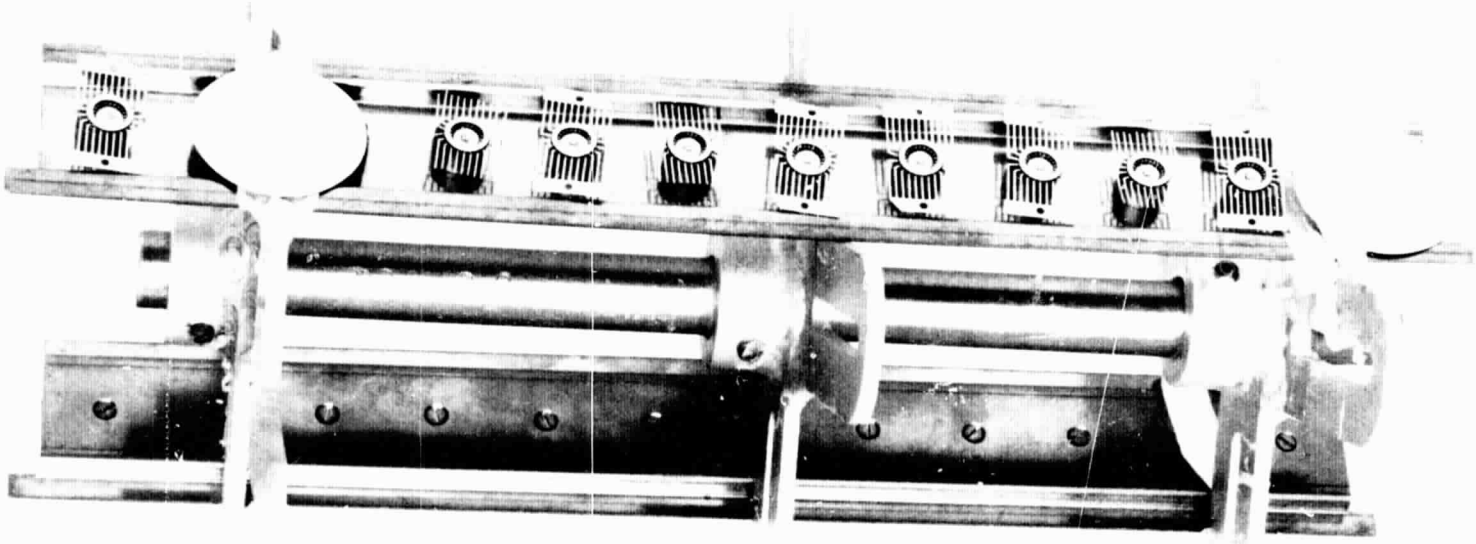


Figure 5. Rack for Holding "Rel-Chips" for Coating

TABLE III
PARYLENE DEPOSITION STUDIES

Run No.	Parylene		Pressure (μ)	Temperature, °C			Test Specimens			Coating Thickness (μ)
	Type	Wt (gms.)	Chamber	Preheat Zone	Cracking Zone	Deposition Chamber	Type	No.	Rotating Speed rpm	
N1866-45	C	10	2 - 30	225	600	25	Reliability Devices	15 (a)	5.75	7.0
N6666-1	D	15	4	200	600	25	Reliability Devices	19 (b)	5.75	4.5
N6666-2	N	13	4 - 40	150	600	25	Reliability Devices	19 (b)	5.75	3.0

(a) All devices treated with A-174 adhesion promoter prior to coating

(b) All devices except two were treated with A-174 adhesion promoter prior to coating

ELECTRICAL STRESS * / PARYLENE	NONE	-25 SOURCE -25 DRAIN 0 GATE	-20 SOURCE -20 DRAIN +20 GATE
NONE	I	II	III
C	IV	V	VI
D	VII	VIII	IX
N	X	XI	XII

*ALL DEVICES WERE SUBJECTED TO ACCELERATED TEMPERATURE STRESSING

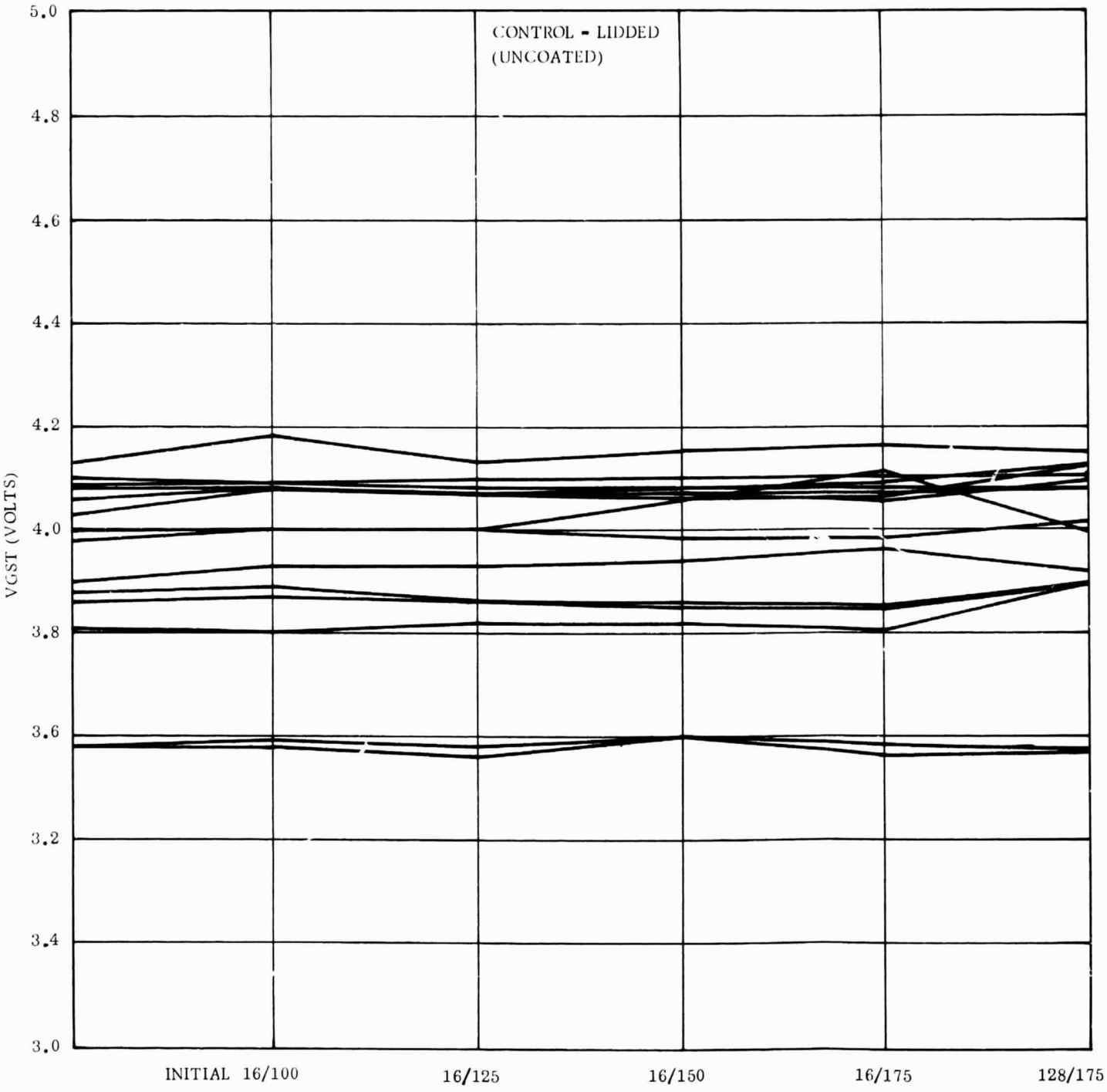
Figure 6. Group Test Matrix Outline

comparison of the different thermal electrical stresses can be made. Again, the only noticeable voltage shift is seen on the most severe thermal stress (i.e., 128 hours, 175 C) on all of the electrical stresses. It is also most pronounced on the devices receiving the highest electrical stress (i.e., -20v on S-D and +20v on gate). These results are as one would expect on any normal devices. The largest average voltage shift of less than 0.1 volts is considered to be quite small on this type of device under "hard" stress.

Figure 10 presents the stability of the drain leakage current (I_{DSS}) for the three different stress conditions. In general, the average variation is quite small except for a small number of devices. As one would expect, the most severe electrical stressed group (i.e., -20v on source and drain and +20v on gate) has higher current instability than the other two groups (see Figure 10(c)).

The Parylene N group indicated slightly inferior values than the other two. This may be attributed to the fact that devices coated with Parylene N had the thinnest coating, viz., 3.0μ thick compared with 4.5μ for Parylene D and 7.0μ for Parylene C.

In a previous study, two other polymeric coatings, a silicone and an epoxy, were considered as encapsulation candidates for semiconductor devices. It was observed that Rel-chips coated with the silicone and epoxy showed a greater instability than those sealed hermetically in metal cans.



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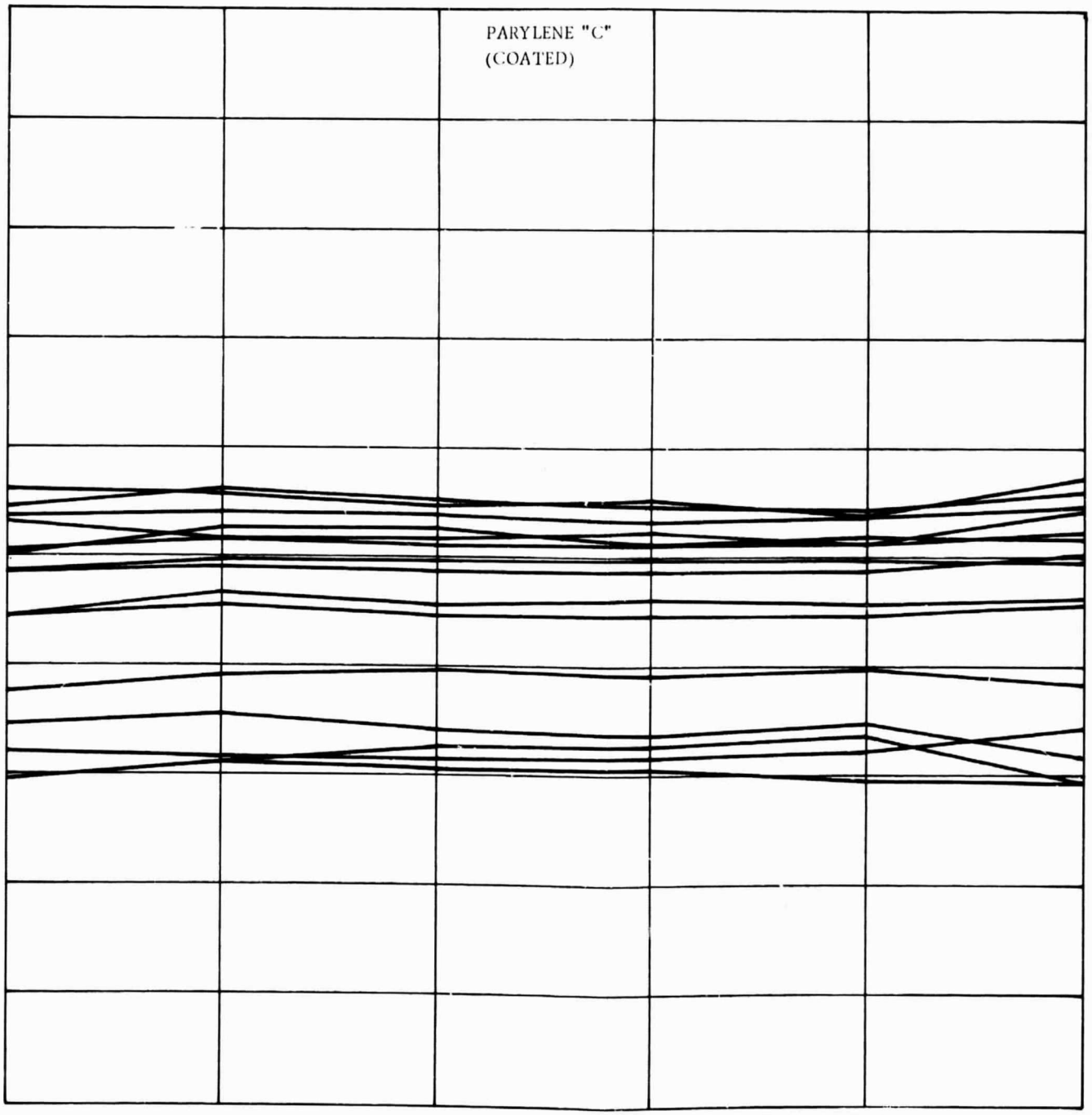

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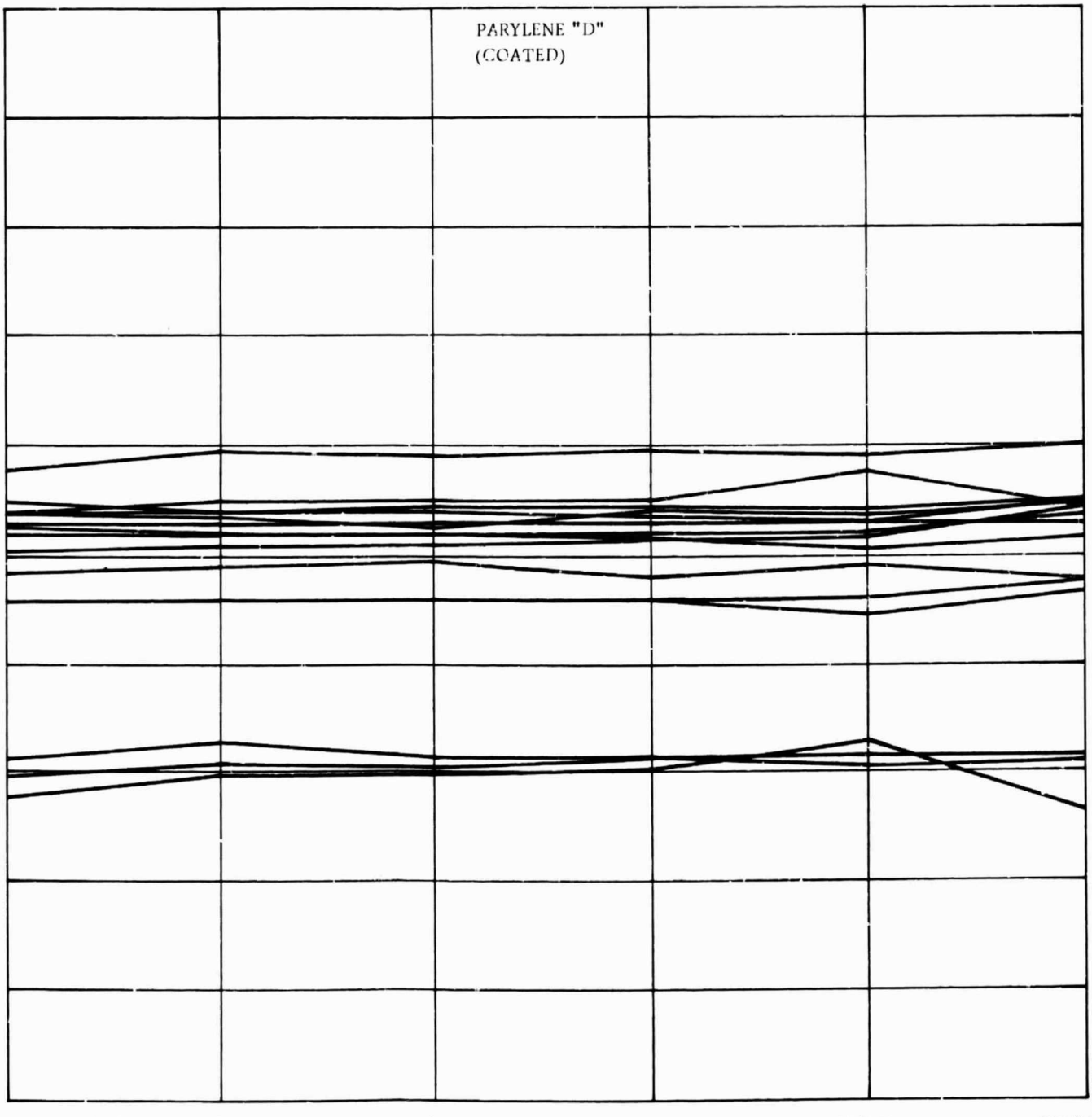

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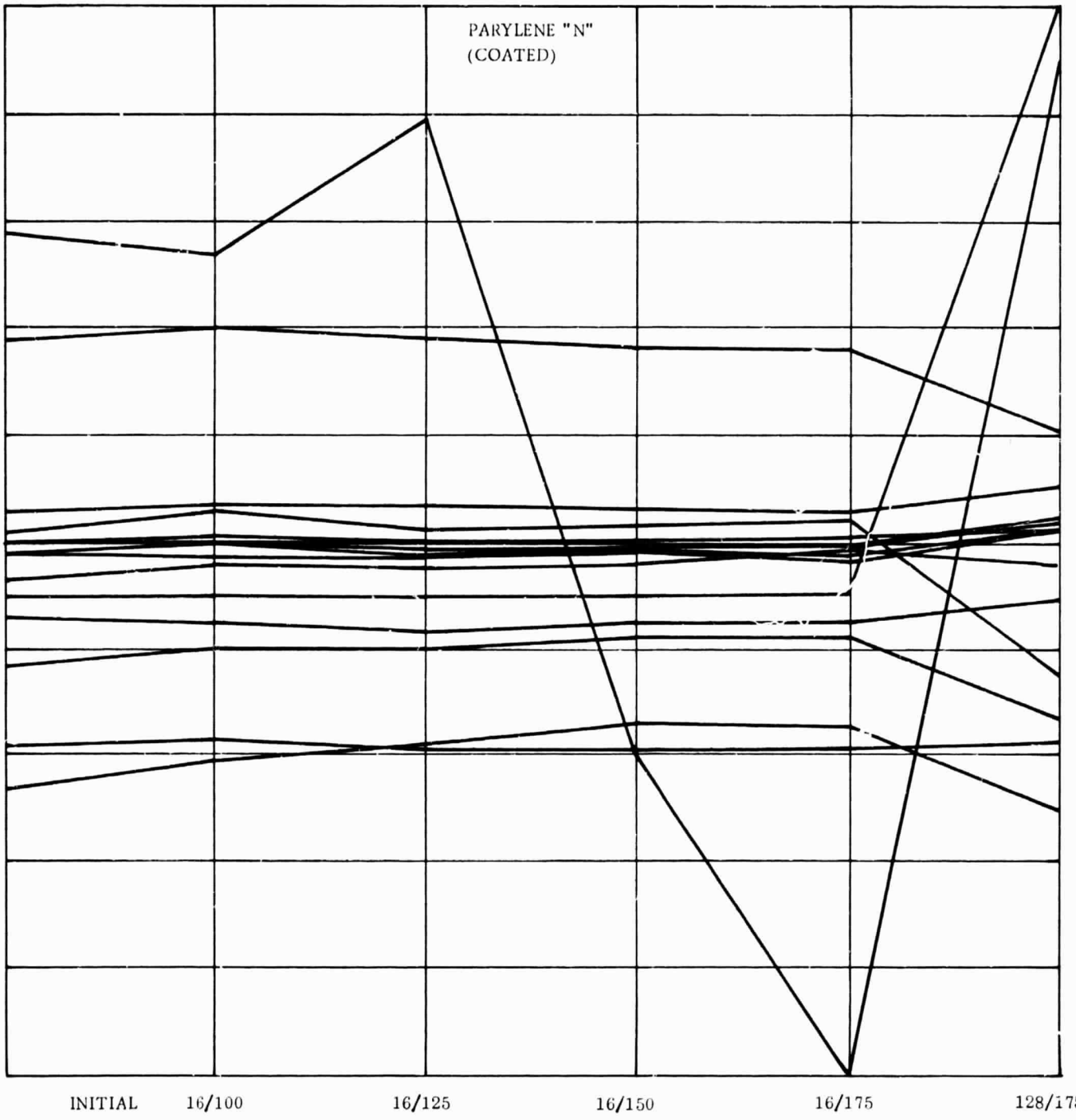

Figure 7. Parylene-Coated Rel-Chips - All Stresses (V_{GST} Volts)

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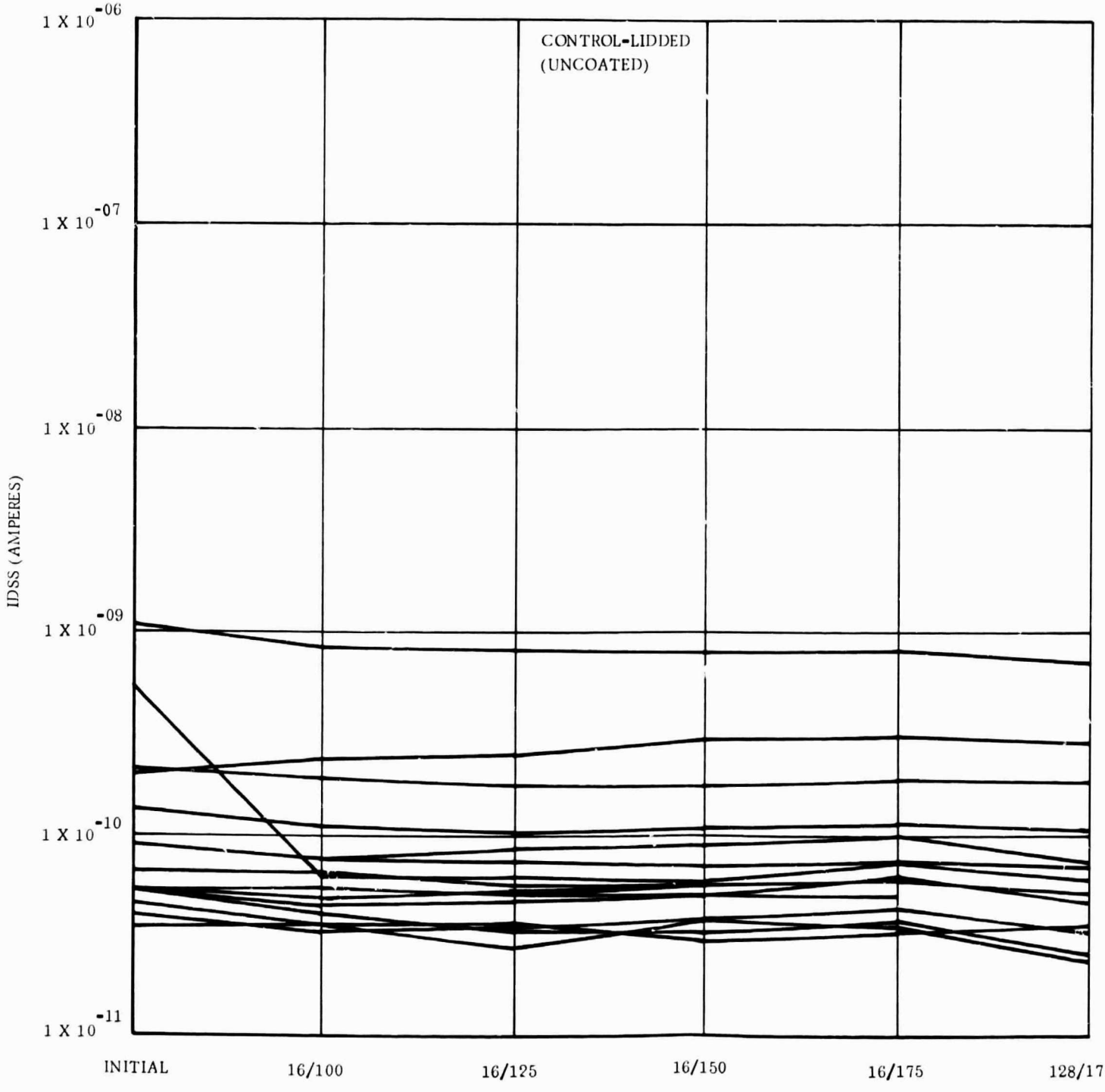

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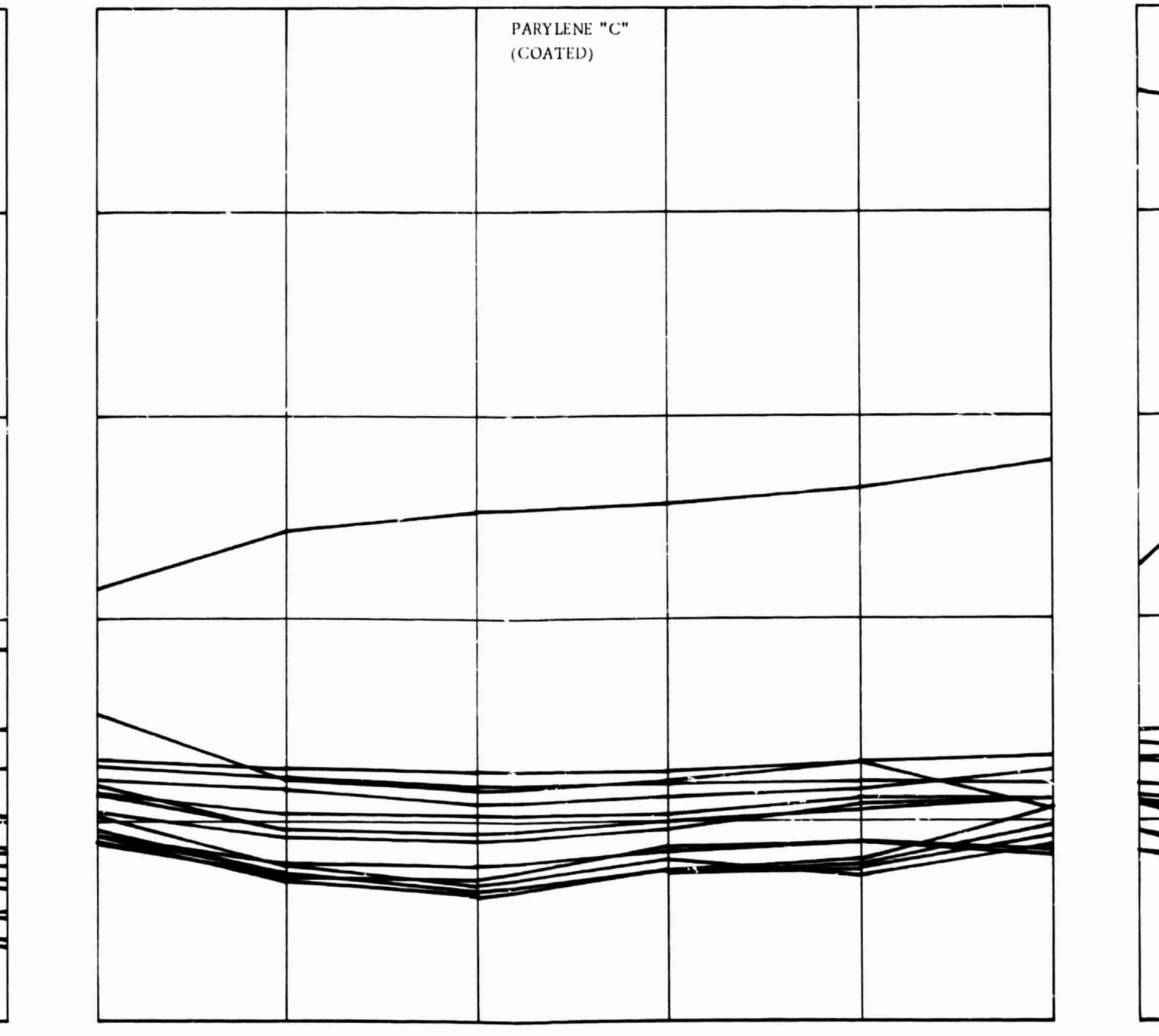

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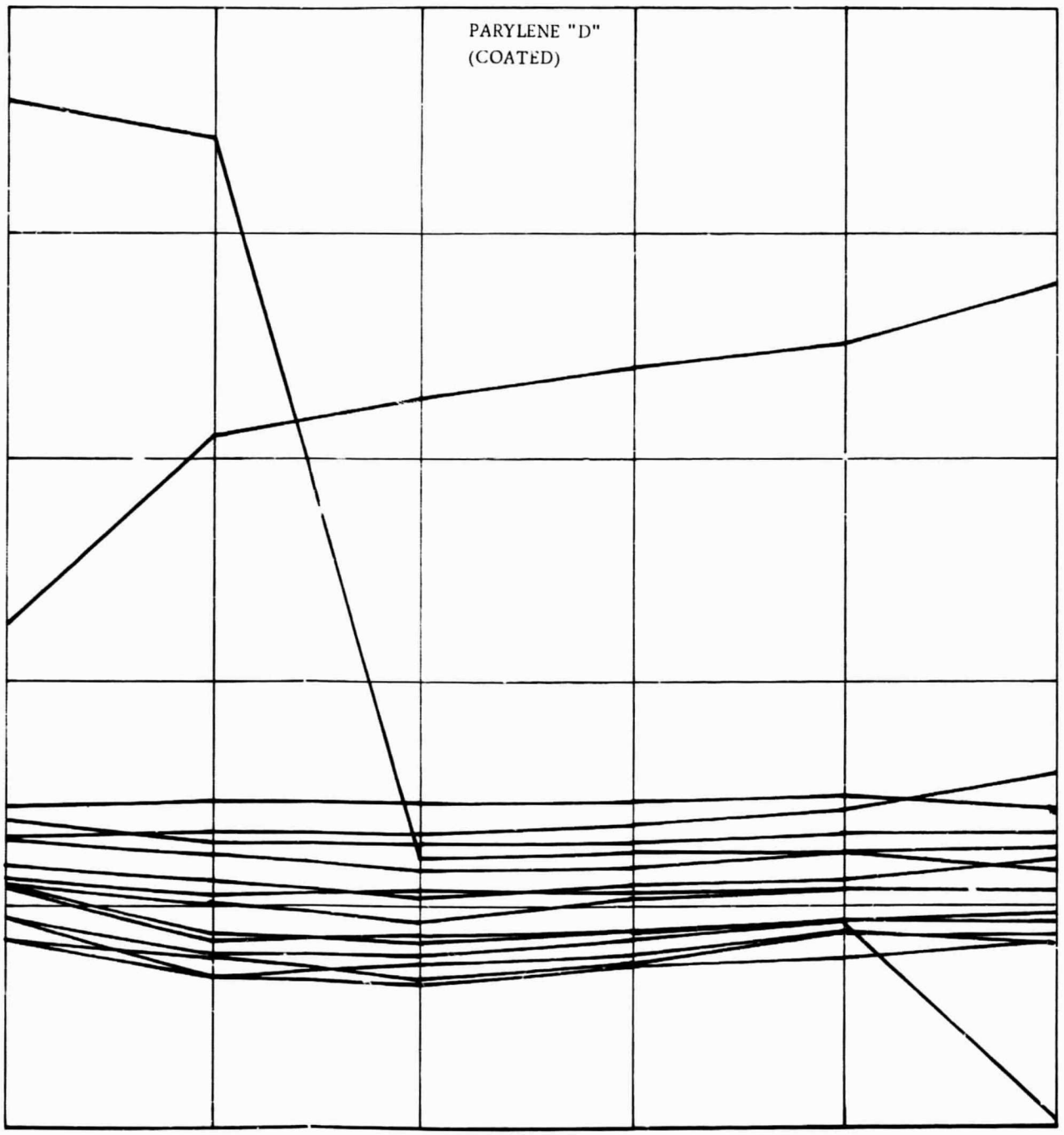
HOURS TEMPERATUR



INITIAL 16/100 16/125 16/150 16/175 128/175 INITIAL

RATURE, °C

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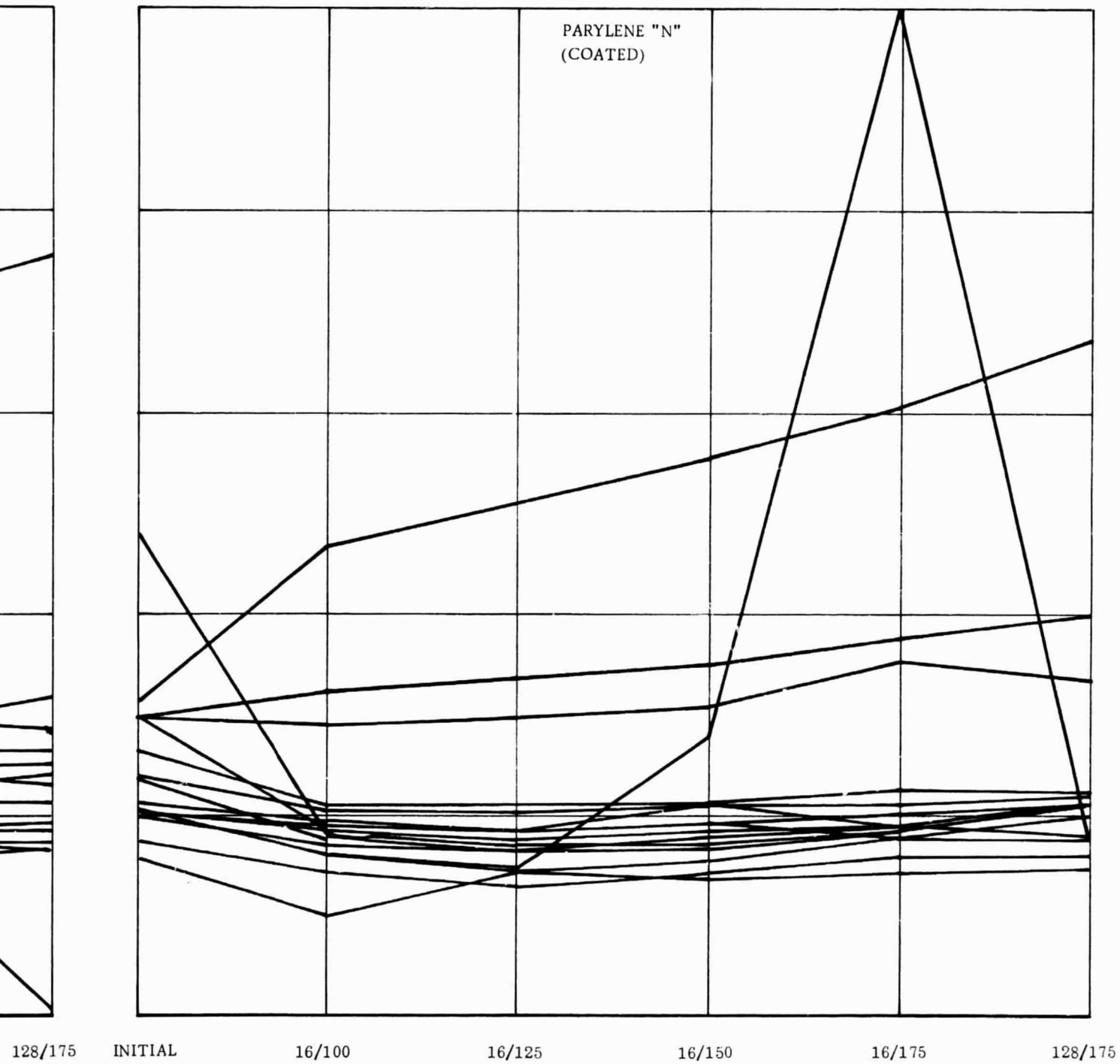

Figure 8. Parylene-Coated Rel-Chips - All Stresses (I_{DSS}-Amperes)

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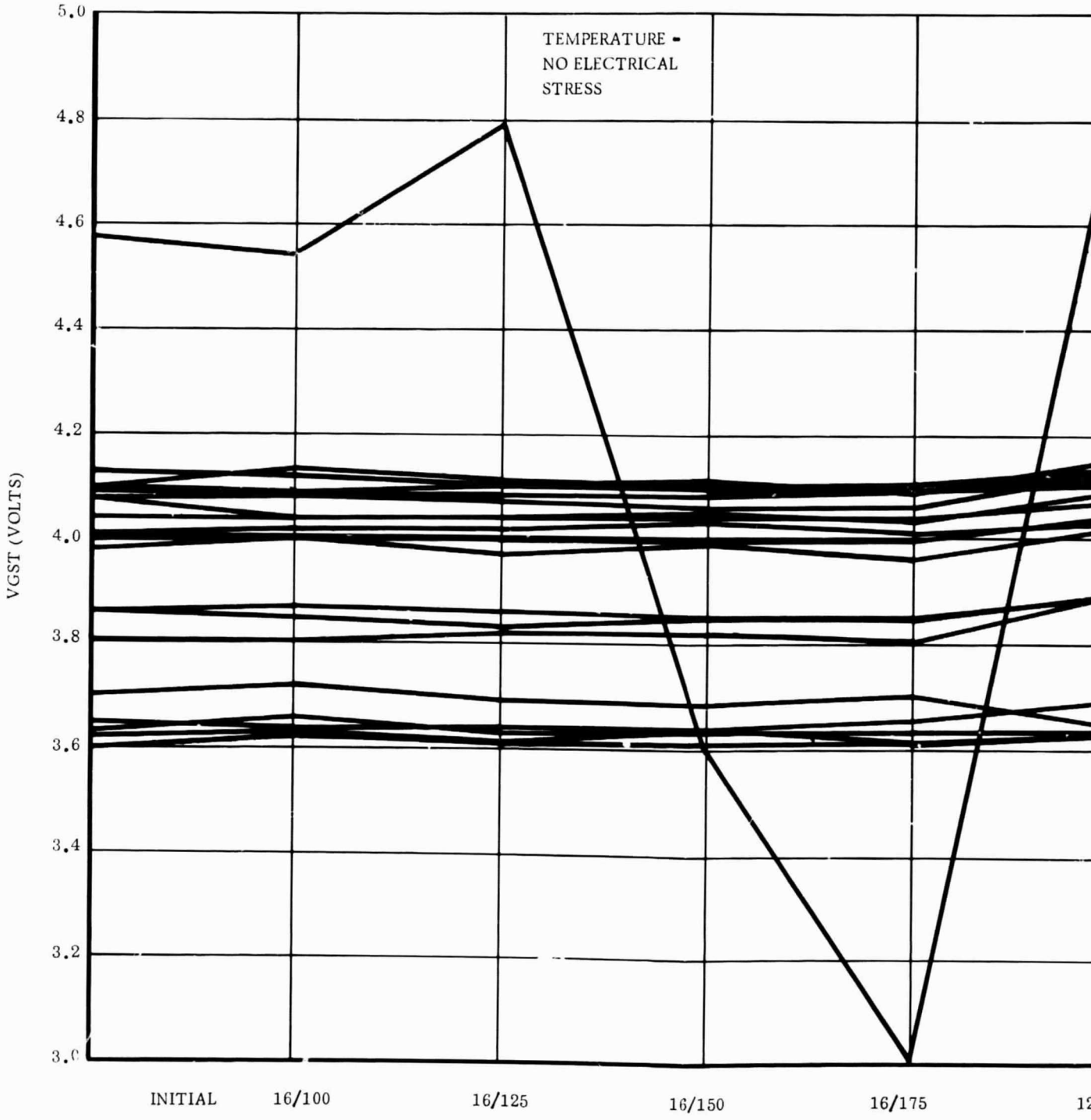

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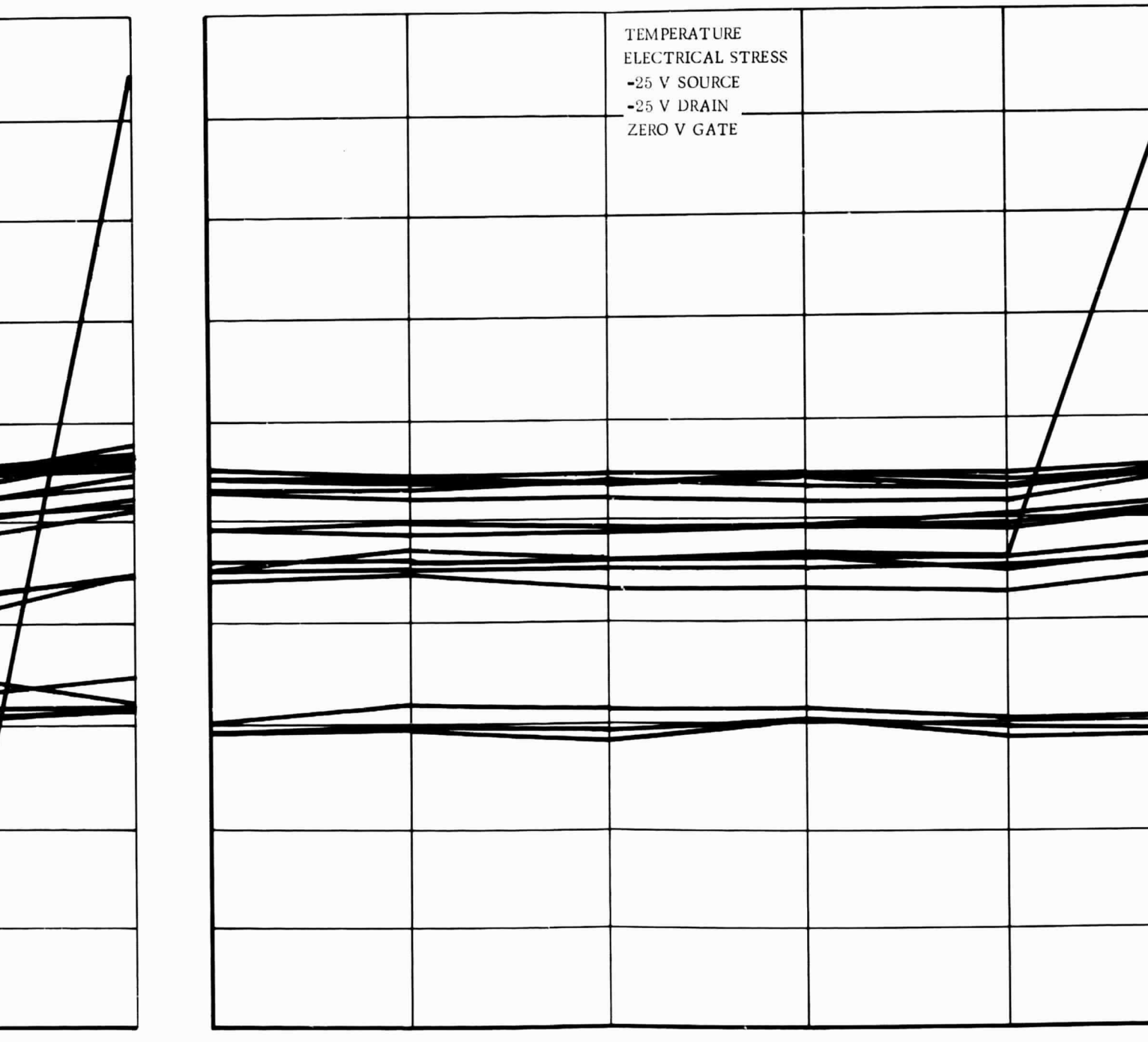

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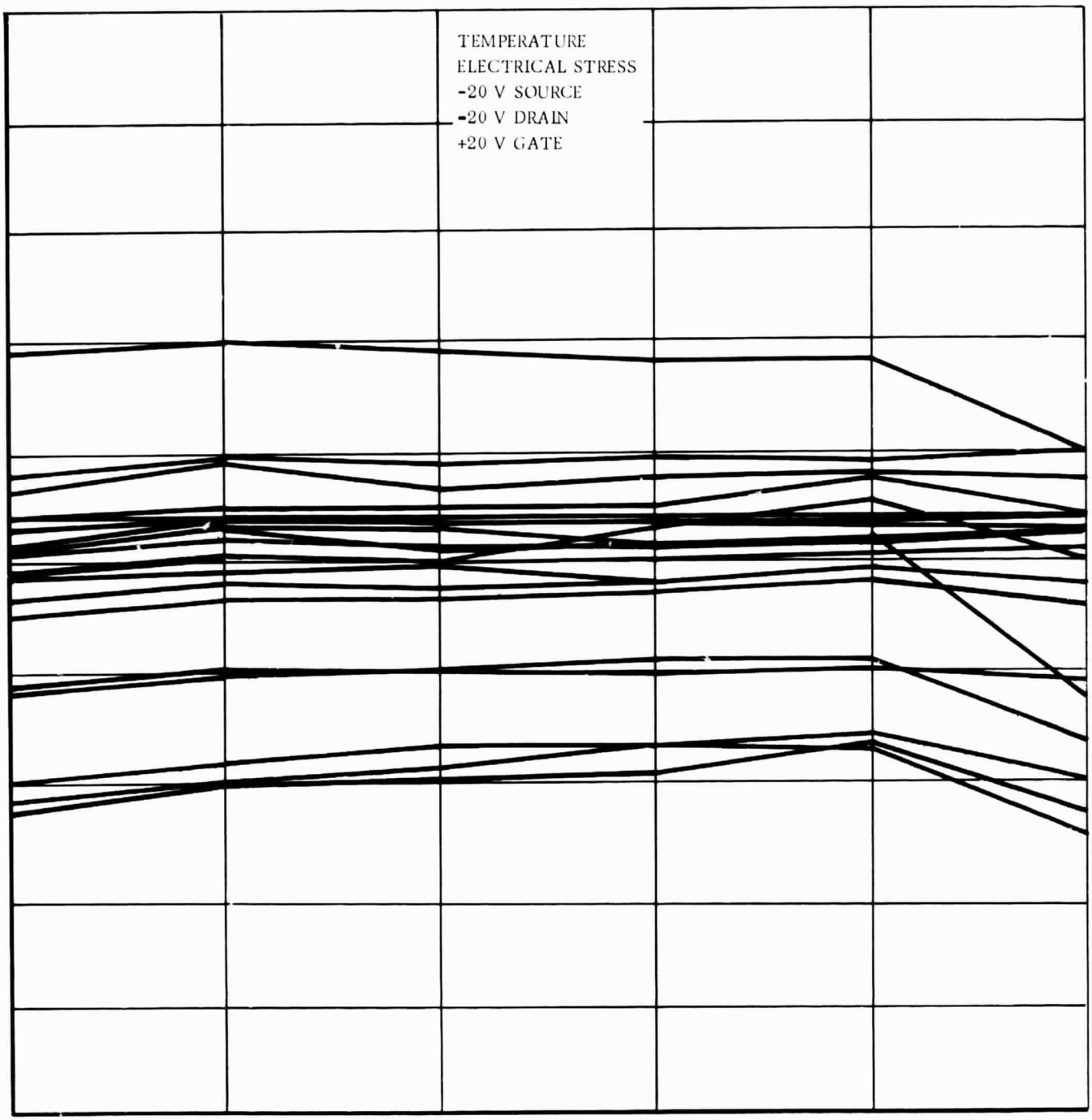

Figure 9. Parylene-Coated Rel-Chips - All Processes (V_{GST} Volts)

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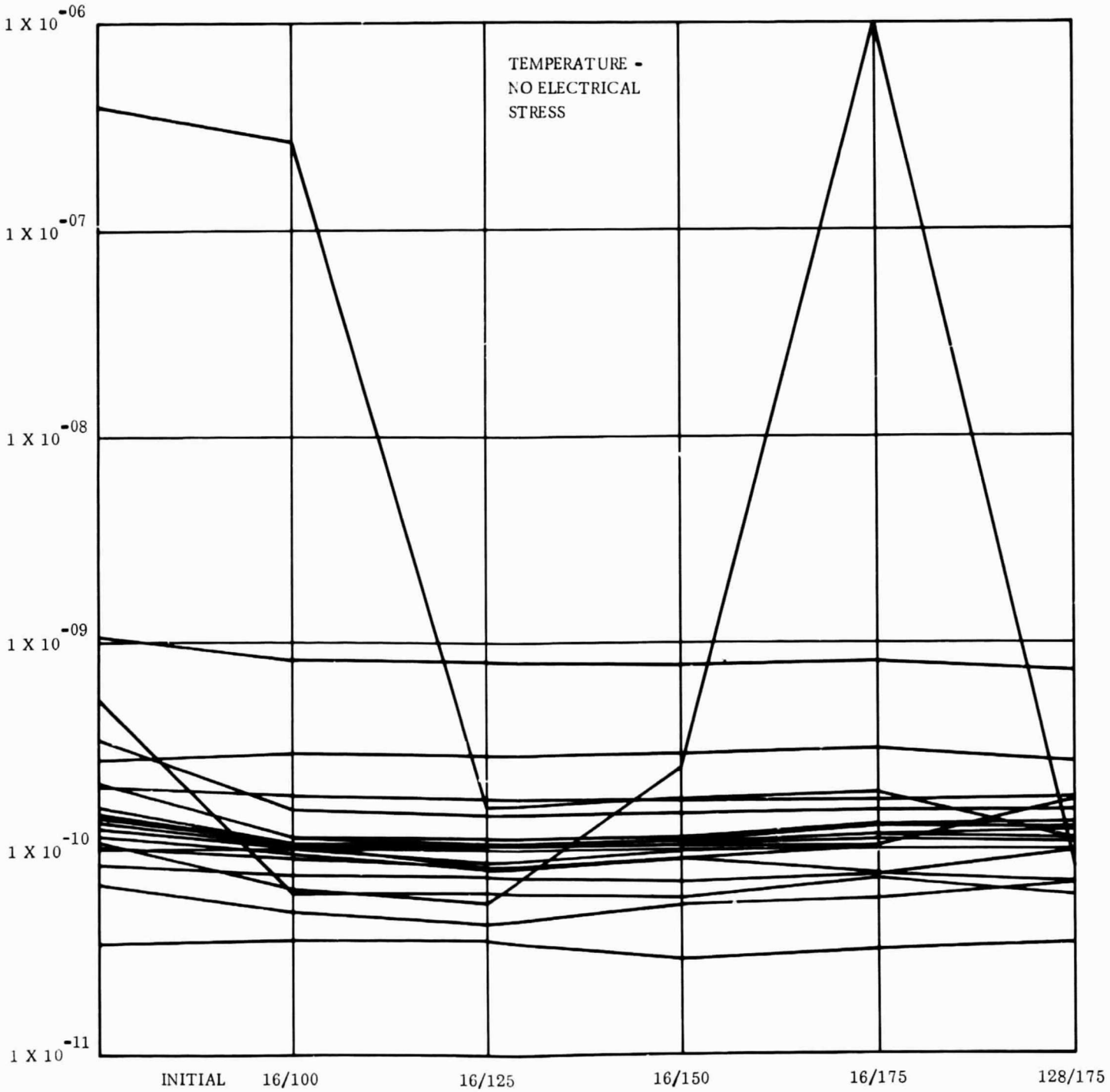

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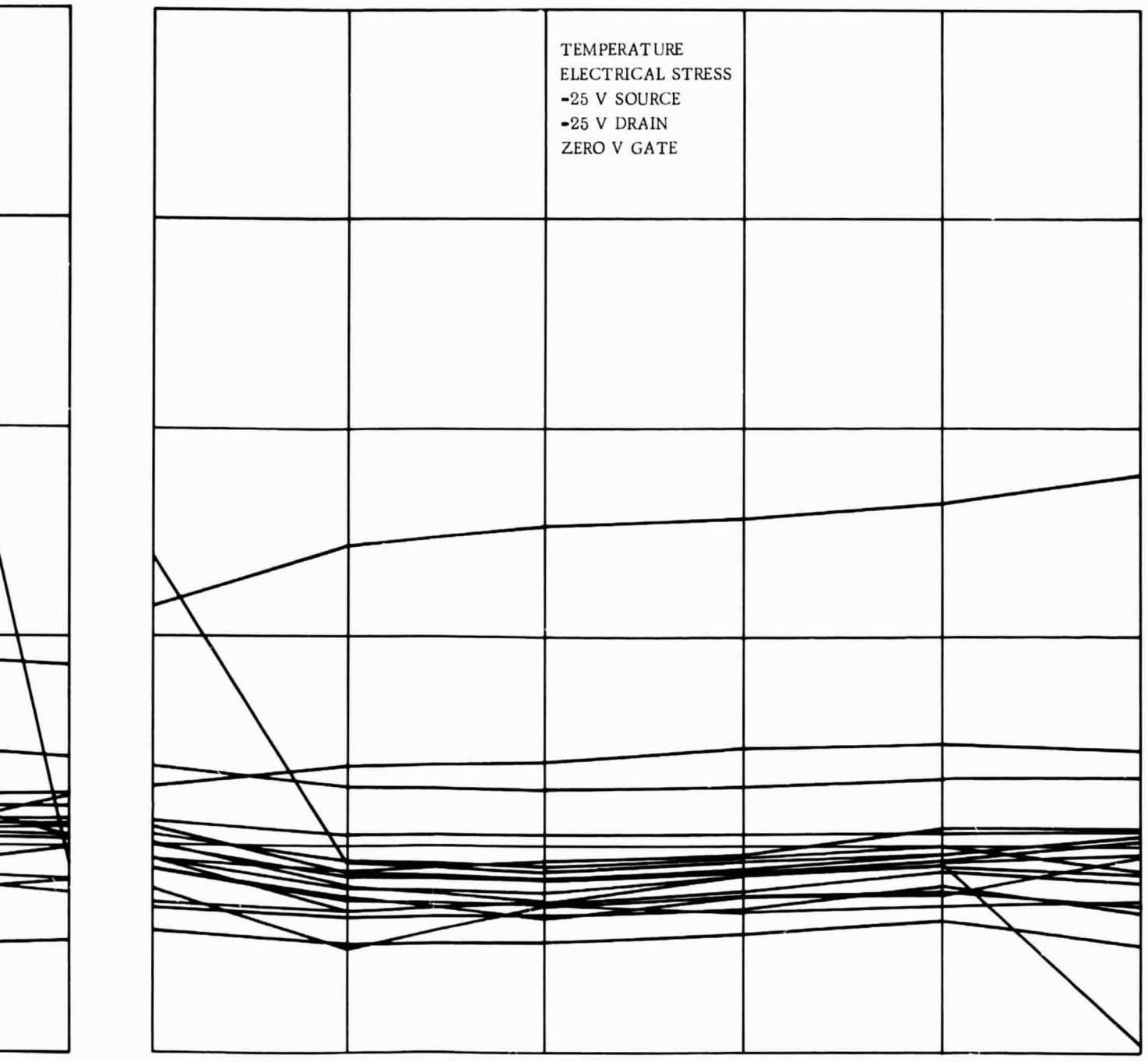

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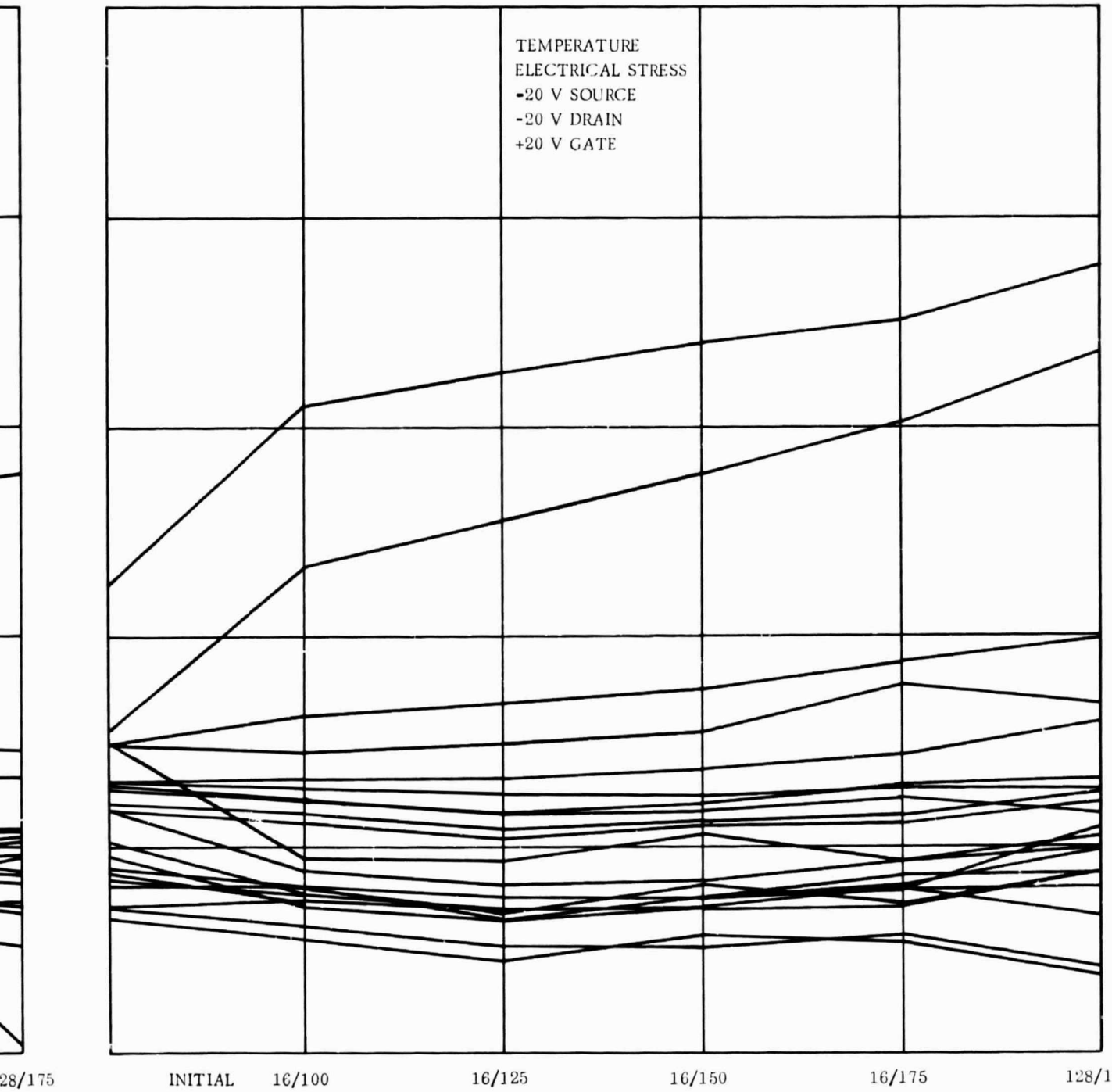

Figure 10. Parylene-Coated Rel-Chips - All Processes (I_{DSS} Amperes)

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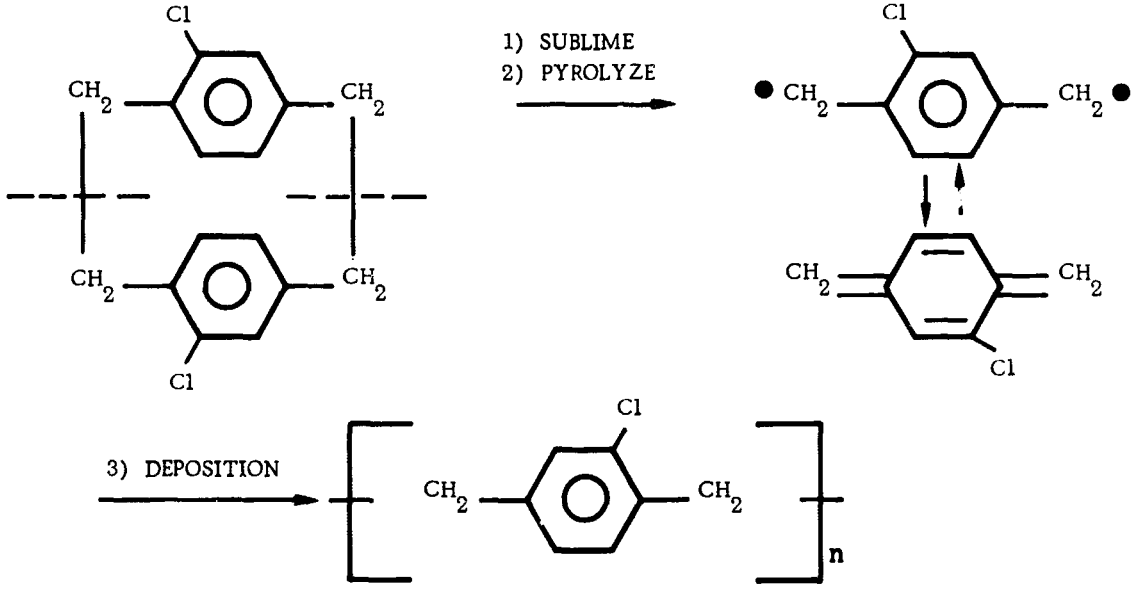
No significant difference in electrical properties after electrical/temperature stressing was observed between the Rel-chips which were treated with A-174 silane adhesion promoter prior to coating and the untreated ones.

VACUUM DEPOSITION OF PARYLENE

The initial vacuum deposition equipment was designed (Figure 11) and fabricated as shown in Figure 12. The equipment consisted of a 20-in. Vycor tube with ground glass joints in a two zone furnace. A weighed amount of Parylene dimer was placed in the vaporization or preheat zone under vacuum and the vapors then conducted through the pyrolysis or cracking area. As the vapors entered the cracking area at about 600 C, cleavage resulted specifically at the methylene-to-methylene bond yielding monomeric chloro-p-xylylene diradicals.

The monomeric chloro-p-xylylene diradical after entering the cooler deposition zone consisting of a 9-in. section of Pyrex pipe with a 2-in. inlet and outlet polymerized instantaneously. Rotation of samples with a variable speed controlled motor was provided to allow for a more even distribution of the polymeric coating. The equations involved in the chemical transformation were as follows for the chloro derivative:



Vacuum deposition of all three types: Parylene C (chloro-p-xylylene), Parylene D (dichloro-p-xylylene) and Parylene N (p-xylylene) were studied (Table IV) utilizing the equipment as described in the previous paragraph. Two modifications in equipment design were made to yield improved coatings. The first involved lengthening the pyrolytic or cracking zone from 9 to 18 in. The extension of the pyrolysis zone resulted after noticing a slight opalescence in thicker Parylene films. To determine whether this haziness was the result of the presence of undissociated Parylene C dimer (starting material), a sample of a film was subjected to infrared analysis. The results (Figure 13) showed the two unmistakable and characteristic strong bands of the

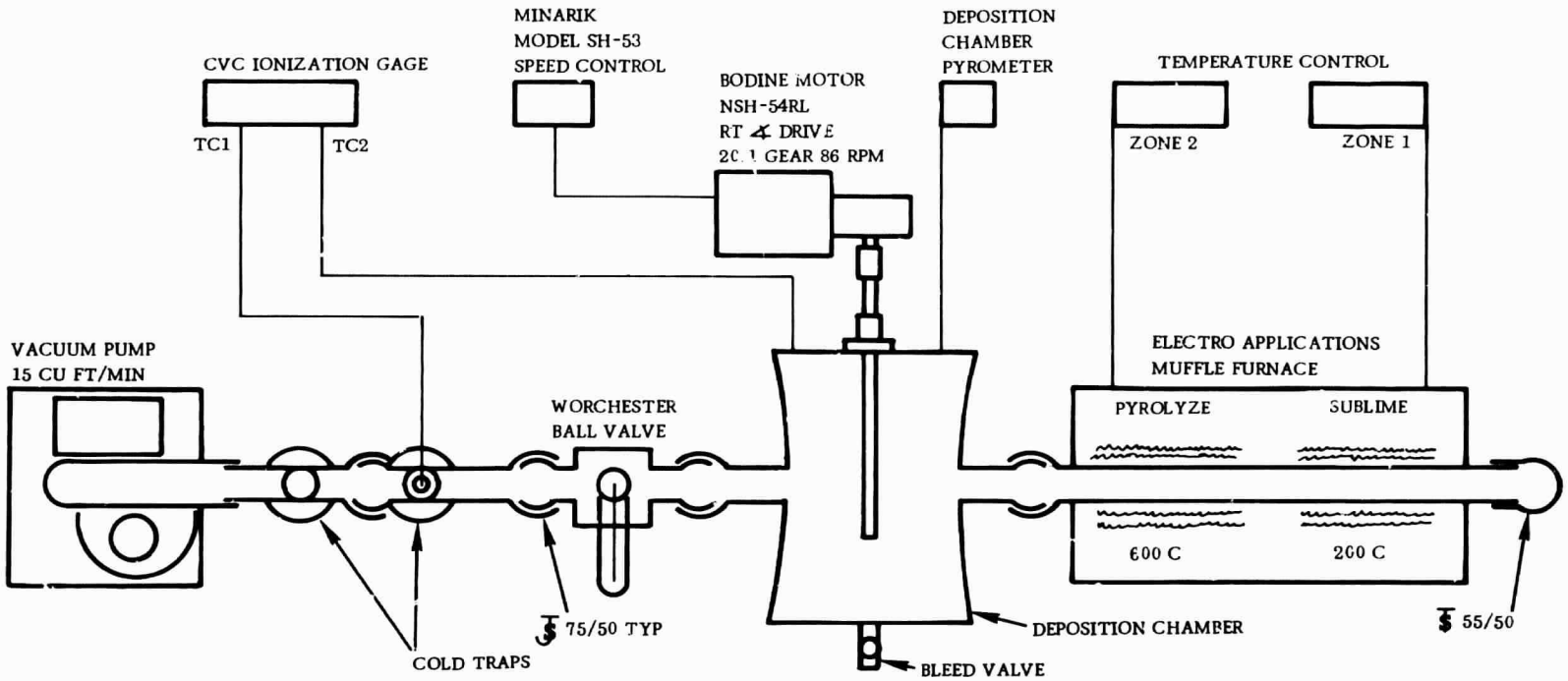


Figure 11. Vapor Deposition of Poly-p-Xylylene (Diagram)

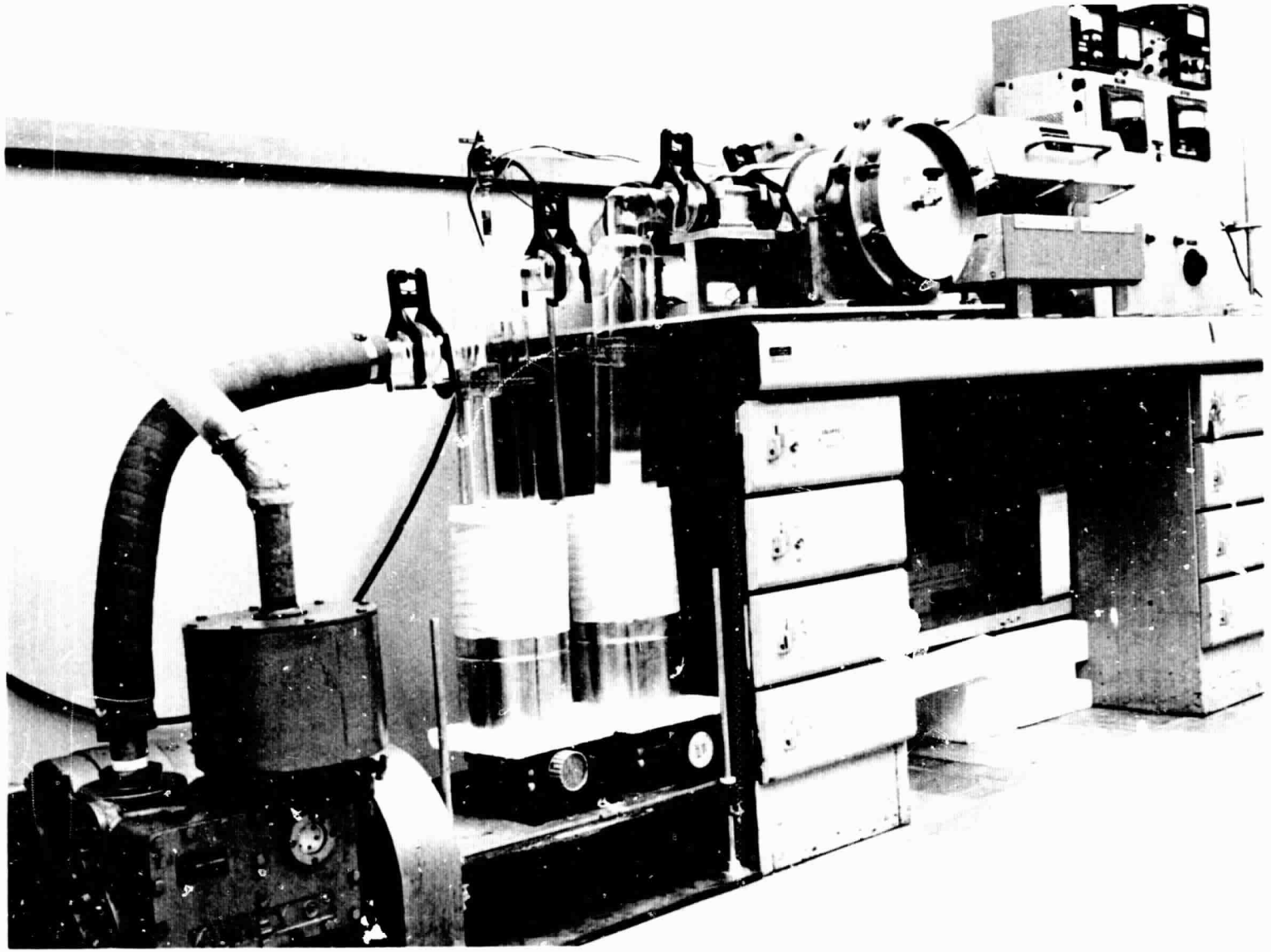


Figure 12. Parylene Vacuum Deposition Equipment

TABLE IV
PARYLENE DEPOSITION STUDIES

Run No.	Parylene		Pressure (μ)		Temperature, °C			Test Specimens			(a) Coating Thickness (μ)
	Type	Wt (gms)	Trap	Chamber	Preheat Zone No. 1	Cracking Zone No. 2	Deposition Chamber	Type	No.	Rotating Speed (RPM)	
N1355-16	C	5.0001	2	50-100	200	600	26	Glass slides. "Y" Fiberglass Board	5 1	5.75	R - 0.3 F - 0.3 B - 0.3 T - 0.3 RS - 0.2
N1355-19	C	10.0167	<1	50-100	200	600	26	Glass slides "Y" Fiberglass Board	6 1	5.75	R - 0.4 F - 0.3 B - 0.1 T - 0.6 RS - 0.9 RS - 1.1
N1355-21	C	5.0087	<1	50-100	200	600	26	Glass slides Ceramic chips	6 2	5.75	R - 0.3 F - 0.2 B - 0.3 T - 0.2 RS - 0.9 RS - 0.3
N1355-22	C	5.0942	20	50-100	200	600	26	Glass slides	6	5.75	R - 1.9 F - 1.0 B - 4.4 T - 2.9 RS - 4.1 RS - 3.8
N1355-24	C	5.0370	20	50-100	200	600	26	Glass slides	6	5.75	R - 0.9 R - 0.5 B - 3.6 T - 5.4 RS - 3.0 RS - 3.0
N1355-25	C	5.0112	18	50-100	200	600	26	Glass slides ceramic chips	6 2	71.0	R - 1.1 R - 0.7 B - 10.1 T - 4.8 RS - 4.4 RS - 1.5
N1355-27	C	4.99	18	50-100	200	600	26	Glass slides	6	5.75	R - 0.6 F - 0.8 B - 4.4 T - 6.4 RS - 3.0 RS - 3.2

TABLE IV (Cont)

Run No.	Parylene		Pressure (μ)		Temperature, °C			Test Specimens			(a) Coating Thickness (μ)
	Type	Wt (gms)	Trap	Chamber	Preheat Zone No. 1	Cracking Zone No. 2	Deposition Chamber	Type	No.	Rotating Speed (RPM)	
N1355-28	C	5.0097	18	500-100	150	450	26	Glass slides	3	5.75	B - (b) F - nil RS - 0.4
N1355-29	C	5.0150	18	50-100	150	500	26	Glass slides	3	5.75	B - (b) F - (b) RS - 1.7
N1355-30	C	5.0024	20	50-100	150	550	26	Glass slides	3 1	5.75	B - 1.6 F - (b) RS - 2.2
N1355-33	C	5.0	15	50	200	600	26	Glass slides	3	5.75	B - 0.04 RS - 0.3 RS - 0.08
N1355-34	C	5.0	12	50	225	600	25	Glass slides	4	5.75	OT - 0.4 RS - 0.8 RS - 0.5 IT - 4.5
N1355-36	C	5.0	17	65	225	600	70	Glass slides	4	5.75	OT - Nil RS - 0.08 RS - Nil IT - 1.0
N1355-38	C	5.0	<1	50	225	600	27	1-1/4 in. S.S. disks 3 in. x 2 in. glass slides	2 6 6	5.75	RS - 1.0 RS - 1.0 RS - 1.0 RS - 1.0 RS - 0.8 RS - 0.7
N1355-40	C	5	<1	50	225	600	24	Glass slides Transfer molding spec. "Y" pattern fiberglass bds.	5 2 8	5.75	RS - 0.9 RS - 0.9 RS - 0.7 RS - 0.7 B - 0.5
N1355-43	C	10	<1	50	225	600	25	Glass slides "Y" pattern boards Pinhole test Disks Ceramic chips	4 4 2 4	5.75	RS - 2.5 RS - 2.7 RS - 2.8 RS - 2.5

TABLE IV (Cont)

Run No.	Parylene		Pressure (μ)		Temperature, °C			Test Specimens			(a) Coating Thickness (μ)
	Type	Wt (gms)	Trap	Chamber	Preheat Zone No. 1	Cracking Zone No. 2	Deposition Chamber	Type	No.	Rotating Speed (RPM)	
N1355-46	C	20	40	50	225	600	25	Glass slides "Y" pattern boards Pinhole disks	4 8 4	5.75	RS - 5.0 RS - 5.0 RS - 5.0 RS - 5.0
N1355-48	C	10	40	25 to 50	170	600	25	Glass slides	4	5.75	RS - 10.0 RS - 10.0 RS - 10.0 RS - 10.0
N1355-50	C	10	10	25 to 40	175	600	25	"Y" Pattern Boards Glass slides	4	5.75	10.0
N1866-4	C	5	10	25 to 40	175	600	25	"Y" Boards Glass slides Stainless Steel Disks 1-1/4 in. Dia	4 4 4	5.75	1.0
N1866-5	D	5	<1	1 to 5	190	600	25	"Y" Boards Glass slides Stainless Steel Disks 1-1/4 in. Dia	4 8 4	5.75	5.0
N1866-6	D	10	1	1 to 5	190	600	25	"Y" Boards Glass slides Stainless Steel Disks 1-1/4 in. Dia	4 6 4	5.75	10.0
N1866-9	N	10	1	15 to 50	150	600	25	"Y" Boards Glass slides Stainless Steel Disks 1-1/4 in. Dia	4 8 4	5.75	10.0
N1866-12	C	10		25	225	600	25	"Y" Boards S.S. Disks Platinum Disks Glass Slides	4 4 2 4	5.75	5.0

TABLE IV (Concluded)

Run No.	Parylene		Pressure (μ)		Temperature, °C			Test Specimens			(a) Coating Thickness (μ)
	Type	Wt (gms)	Trap	Chamber	Preheat Zone No. 1	Cracking None No. 2	Deposition Chamber	Type	No.	Rotating Speed (RPM)	
N1866-15	D	2		6	235	600	25	"Y" Boards S.S. Disks Glass Slides	4 4 6	5.75	<1.0
N1866-19	C	10		12	225	600	25	Matrix Boards Glass Slides S.S. Disks Rel-Chips	6 6 6 6	5.75	5.0
N1866-27	C	5.0		6 - 18	225	600	25	Glass slides Stainless Steel disks	4 8	5.75	3.0
N1866 - 29	C	3.0		10 - 20	225	600	25	Glass slides Stainless steel disks	3 6	5.75	2.0
N1866-34	C	4.0		8 - 19	225	600	25	Glass slides Stainless steel disks Integrated circuit packages	4 6 5	5.75	2.5
N1866-36	C	7.5		19 - 40	225	600	25	Glass slides	4	5.75	4.5

(a) Location of specimens in deposition chamber: R - rear, F - front, T - top, B - bottom, RS - rotating shaft, IT - inlet tube, OT - outlet tube.

(b) Coating too soft to measure.

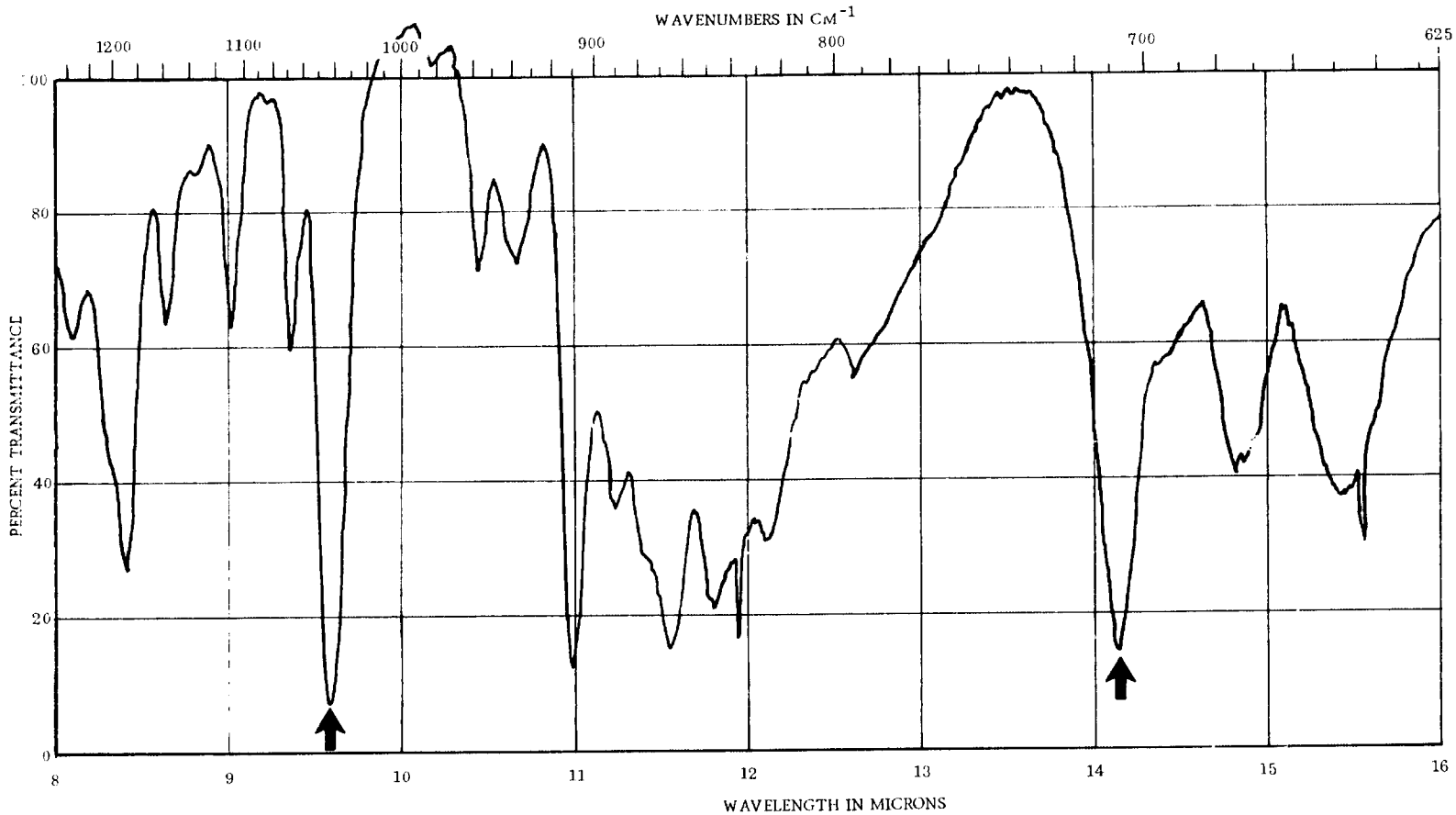


Figure 13. Deposited Parylene C Polymer Infrared Spectrum (With Dimer)

dimer starting material at 11.0 and 14.15 microns (infrared spectrum of Parylene C dimer in Nujol - Figure 14).

Based on the infrared results, which indicated the presence of unreacted dimer in the deposited films, the apparatus was then redesigned to minimize any change of unreacted dimer appearing in the deposition zone. The pyrolytic tube length was extended from 9 to 18 in., and an additional 9 inches of tube heated with an external heating mantle was added to the overall length (Figure 15). In addition, a baffle plate was placed across the entrance of the coating chamber (Figure 16). This equipment was utilized with a lower vaporization temperature in experiment 48 to yield the clearest and best film thus far obtained. This 100,000 A° thick film, when scanned with infrared, showed no characteristic absorption of unreacted starting dimer at 11.0 and 14.15 microns (Figure 17). It appears that lengthening the cracking zone achieved complete cleavage of the starting material resulting in a pure Parylene polymeric film.

A series of preliminary experiments using Parylene C was conducted to optimize experimental coating variables. Glass slides, ceramic chips, "Y" connector board, stainless steel disk, and reliability chips were coated under varying experimental conditions of temperature, vacuum, speed of rotation, residence time, heat-up-sequence of vaporizer and pyrolysis zones, and temperature inside the coating chamber. In addition, glass slides were placed throughout the Parylene deposition furnace, including the top, bottom ends, and positions on the rotating frame as shown in Figure 18 to ascertain the varying thicknesses of Parylene throughout the chamber. The results of the profiled film thicknesses utilizing Parylene C in the deposition chamber containing a baffle are as follows:

Front End Plate	5.0 microns
Rear End Plate	5.0 microns
Top of Chamber	5.5 microns
Bottom of Chamber	4.5 microns
Rotating Shaft	5.0 microns
Rotating Shaft	5.0 microns

It thus appears that a fairly uniform coating of Parylene can be obtained throughout this 9-in.-glass deposition chamber with its incorporated baffle.

A series of experimental runs was made to deposit varying thickness of Parylene C film as a function of charge (Figure 19). It was found that thickness of Parylene C film below 2 microns was not desirable due to presence of pinholes.

MEASUREMENT OF THIN FILMS OF PARYLENE

Talysurf

In preliminary experiments, a Taylor-Hobson, Model-3 Talysurf measuring instrument (Figure 20) with a strip chart recorder utilizing a diamond tip 0.00005 inch in diameter was used to measure film thicknesses. The sensitivity of this instrument is > 1/4 microinch (60 A°).

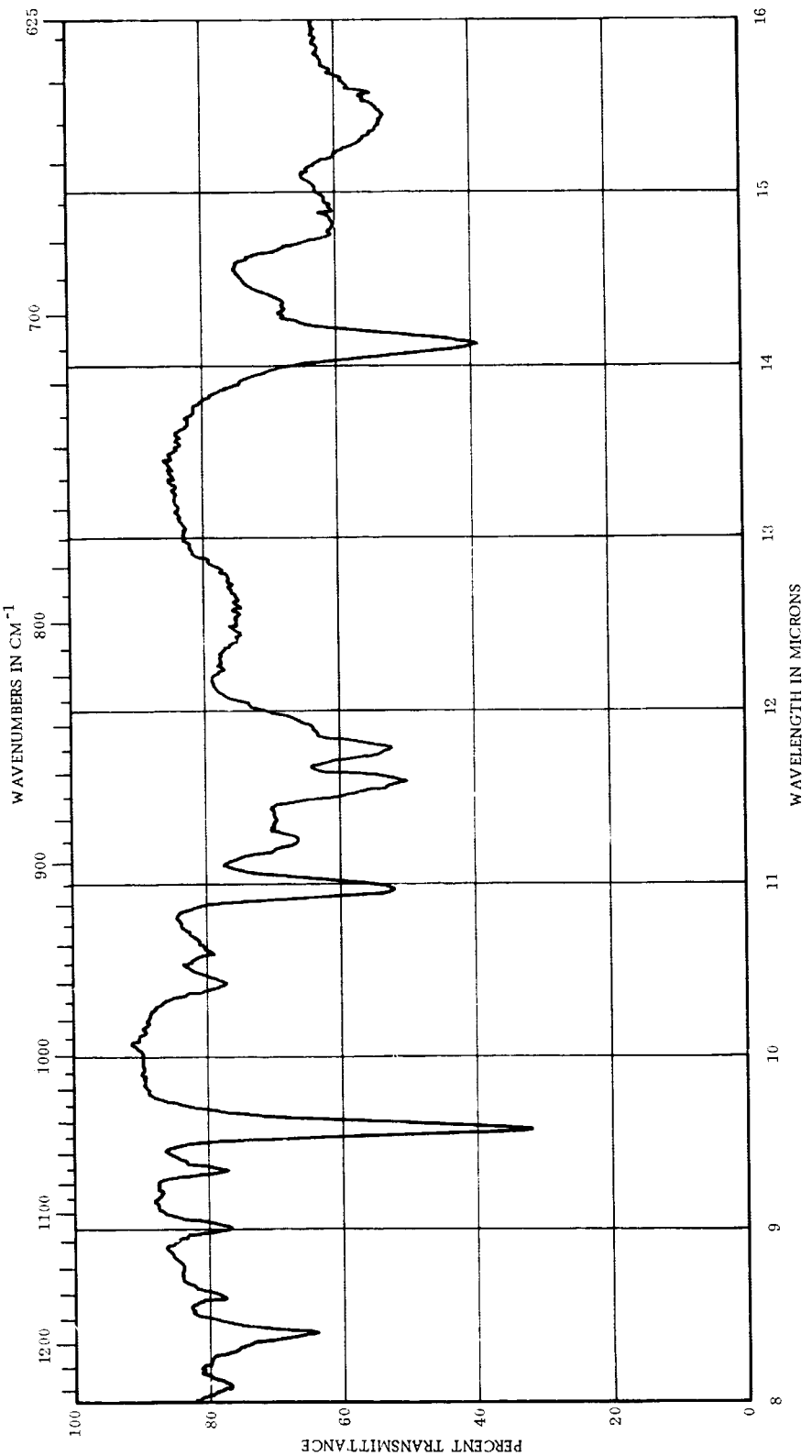


Figure 14. Parylene C Dimer Infrared Spectrum

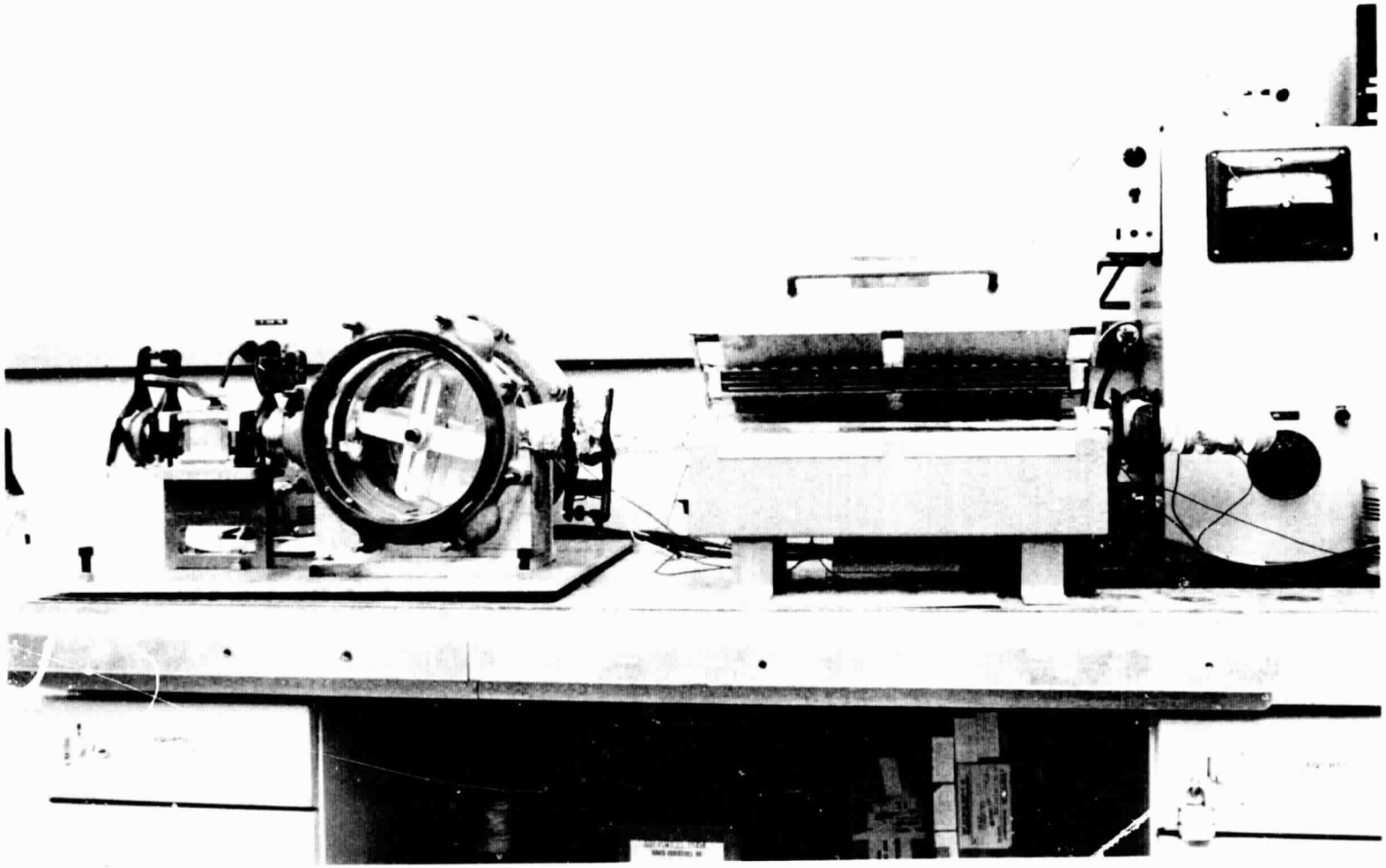


Figure 15. Modified Parylene Vacuum Deposition Equipment

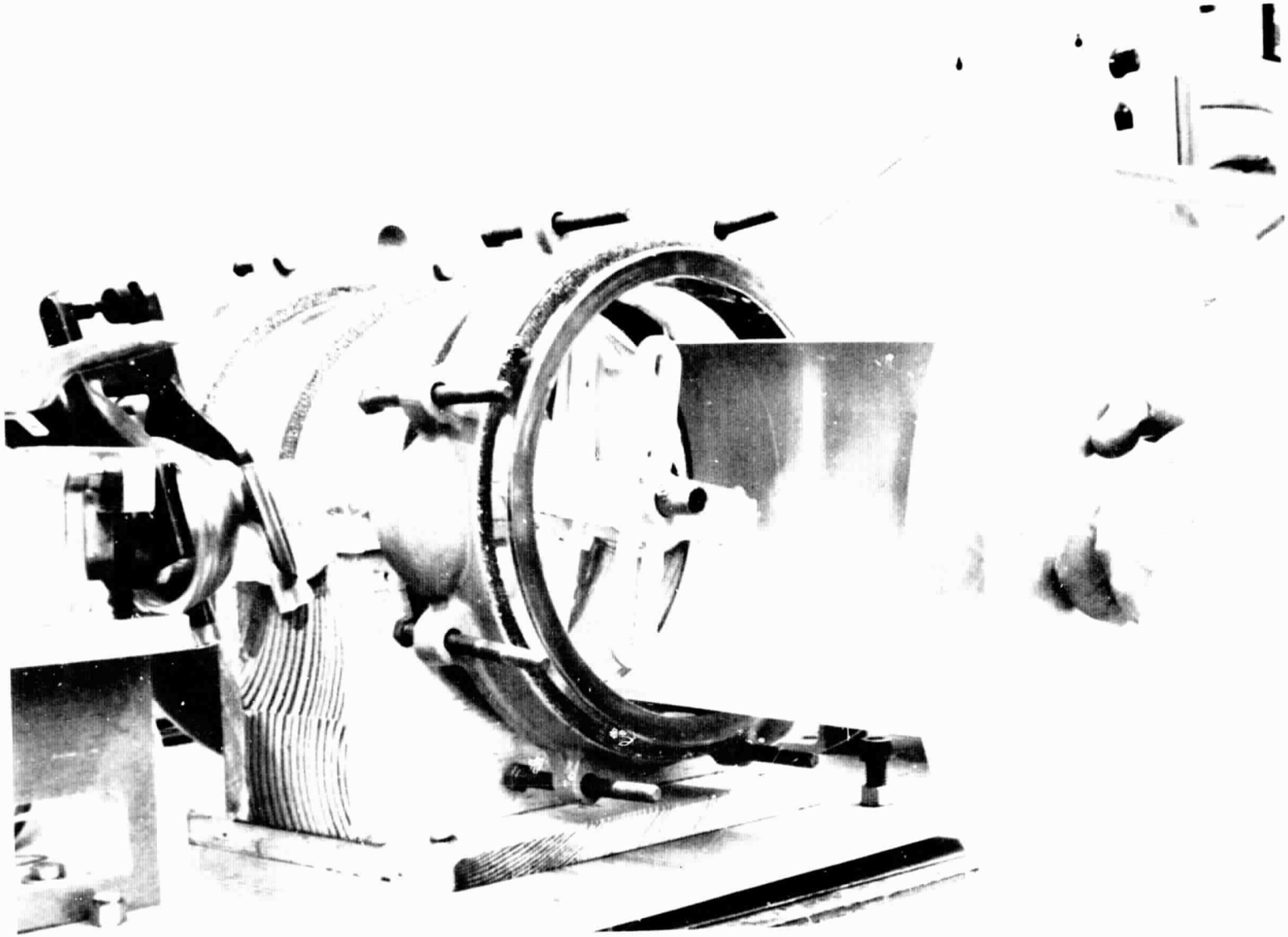
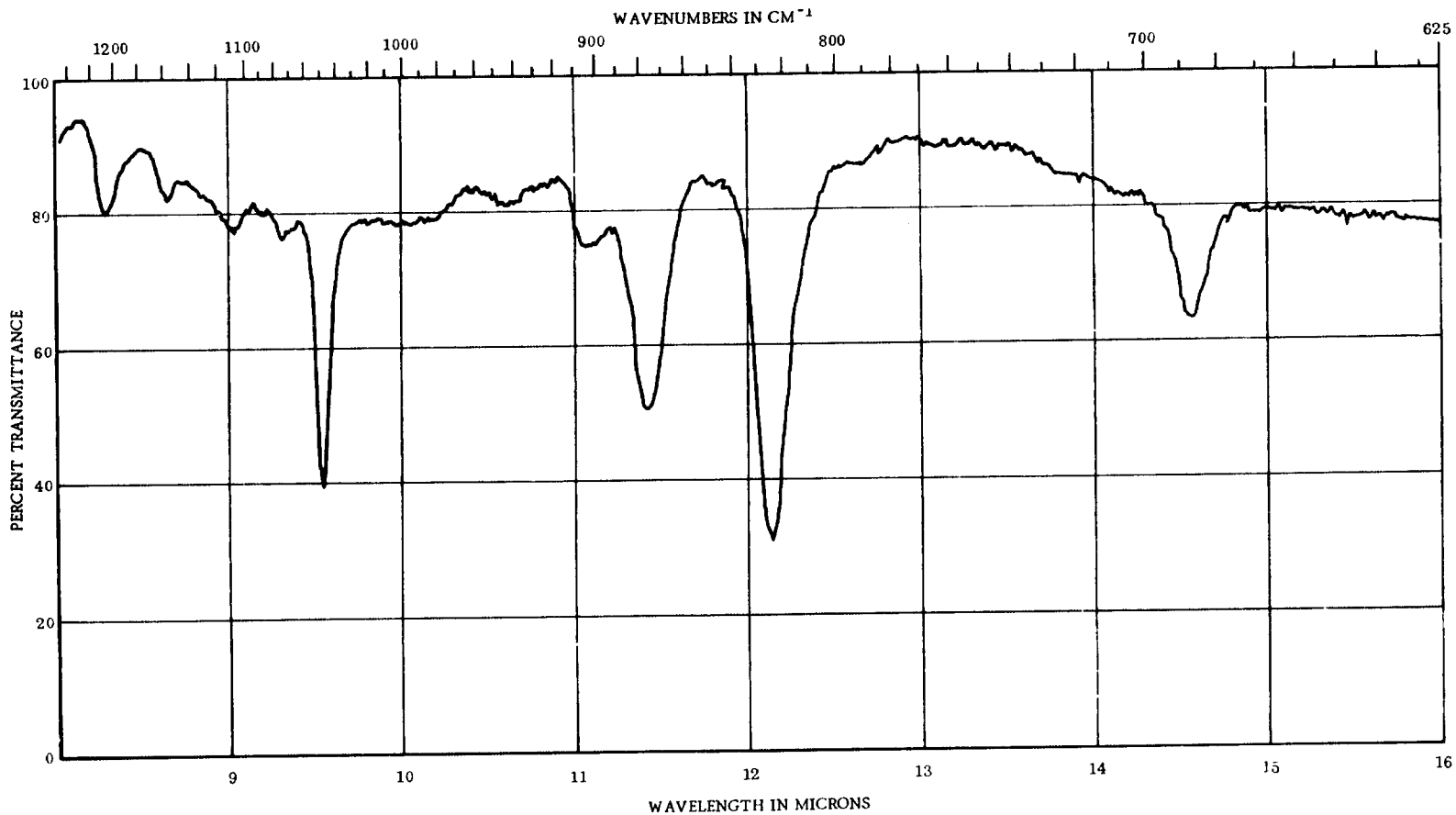


Figure 16. Closeup of Baffle Plate

Figure 17. Parylene C Polymer (Pure) Infrared Spectrum



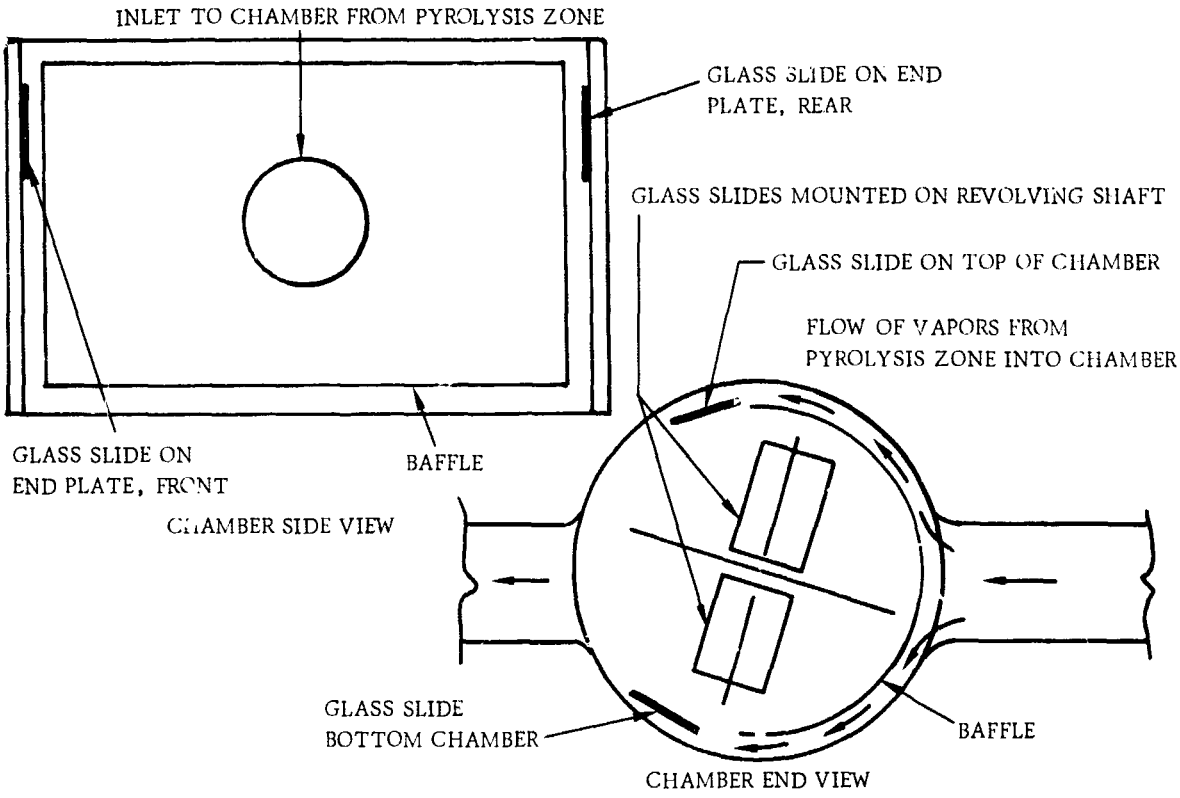


Figure 18. Film Thickness Profile

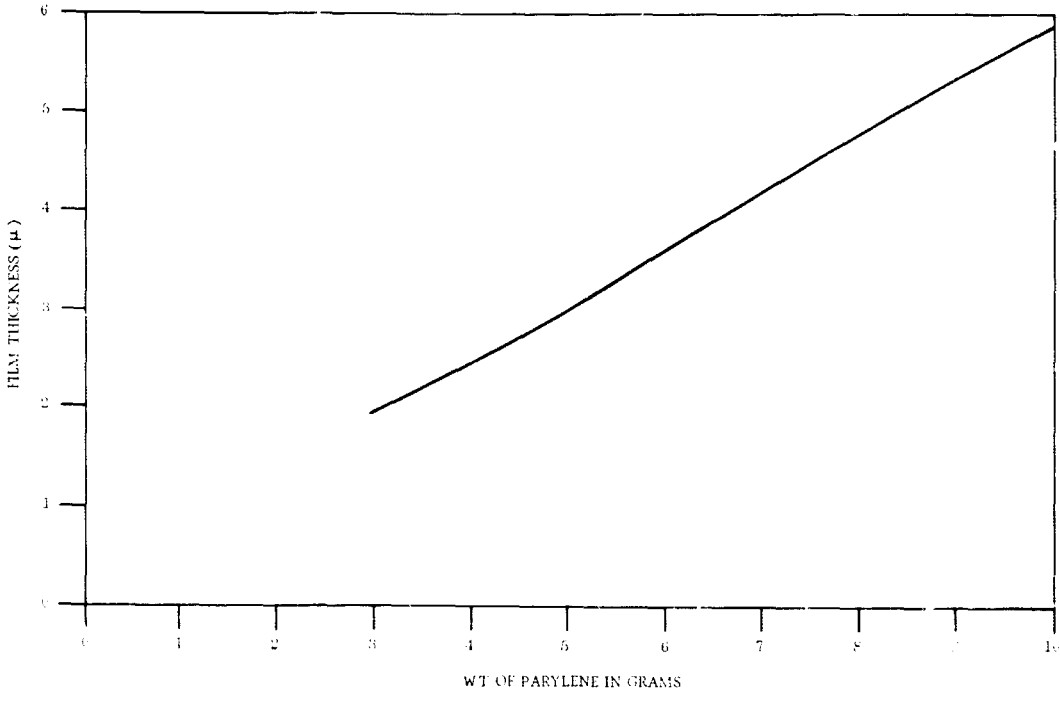


Figure 19. Parylene C Film Thickness as Function of Charge (Quantity of Dimer)

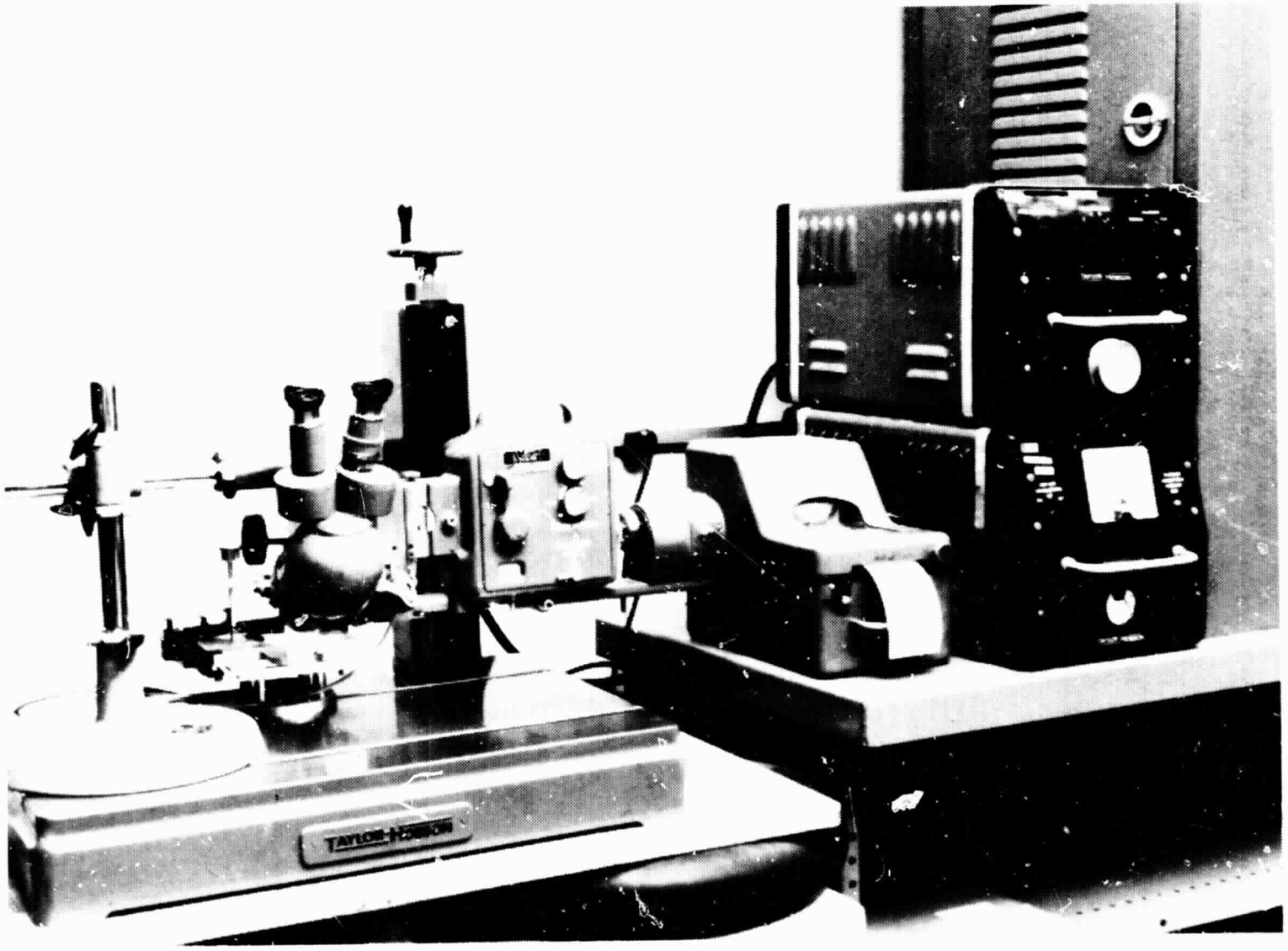
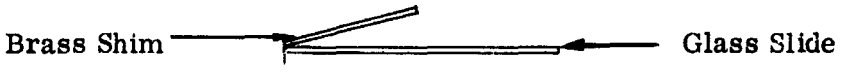


Figure 20. Talysurf Thickness Measurement Equipment

Visual Estimation

Sample specimen films were prepared on glass slides using a wedge arrangement as shown.



If the film is not plane parallel, which would result using the sample film collector as shown, the surfaces make an appreciable angle with each other when the brass shim is removed. The interfering rays do not enter the eye parallel to each other but appear to diverge from a point near the film. The resulting fringes resemble the localized fringes in a Michelson interferometer, and appear to be formed in the film itself. If the two surfaces are plane, so that the film is wedge shaped, the fringes will be practically straight following the lines of equal thickness. In this case, the path difference for a given pair of rays is practically given by

$$2\,nd = \left(m + \frac{1}{2}\right)\lambda$$

n = index of refraction

d = film thickness

λ = wavelength of light

m = integral value

provided the observations are made almost normal to the film. In going from one fringe to the next, m increases by 1; and this requires that the optical thickness of the film nd should change by $\lambda/2$.

In estimating the thickness of Parylene films below 10,000 A°, the 5461 A° green line wavelength at a quarter wavelength and index of refraction were employed to yield:

$$\frac{\lambda}{(4)\,(n)} = \frac{5461\ A^\circ}{(4)\,(1.63)} = 840\ A^\circ$$

Each green line appears at N x 840. To estimate the Parylene film thickness, we count the number of green lines up to the wedge of Parylene film under the fluorescent light, substract one, and multiply by 840. Thus the formula (2N-1) x 840 was found to give a very good thickness value for thin polymeric films in A°.

Inspector Thickness Gage

This device, manufactured by Gardner Laboratories was used in the latter phase of this program. It measures dry film thickness by the magnetic attraction principle and consists basically of a balanced arm, pivoted at its center. One end of the arm carries a permanent magnet, while the other end has a coiled spring. The spring is attached at its opposite end to a graduated scale ring. Rotation of the scale ring

measures deflection of the spring. During operation, the magnet is placed vertical to the surface of film in contact with a ferromagnetic base. Variations in film thickness tend to alter the attractive force of the magnet. The unknown force is then determined by turning the scale ring by hand to apply tension to the spring. When the spring tension just exceeds the unknown magnetic attractive force, the magnet breaks contact with the coated surface. The film thickness is read directly in microns from the calibrated scale.

Silane Adhesion Promoter. - In an effort to ensure good adhesion, silane adhesion promoters were considered for application to both stainless steel disks and epoxy-glass "Y" connector boards. These silane adhesion promoters are molecules functioning as coupling agents containing two different types of reactivity. They establish a "bridge-type" chemical bond between the inorganic and organic surfaces because of the unique affinity of both portions of the molecule. The silicon part of the molecule can attach or bond to the inorganic, metallic, or glass surface while the organic portion is tailored to combine with the polymeric surface.

The general formula of most coupling agents of this type is $R\text{-}Si(OCH_3)_3$ where R is a reactive organic group engineered to match the reactivity of the system to be used.

The mechanism of coupling requires that the silane coupling agent undergo hydrolysis, which necessitates a combination of water and acid or base catalyst.

$$-Si(OCH_3)_3 + 3H_2O \longrightarrow Si(OH)_3 + 3CH_3OH$$

The water for effecting this required hydrolytic step can originate from the application medium, the atmosphere, or from the substrate. Application of anhydrous coupling agent to a completely dry surface fails to improve adhesion.

After considering the postulated mechanism of both the candidate silanes, vinyltrichlorosilane and γ-methacryloxpropyltrimethoxysilane, onto the substrate surface, it was decided not to use the vinyltrichlorosilane. This chlorinated silane reacts with surface moisture to form hydrogen chloride. The presence of HCl besides being a potent corrosive chemical is a source of chloride ion, which has been shown to be a most serious source for adverse effects on semiconductor surfaces.

$$CH_2 = CHSiCl_3 + 3H_2O \longrightarrow CH_2 = CHSi(OH)_3 + 3HCl$$

Pretreatment

In an effort to remove surface glaze, "Y" connector boards were pretreated by gently scouring with a Nylon fibered pad and isopropanol, followed by a thorough rinsing with isopropanol.

In addition, in order to evaluate the comparative merits of the scoured method of pretreatment, a series of "Y" connector boards was only rinsed with isopropanol and another series dry honed. The latter operation was performed using fine walnut shells (No. 10.5) under 40 lb pressure in the Uni-Hone (Universal Finishing Machines, Inc., Los Angeles). The three types of pretreated samples were subjected to adhesion tests.

Application of Adhesion Promoter (Modified Method)

A solution of Union Carbide A-174 (λ-methacryloxypropyl trimethoxy silane) was prepared in methanol. The solution was prepared by mixing 1.0 ml A-174, 5.0 ml H_2O in 1000 ml methanol. The resultant solution was then allowed to remain at room temperature for two hours prior to use. The cleaned substrate was then immersed in this solution at room temperature for 10 minutes, then removed and allowed to air dry for 30 minutes. At the end of this time, the substrate was rinsed in agitated methanol for five minutes and then allowed to air dry for 30 minutes. The storage life of this solution of A-174 silane adhesion promoter is one day, and a fresh solution was prepared every day.

Adhesion Test Results

To determine the effects of surface pretreatment on adhesion, a series of "Y" connector boards were subjected to three different pretreatments prior to application of A-174 silane adhesion promoter. Pretreatment included either scouring with a Nylon fibered pad and isopropanol, dry honing with walnut shells, or merely rinsing with isopropanol. The three series of Parylene C coated "Y" connector boards consisting of two sets, five microns thick and one thin set of < 1 micron were subjected to an adhesion tape test. The adhesion test chosen consisted of scoring the coated surface of each specimen with a single X cut of approximately 0.01 inch deep. A three-inch portion of a five-inch length of masking tape was then pressed onto the scored surface at a 45 deg angle with respect to the cuts. The tape was then rapidly peeled from the specimen surface pulling in a direction perpendicular to the surface. This adhesion test was conducted on "Y" connector boards that were coated with Parylene C and D before and after subjection to the 240-hour humidity exposure tests. The results thus far (Table V) have indicated excellent adhesion between the glass epoxy boards and the Parylene coating for all three types of pretreatment.

Determination of Pinholes. - The problem of pinholes is most acute in thin films and especially in organic types where self healing does not usually result as is the case with the inorganic anodize and thermal oxidation oxide films. The location of surface defects such as pinholes in early production stages has been a problem since electrical failures can subsequently occur when vacuum deposited interconnects placed over the holes are short circuited to the conductive substrate below. A simple nondestructive electrograph procedure developed at Autonetics locates pinholes in passivation layers of silicon wafers and has been adopted for use on polymeric thin films for the first time.

This method utilizes a colorless organic reagent, viz., benzidine which is anodically oxidized to a colored product only at conductive sites such as pinholes (Figure 21). Application of a suitable anodic potential to the Parylene coated 1-1/4-in.-dia stainless steel disk results in the formation of dark blue to black oxidation product at the conductive sites, which are readily visible against the white background of the filter paper. This method was published in Insulation 15, 40 (1968) by S. M. Lee, J. P. McCloskey, and J. J. Licari entitled "New Technique Detects Pinholes In Thin Polymer Films."

Disks coated with Parylenes were subjected to the electrographic method of pinhole determination as described in the above. In preliminary experiments (Table VI)

TABLE V
ADHESION TEST RESULTS

Run No.	Parylene	Treatment			%Adhesion (1)	
		Surface Preparation	Adhesion Promoter	Post Cure (2)	Before	After
N1866-12-A	C	Scoured (3)			0	0
N1866-12-B		Scoured		X	0	0
N1866-12-C		Scoured	X		0	0
N1866-12-D		Scoured	X	X	0	0
N1866-15-A	D	Dry Honed (4)			0	
N1866-15-B		Dry Honed	X		0	
N1866-15-C		Dry Honed		X	0	
N1866-15-D		Dry Honed	X	X	0	
N1866-19-A-1	C	Solvent Rinse			0	100
N1866-19-A-2					0	100
N1866-19-A-3					0	100
N1866-19-B-1			X		0	50
N1866-19-B-2			X		0	25
N1866-19-B-3			X		0	50

(1) Represent percent of film removed by tape before and after 240 hour humidity exposure

(2) Treated for 90 minutes at 66 C/44 mm

(3) With Nylon fibered pad and isopropanol

(4) With walnut shell abrasive

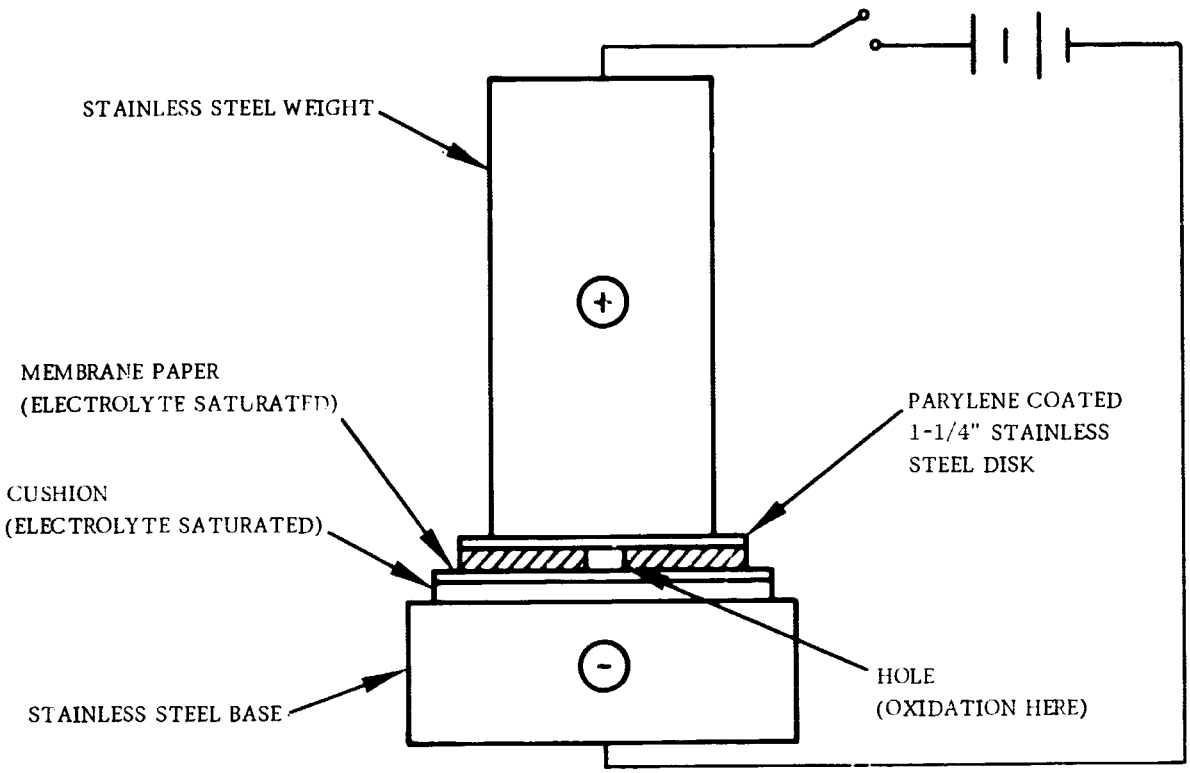


Figure 21. Electrograph Assembly Diagram

a series of stainless steel disks were coated with Parylene C, D, and N. Results from these experiments showed the number of pinholes to range from 15 to 85. No simple correlation was observed relating the type of Parylene used and the number of pinholes, although initial experiments showed the smallest number of pinholes to be present using Parylene N. In addition, post curing of Parylenes for 100 C for one hour did not change the number of pinholes but rather reduced the pinhole diameters by one half.

Efforts were instituted to eliminate the presence of pinholes. It was thought that the presence of pinholes originated from particulate or foreign matter on the substrate surface or from the presence of foreign material or even some oxide on the surface, or was introduced during handling and/or surface rinse. To ascertain whether oxide or other foreign material inherent to the stainless steel material was causing this problem, platinum disks were coated (experimental run 12) to ascertain whether oxide or other foreign material inherent to stainless steel material was responsible for the pinhole problem. Stainless steel and platinum disks prepared for pinhole determination studies were subjected to the modified A-174 silane adhesion promoter treatment. No pinholes were observed when a significant coating of five microns was applied over both stainless steel and platinum disks. However, as expected when a very thin coating was deposited of <1 micron a 20-33 percent area of the disk was found to have very small pinhole clusters. In addition, as expected in the absence of pinholes, samples were not affected by further post curing.

TABLE VI
PINHOLE TEST RESULTS

Run No. (3)	Parylene	Film Thickness (μ)	Treatment		Pinholes		Comments
			Adhesion Promoter (1)	Post Cure (2)	Number	Size (4)	
N1866-2-A	C		X		5	Small	Four near edge
N1866-2-B		< 1.0	X		70	Small	
N1866-2-C			X	X	55	Sm/Med	
N1866-2-D			X	X	200	Assorted	Pattern of cracks and scratches
N1866-5-A	D				25	Sm/Med	Mostly near edge
N1866-5-B			X		40	Sm/Med	Evenly distributed
N1866-5-C		1.0		X	20	Sm/Med	Mostly near edge
N1866-5-D			X	X	4	Sm/Med	Four med in center
N1866-6-A	D				30	Sm/Med	Uneven distribution
N1866-6-B			X		20	Very sm	Evenly distributed
N1866-6-C		2.0		X	150	Assorted	Uneven distribution
N1866-6-D			X	X	200	Assorted	Uneven distribution
N1866-9-A	N				5	Assorted	All near edge
N1866-9-B			X		2	Assorted	Near edge
N1866-9-C		2.0		X	10	Assorted	
N1366-9-D			X	X	10	Assorted	
N1866-12-A	C		---	---	0		
N1866-12-B			---	X	0		
N1866-12-C		5	X	--	0		
N1866-12-D			X	X	0		
N1866-12-Pt.			X	--	0		
N1866-12-Pt.			X	X	0		
N1866-15-A	D	1	--	--	100	V. Small	Pinholes are in groups.
N1866-15-B			X	--	100	V. Small	One group near edge.
N1866-15-C			--	X	75	V. Small	Scratches over entire area.
N1866-15-D			X	X	100	V. Small	Some scratches, pinholes over entire area.
N1866-19-A-1	C		--	--	0		
N1866-19-A-2		5	--	--	0		
N1866-19-A-3			--	--	0		
N1866-19-B-1			X	--	0		
N1866-19-B-2			X	--	0		
N1866-19-B-3			X	--	0		

TABLE VI (Concluded)

Run No. (3)	Parylene	Film Thickness (μ)	Treatment		Pinholes		Comments
			Adhesion Promoter	Post Cure	Number	Size (4)	
			(1)	(2)			
N1866-27-A-1	C			--	3	Small	All near edge
N1866-27-A-2		3.0		--	1	Small	
N1866-27-A-3				--	1	Small	
N1866-27-B-1			X	--	9	Small	All near edge
N1866-27-B-2			X	--	5	Small	All near edge
N1866-27-B-3			X	--	3	Small	All near edge
N1866-29-A-1	C	2.0		--	3	Sm/Med	Two near edge
N1866-29-A-2				--	2	Sm/Med	Both near edge
N1866-29-A-3				--	3	Sm/Med	
N1866-29-B-1			X	--	15	Sm/Med	Majority near edge
N1866-29-B-2			X	--	5	Sm/Med	Near center
N1866-29-B-3			X	--	9	Sm/Med	Near center
N1866-34-A-1	C	2.5		--	14	Sm/Med	All in one group near edge
N1866-34-A-2				--	2	Sm/Med	One near edge
N1866-34-A-3				--	1	Sm/Med	Near edge
N1866-34-B-1			X	--	2	Sm/Med	Near center
N1866-34-B-2			X	--	0	Sm/Med	
N1866-34-B-3			X	--	8	Sm/Med	Majority in one group near edge.

(1) Treatment with Union Carbide A-174 Silane Adhesion Promoter
(2) Treated for 90 minutes at 66 C/44 mm
(3) A, B, C, D, refer to stainless steel disk samples used for coated. Pt is platinum
(4) Assorted represents mixture of small, medium, and large.

Moisture Insulation Studies. - A series of experiments was designed to determine the effects of moisture at elevated temperatures on Parylene C coated epoxy-glass circuit boards containing "Y" connector patterns. Coated circuit boards were subjected to Military Spec. MIL-I-46058B (12-22-66, superseding MIL-I-46058A, 24 June 1964). This specification, although designed for epoxy, polyurethane, silicone, and polystyrene coatings of 0.001 - 0.006 in., was adopted for determining the effects of humidity at elevated temperatures on Parylenes.

Epoxy glass circuit boards containing "Y" connector patterns with soldered leads were placed inside a humidity chamber with the test leads extending outside for a total of ten cycles of 24 hours each or 240 hours. Each 24-hour cycle involved both dry and humid exposure subcycles. The sequence combined an initial 4-hour humid subcycle followed by a 2-hour dry subcycle, then a 4-hour humid, and finally a remaining 14-hour dry cycle. During this time, a 100 vdc polarizing voltage was continuously applied. Insulation resistance measurements are made initially; then after the first, fourth, seventh, and tenth cycles at the end of the first four hours humid period.

The results of these experiments were compiled in Table VII. However, in order to obtain a trend, average values were assigned to the various Parylenes with differing thickness. These values were obtained by averaging the insulation resistance measurement after 4-, 24-, 96-, 168-, and 240-hour exposure. Both the initial and recovered measurements were not used because of their relative lack of significance. Readings of "open" were not included in order to obtain the average resistance.

In addition, where postcuring was employed, it was not considered a factor because it was shown that post curing for 1.5 hours at 66 C/20 mm did not affect moisture resistance, i.e., samples 12-C, which was not subjected to the post cure, indicated $1.5 \times 10^{10}\Omega$, while samples 12-0, which were subjected to the post cure, gave $1.3 \times 10^{10}\Omega$ after the test. Both samples were from the same experimental run.

Based on the above described approach, a series of average values were obtained and are listed in Table VIII. The effects of moisture environment on varying thickness of Parylene C are depicted in a semilog plot (Figure 22) and a log-log plot (Figure 23). Insulation resistance on connector boards coated with Parylene C appears to reach a maximum value of $40 \times 10^{8}\Omega$ with coatings of about 10 microns.

Connector boards that have been treated with Union Carbide A-174 prior to coating with Parylene exhibit an improved moisture resistance from the untreated boards when exposed to humidity. The results, as shown in Table IX, indicate that one order of magnitude difference is evident between the treated and untreated boards in both the 1 and 2μ thick Parylene D samples. However, the effect appears to be not significant with both Parylene N and C.

An effort was made to correlate the Parylene type coating employed on the connector board with the insulation resistance measurement value after exposure to humidity. The values chosen in Table X are for boards that have not been treated with adhesion promoter.

From the results obtained to date, Parylenes appear comparable or better than some materials; e.g., polyurethanes and epoxies. In Figure 24, the change in insulation resistance of a polyurethane is compared to a Parylene C coating which have been exposed to humidity. The Parylene C coating exhibited superior insulation resistance.

TABLE VII
MOISTURE INSULATION RESISTANCE

Run No. (b)	Film Thickness (μ)	Adhesion Promoter	Post Cure Hr at °C	Measurement After Hours of Exposure (Ω)						
				Initial	4	24	96	168	240	(d) Recovered
N1355-16	0.2	No	None							
(a) -1				2.0×10^{12}	Open	4.0×10^{7}	1.8×10^{7}	3.0×10^{7}	9.0×10^{6}	1.3×10^{11}
-2				2.0×10^{12}	Open	2.7×10^{7}	2.0×10^{7}	2.6×10^{7}	Open	1.1×10^{10}
-3				2.0×10^{12}	7.0×10^{6}	1.3×10^{7}	1.3×10^{7}	1.0×10^{7}	5.0×10^{6}	4.5×10^{7}
-4				1.5×10^{12}	2.0×10^{7}	5.0×10^{7}	1.7×10^{7}	4.5×10^{7}	1.6×10^{7}	7.0×10^{9}
N1355-19	1.0	No	None							
-1				2.0×10^{12}	4.0×10^{7}	(c)	(c)	(c)	(c)	(c)
(a) -2				2.0×10^{12}	1.5×10^{8}					
-3				2.0×10^{12}	5.0×10^{7}					
-4				2.0×10^{12}	7.0×10^{7}					
N1355-40 (b)		No								
Control-1-R	0.7	No	None	$5.0 \times$	No	7.0×10^{7}	4.0×10^{7}	Open	Open	4.0×10^{8}
-L				2.0×10^{12}	measure-	1.5×10^{8}	Open	Open	Open	1.2×10^{10}
Control-2-R	0.9	No	None	2.0×10^{12}	ments made	3.5×10^{8}	6.0×10^{7}	6.0×10^{7}	6.0×10^{7}	3.2×10^{11}
-L				2.0×10^{12}		4.5×10^{7}	1.5×10^{7}	Open	Open	1.6×10^{11}
50°C-1-R	0.9	No	1 at 50	2.0×10^{12}		3.2×10^{8}	4.0×10^{7}	Open	Open	Open
-L				1.8×10^{12}		3.0×10^{8}	4.0×10^{7}	2.0×10^{7}	Open	4.0×10^{11}
50°C-2-R	0.7	No	1 at 50	2.0×10^{12}		3.0×10^{8}	1.0×10^{7}	Open	Open	5.0×10^{8}
-L				2.0×10^{12}		2.8×10^{8}	4.0×10^{7}	4.0×10^{7}	1.8×10^{7}	3.0×10^{11}
100°C-1-R	0.7	No	1 at 100	2.0×10^{12}		3.0×10^{8}	1.5×10^{8}	1.8×10^{8}	1.3×10^{8}	6.0×10^{11}
-L				2.0×10^{12}		4.5×10^{8}	1.8×10^{8}	1.8×10^{8}	1.4×10^{8}	7.0×10^{11}
100°C-2-R	0.7	No	1 at 100	2.0×10^{12}		2.5×10^{8}	6.0×10^{7}	Open	Open	Open
-L				2.0×10^{12}		5.0×10^{8}	1.2×10^{8}	7.0×10^{7}	Open	3.0×10^{11}
150°C-1-R	0.9	No	1 at 150	2.0×10^{12}		7.0×10^{8}	3.5×10^{8}	3.0×10^{8}	2.0×10^{8}	6.0×10^{11}
-L				1.0×10^{12}		1.0×10^{9}	3.0×10^{8}	1.9×10^{8}	1.5×10^{8}	6.0×10^{11}
150°C-2-R	0.9	No	1 at 150	2.0×10^{12}		2.0×10^{12}	Open	Open	Open	Open
-L				2.0×10^{12}		4.5×10^{8}	2.5×10^{8}	2.5×10^{8}	1.0×10^{8}	5.0×10^{11}

TABLE VII (Cont)

Run No. (b)	Film Thickness (μ)	Adhesion Promoter	Post Cure Hr at °C	Measurement After Hours of Exposure (Ω)						
				Initial	4	24	96	168	240	(d) Recovered
N1355-43	2.7	No					(c)	(c)	(c)	(c)
Control-1-R			None	2.0×10^{12}	6.0×10^{7}	2.0×10^{8}				
-L				2.0×10^{12}	4.0×10^{7}	2.0×10^{8}				
100°C-R	2.7	No	2 at 100	2.0×10^{12}	6.0×10^{7}	2.0×10^{8}				
-L				2.0×10^{12}	5.0×10^{7}	Open				
125°C-R	2.7	No	2 at 125	2.0×10^{12}	5.0×10^{7}	5.0×10^{8}				
-L				2.0×10^{12}	6.0×10^{7}	4.0×10^{8}				
150°C-R	2.7	No	2 at 150	2.0×10^{12}	Open	Open				
-L				2.0×10^{12}	Open	Open				
N1355-50-1	10.0	No	1 at 100							
-R				2.0×10^{12}	2.0×10^{10}	4.5×10^{7}	1.8×10^{8}	Open	Open	2.0×10^{8}
-L				2.0×10^{12}	3.0×10^{10}	3.5×10^{7}	6.0×10^{7}	Open	Open	Open
N1355-50-2	10.0	No	1 at 100							
-R				1.5×10^{12}	8.0×10^{9}	6.0×10^{7}	1.3×10^{8}	8.0×10^{7}	Open	7.0×10^{8}
-L				2.0×10^{12}	1.6×10^{10}	1.9×10^{7}	1.8×10^{7}	5.0×10^{7}	Open	Open
N1355-50-3	10.0	No	None							
-R				2.0×10^{12}	7.0×10^{9}	8.0×10^{7}	3.6×10^{8}	4.0×10^{8}	Open	2.3×10^{10}
-L				2.0×10^{12}	1.2×10^{10}	5.0×10^{7}	3.6×10^{8}	3.0×10^{8}	2.0×10^{8}	2.4×10^{11}
N1355-50-4	10.0	No	None							
-R				2.0×10^{12}	5.0×10^{9}	2.0×10^{7}	1.4×10^{8}	1.2×10^{8}	Open	3.0×10^{8}
-L				2.0×10^{12}	1.8×10^{10}	2.5×10^{7}	Open	2.5×10^{7}	Open	Open
N1866-2-A	1.0	Yes	None							
-R				2.0×10^{12}	6.0×10^{8}	4.0×10^{8}	---	---	Open	2.0×10^{9}
-L				2.0×10^{12}	6.0×10^{8}	4.0×10^{8}	---	---	5.0×10^{8}	1.0×10^{11}
N1866-2-B	1.0	Yes	None							
-R				2.0×10^{12}	6.0×10^{8}	4.0×10^{8}	---	---	Open	2.0×10^{9}
-L				2.0×10^{12}	2.0×10^{9}	4.0×10^{8}	---	---	Open	1.0×10^{10}
N1866-2-C	1.0	Yes	1.5 to 66							
-R				2.0×10^{12}	Open	Open	---	---	6.0×10^{8}	1.5×10^{11}
-L				2.0×10^{12}	Open	Open	---	---	4.0×10^{7}	5.0×10^{11}

TABLE VII (Cont)

Run No. (b)	Film Thickness (μ)	Adhesion Promoter	Post Cure Hr at °C	Measurement After Hours of Exposure (Ω)						
				Initial	4	24	96	168	240	(d) Recovered
N1866-2-D	1.0	Yes	1.5 at 66							
-R				2.0×10^{12}	6.0×10^{8}	6.0×10^{8}	---	---	4.0×10^{8}	1.4×10^{11}
-L				2.0×10^{12}	Open	3.0×10^{8}	---	---	4.0×10^{8}	1.5×10^{11}
N1866-5-A	2.0	No	None							
-R				2.0×10^{12}	3.0×10^{8}	4.0×10^{7}	---	---	Open	2.5×10^{9}
-L				2.0×10^{12}	5.0×10^{7}	Open	---	---	Open	Open
N1866-5-B	2.0	Yes	None							
-R				2.0×10^{12}	Open	Open	---	---	Open	2.0×10^{10}
-L				2.0×10^{12}	2.9×10^{9}	Open	---	---	Open	2.5×10^{10}
N1866-5-C	2.0	No	1.5 at 66							
-R				2.0×10^{12}	5.0×10^{7}	1.0×10^{6}	---	---	Open	Open
-L				2.0×10^{12}	5.0×10^{7}	1.0×10^{6}	---	---	Open	Open
N1866-5-D	2.0	Yes	1.5 at 66							
-R				2.0×10^{12}	Open	Open	---	---	8.0×10^{8}	2.0×10^{11}
-L				2.0×10^{12}	4.0×10^{8}	7.0×10^{8}	---	---	2.0×10^{8}	2.0×10^{9}
N1866-6-A	1.0	No	None							
-R				2.0×10^{12}	Open	1.0×10^{7}	---	---	4.0×10^{7}	3.5×10^{9}
-L				2.0×10^{12}	Open	Open	---	---	8.0×10^{7}	6.0×10^{9}
N1866-6-B	1.0	Yes	None							
-R				2.0×10^{12}	1.2×10^{9}	3.0×10^{8}	---	---	Open	Open
				2.0×10^{12}	8.0×10^{8}	Open	---	---	Open	Open
N1866-6-C	1.0	No	1.5 at 66							
-R				2.0×10^{12}	1.0×10^{8}	Open	---	---	Open	Open
-L				2.0×10^{12}	1.0×10^{8}	1.0×10^{6}	---	---	Open	Open
N1866-6-D	1.0	Yes	1.5 at 66							
-R				2.0×10^{12}	4.0×10^{8}	3.6×10^{8}	---	---	5.0×10^{8}	4.0×10^{10}
-L				2.0×10^{12}	3.0×10^{8}	Open	---	---	5.0×10^{8}	8.0×10^{10}
N1866-9-A-R	2.0	No	None	2.0×10^{12}	---	8.0×10^{7}	---	1.8×10^{8}	Open	2.0×10^{4}
-L				2.0×10^{12}	---	3.4×10^{8}	---	1.5×10^{8}	Open	1.3×10^{10}
N1866-9-B-R	2.0	Yes	None	2.0×10^{12}	---	8.0×10^{8}	---	1.0×10^{8}	Open	1.5×10^{10}
-L				2.0×10^{12}	---	3.8×10^{8}	---	4.0×10^{8}	3.0×10^{7}	1.5×10^{10}

TABLE VII (Concluded)

Run No. (b)	Film Thickness (μ)	Adhesion Promoter	Post Cure Hr at °C	Measurement After Hours of Exposure (Ω)						
				Initial	4	24	96	168	240	(d) Recovered
N1866-9-C-R	2.0	No	1.5 at 66	2.0×10^{12}	---	1.8×10^{8}	---	2.2×10^{8}	Open	4.0×10^{4}
-L				2.0×10^{12}	---	2.5×10^{8}	---	3.0×10^{8}	1.5×10^{4}	2.0×10^{4}
N1866-9-D-R	2.0	Yes	1.5 at 66	2.0×10^{12}	---	5.0×10^{8}	---	9.0×10^{7}	1.7×10^{6}	4.0×10^{10}
-L				2.0×10^{12}	---	Open	---	Open	Open	Open
N1866-12-A-R	5.0	No	None	2.0×10^{12}	---	5.0×10^{9}	---	3.0×10^{9}	3.7×10^{3}	1.4×10^{10}
-L				2.0×10^{12}	---	3.7×10^{9}	---	2.2×10^{9}	4.0×10^{8}	2.8×10^{10}
N1866-12-B-R	5.0	No	1.5 at 66	1.5×10^{12}	---	2.0×10^{9}	---	1.0×10^{9}	2.0×10^{8}	1.4×10^{10}
-L				2.0×10^{12}	---	2.0×10^{9}	---	1.2×10^{9}	Open	1.5×10^{10}
N1866-12-C-R	5.0	Yes	None	2.0×10^{12}	---	2.0×10^{9}	---	1.0×10^{9}	8.0×10^{7}	9.0×10^{9}
-L				2.0×10^{12}	---	2.0×10^{9}	---	1.0×10^{9}	Open	Open
N1866-12-D-R	5.0	Yes	1.5 at 66	2.0×10^{12}	---	4.5×10^{9}	---	3.0×10^{9}	4.0×10^{8}	1.5×10^{10}
-L				2.0×10^{12}	---	3.0×10^{9}	---	2.0×10^{9}	2.0×10^{8}	1.3×10^{10}

NOTES:

(a) One board test specimen with 4 "Y" test sites.

(b) Each of the eight test boards has 2 "Y" test sites, R = right site, L = left site.

(c) Test incomplete

(d) Measured outside chamber after one hour

TABLE VIII
MOISTURE INSULATION STUDIES

Run No.	Parylene	Adhesion Promoter	Thickness (μ)	Resistance ($10^8\Omega$)	Remarks
1355-16	C	No	0.2	0.21	
19	C	No	1.0	0.78	Dimer in coating
40	C	No	0.8	2.10	
43	C	No	2.7	1.60	Dimer in coating
50	C	No	10.0	40.00	
1866-2	C	Yes	1.0	5.50	
5	D	No	2.0	0.85	
		Yes	2.0	8.00	
6	D	No	1.0	0.55	
		Yes	1.0	5.45	
9	N	No	2.0	2.1	
		Yes	2.0	3.2	
12	C	No	5.0	19.0	
		Yes	5.0	17.0	

In addition, it should be pointed out that the Parylene coating usually have an average thickness of about five microns, while the polyurethanes and allied materials are applied in 2-5 mil thicknesses. These coatings are 5 to 25 times thicker than our vacuum deposited Parylenes.

Physical Measurements

Water Extract Electrical Resistivity.

Method: Reliability Series "Physics of Failure in Electronics," Vol. 4, pages 464-492, by S. M. Lee, J. J. Licari, and A. G. Valles.

Procedure: A weighed sample of the test film was placed in a flask with 100 ml of deionized water. The electrical resistivity of the deionized water had been previously measured. The flask was maintained at 165 F for seven days, and the electrical resistivity of the water at room temperature was then measured.

Average Results:

Sample	Wt of Film (gms)	Resistance (ohms) Initial	Final
Blank	---	2.38×10^6	3.25×10^5
Parylene C	0.50	2.25×10^6	2.38×10^5
Parylene D	0.6624	5.0×10^6	0.63×10^5
Parylene N	0.1129	4.5×10^6	2.1×10^5

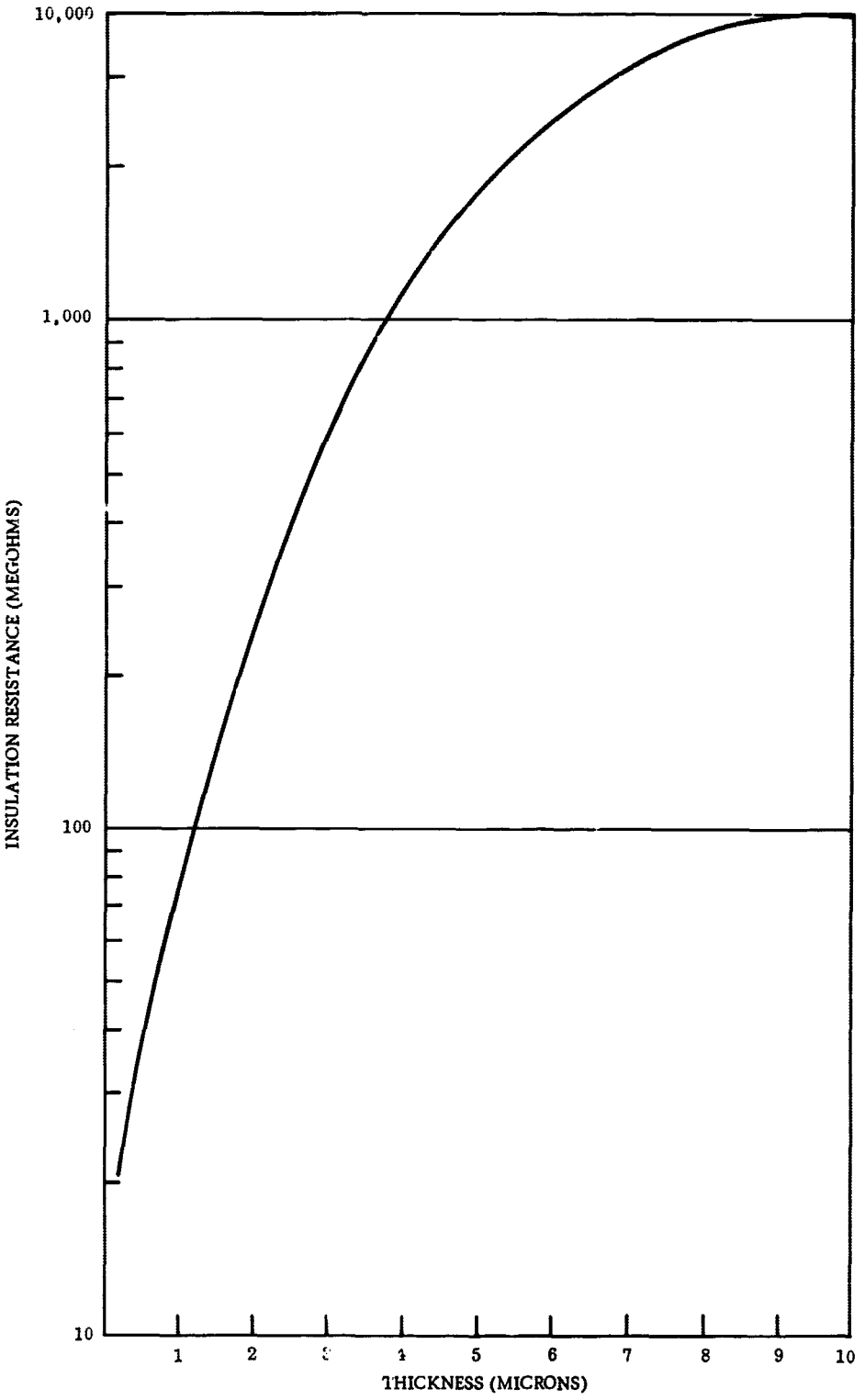


Figure 22. Parylene C - Effect of Coating Thickness on Moisture Insulation Resistance

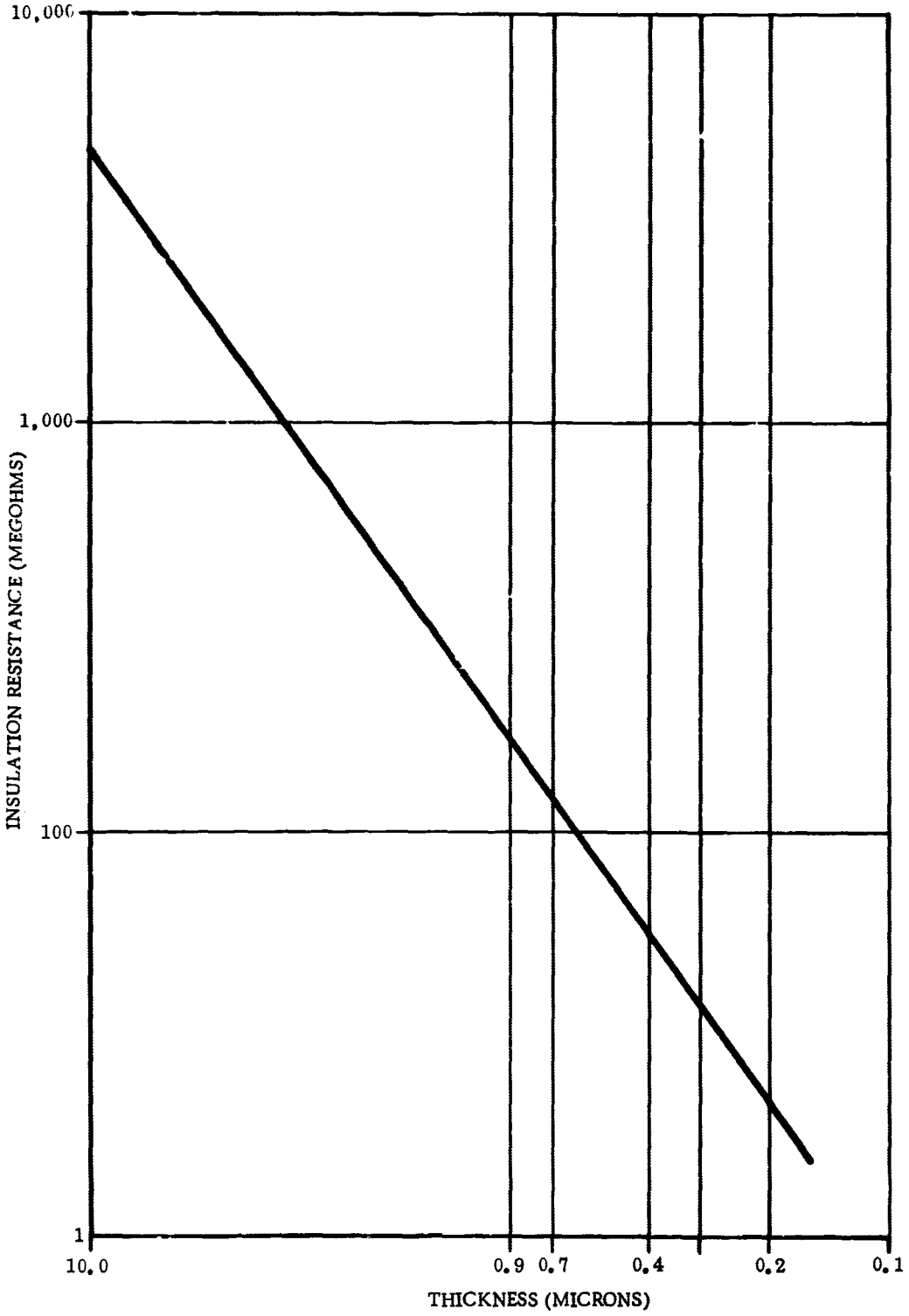


Figure 23. Parylene C - Effect of Coating Thickness on Moisture Insulation Resistance

TABLE IX
MOISTURE INSULATION STUDIES

Parylene	Adhesion Promoter	Thickness	Resistance ($10^8\Omega$)
D	No	1.0	0.55
D	Yes	1.0	5.45
D	No	2.0	0.85
D	Yes	2.0	8.00
N	No	2.0	3.20
N	Yes	2.0	2.10
C	No	5.0	19.00
C	Yes	5.0	17.00

TABLE X
MOISTURE INSULATION STUDIES

Parylene	Thickness (μ)	Resistance ($10^8\Omega$)
C	2.7	1.60
D	2.0	0.85
N	2.0	2.10

Water Vapor Permeability.

Method: MIL-I-16923E

Procedure: A sample of the test film is securely clamped over the mouth of a Payne permeability cup containing 10 ml of distilled water. The assembled cup is weighed and placed in a desiccator over dry $CaCl_2$. The cups are then removed and weighed at 24-hour intervals until a constant rate of loss in grams is attained.

Results: The rate of water vapor permeability is calculated as follows:

$$D = \frac{g \times th}{T \times A}$$

where:

D = rate of water vapor permeability
g = wt. loss in grams
T = time in hours
th = thickness of specimen in cm
A = exposed area of specimen in sq cm

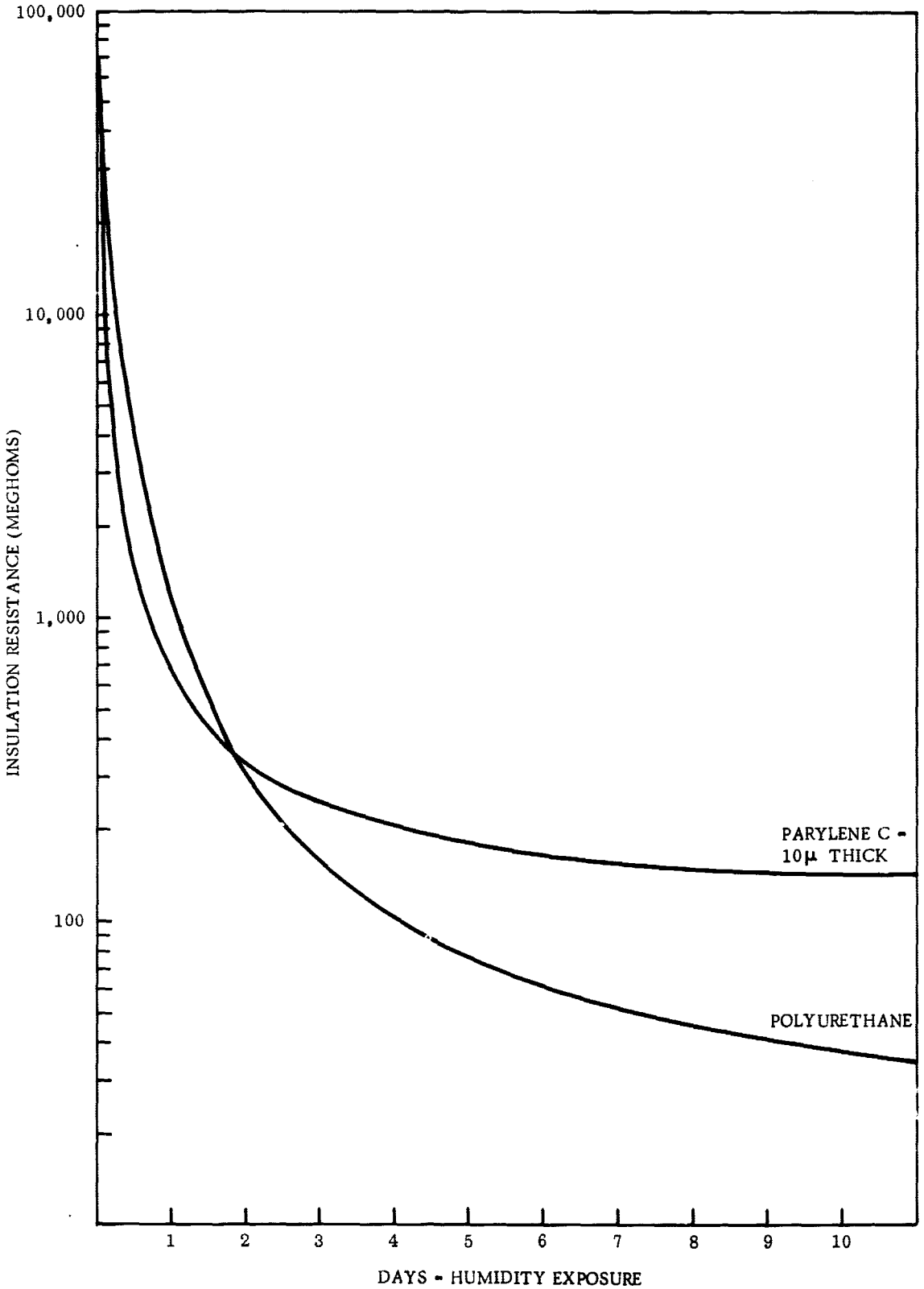


Figure 24. Comparison of Parylene C and Polyurethane Coating

Parylene (1)	Film Thickness (cm)	Rate of Water Vapor Permeability (g-cm/hr-cm^2)
C	2.0×10^{-3}	2.42×10^{-8}
D	2.0×10^{-3}	2.47×10^{-8}
N	1.3×10^{-3}	16.95×10^{-8}

(1) Each sample result represents an average of two test specimens.

The rate of change, i.e., weight loss as a function of time is graphically expressed in Figure 25.

Typical values of rates of water vapor permeability for a polyurethane and silicone as measured in our laboratories are 1×10^{-6} and 2×10^{-5} g-cm/hr-cm^2 respectively.

Thermal Conductivity.

Method: Cenco-Fitch MIL-I-16923E

Procedure: A 3 X 3 in. sample of the test film is mounted on a plate maintained at approximately 210 F. The test film is sandwiched between the heated plate and one exposed to room temperature. A microammeter connected to both plates measures the current differences due to the temperature differential. As the heat flows through the film to the cooler plate, the microammeter deflection is measured at 30-second intervals until the rate of change of the deflection becomes constant.

Results: The coefficient of thermal conductivity is calculated as follows:

$$K = 4.708 \frac{1}{m}$$

where:

K = coefficient of thermal conductivity
4.708 = constant for apparatus used
1 = thickness of specimen in centimeters
m = slope of curve (microamperes/minute)

Parylene (1)	Film Thickness (cm)	K (2) (cal/sec/cm^2/°C/cm)
C	4.45×10^{-3}	6.30×10^{-5}
D	6.99×10^{-3}	5.92×10^{-5}
N	1.27×10^{-3}	2.25×10^{-5}

(1) Each sample represents an average of two test specimens.

(2) The observed values appear lower than expected, probably due to the Cenco Fitch apparatus requiring a 1/8-in.-thick sample.

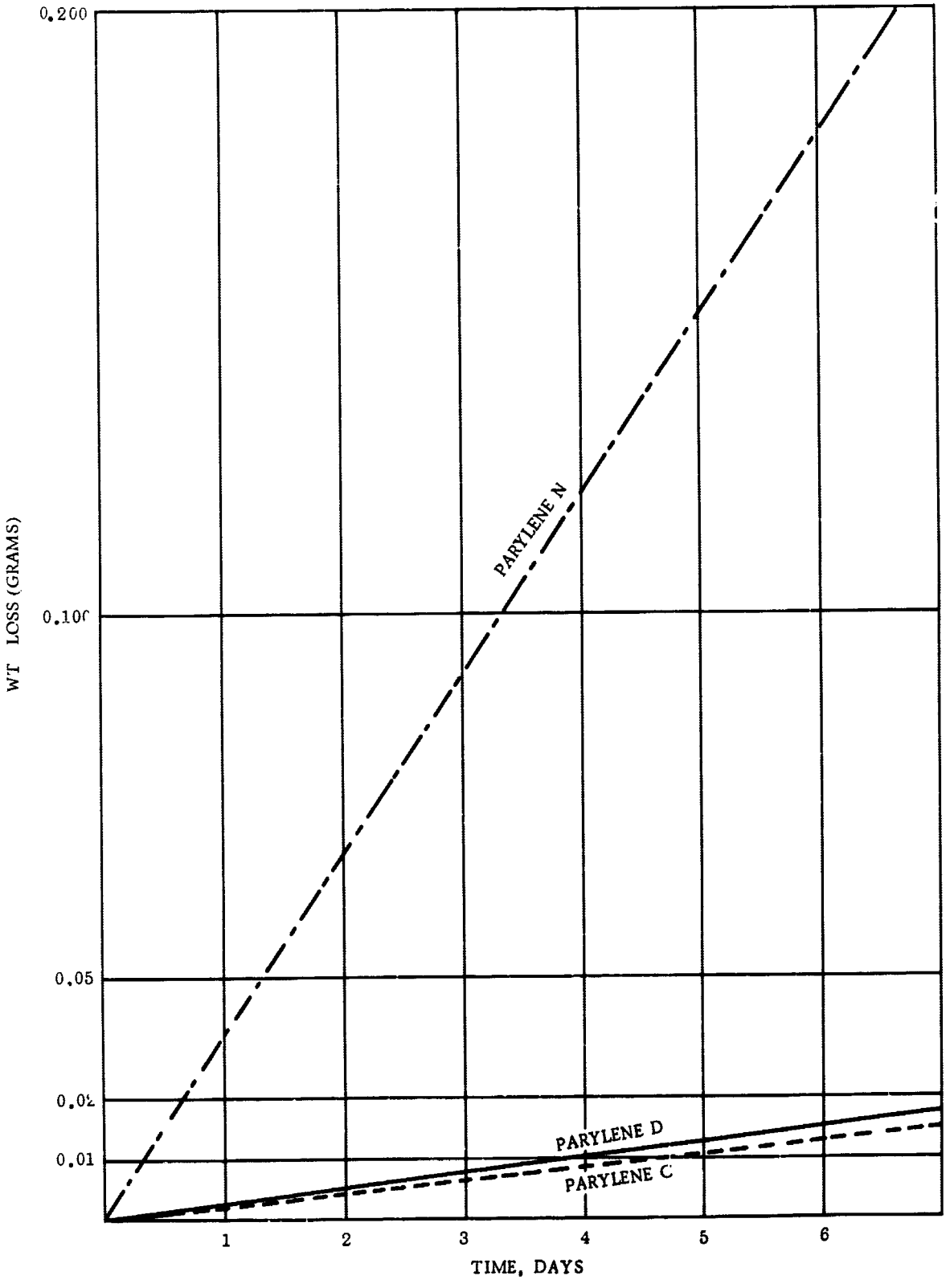


Figure 25. Water Vapor Permeability of Parylenes

Parylene thermal conductivity data is shown in Figure 26. For comparative purposes, thermal conductivity data for a silicone, epoxy, and polyurethane are 3.3×10^{-4}, 4.0×10^{-4}, and 4.2×10^{-4}, cal/sec/cm^2°C/cm respectively.

Outgassing. - Parylene samples were sealed in glass tubes and connected to a vacuum system in conjunction with gas chromatographic apparatus. After "pumping down" the gaseous products for about a half hour at room temperature, the total hydrocarbon outgassing products were analyzed as methane. The results are as follows:

Parylene Type	Total Hydrocarbons as CH_4 (ppm) of Parylene
N	1.2
D	5.5
C	6.9

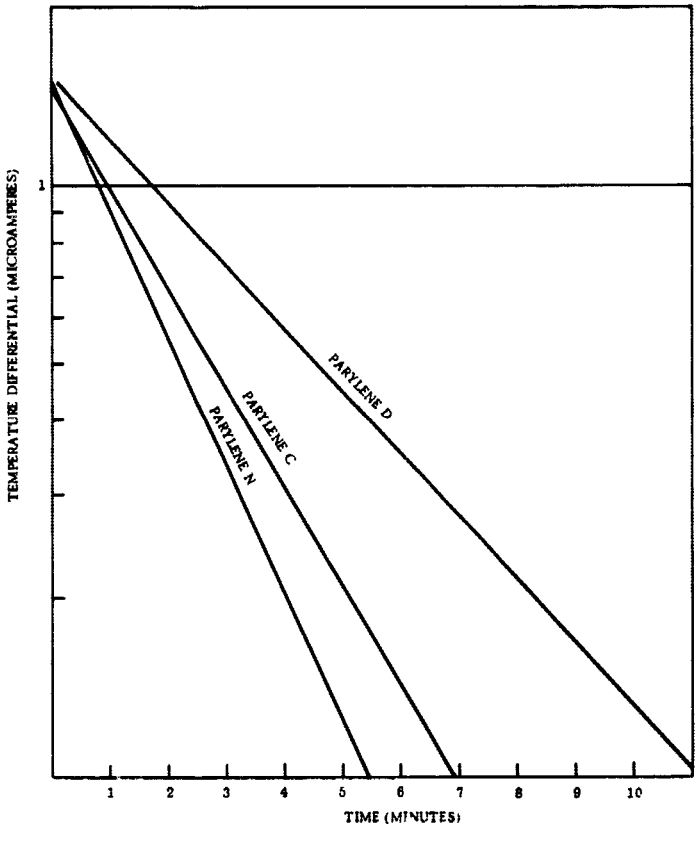


Figure 26. Thermal Conductivity of Parylenes

A. NEW TECHNOLOGY APPENDIX

Pages 6 and 12 and Figures 7 - 10 indicate improvements or innovations in the state of the art on the deposition of thin polymeric barrier coatings on semiconductor devices.