

COMPLIMENTS OF

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PARYLENE FOR ELECTRONICS

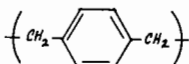


## I. Introduction

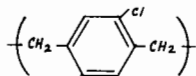
Parylene is the generic name for members of a unique polymer series developed by Union Carbide Corporation. The basic member of the series, called parylene N, is poly-p-xylylene, a completely linear, highly crystalline material.

Parylene C, the second member of the series commercially available, is produced from the same monomer modified only by the substitution of a chlorine atom for one of the aromatic hydrogens. The structures are shown in Figure 1.

FIGURE 1



PARYLENE N



PARYLENE C

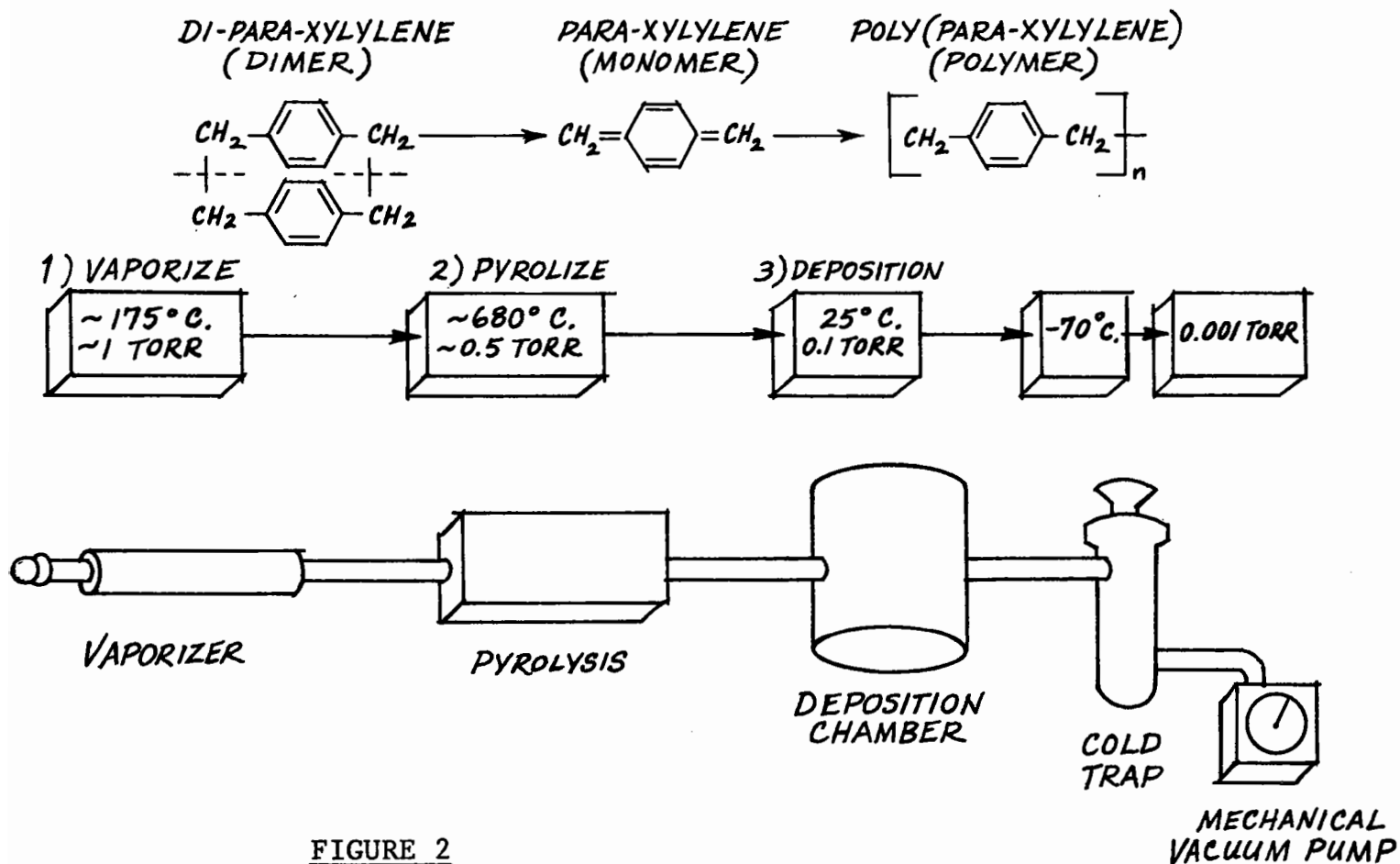
Parylene N is a primary dielectric, exhibiting a very low dissipation factor, high dielectric strength and a dielectric constant invariant with frequency. It is currently used as the dielectric in extended foil Flat Kap capacitors marketed by Union Carbide. Parylene C has a useful combination of electrical and physical properties plus a very low permeability to moisture and other corrosive gases. Along with its ability to provide a true pinhole-free conformal insulation, parylene C is the material of choice for the coating of critical electronic assemblies.

Due to the uniqueness of the vapor phase deposition, the parylene polymers can be formed as structurally continuous films from as thin as a fraction of a micron to as thick as several mils.

## II. The Deposition Process

The parylene polymers are deposited from the vapor phase by a process which in some respects resembles vacuum metallizing. Unlike vacuum metallization, however, which is conducted at pressures of  $10^{-5}$  torr or below, the parylenes are formed at around 0.1 torr. Under these conditions the mean free path of the gas molecules in the deposition chamber is in the order of 0.1 cm., therefore, unlike vacuum metallizing, the deposition is not line-of-sight and all sides of an object to be encapsulated are uniformly impinged by the gaseous monomer. This is responsible for the truly conformal nature of the coating.

The process consists of three distinct steps as outlined on Figure 2.



The first step is vaporization of the solid dimer at  $\sim 175^{\circ}$  C. The second step is the quantitative cleavage (pyrolysis) of the dimer at the two methylene-methylene bonds at about  $680^{\circ}$ C. to yield the stable monomeric diradical, p-xylylene. Finally, the monomer enters the room temperature deposition chamber where it simultaneously absorbs and polymerizes on the substrate. No liquid phase has ever been isolated and the substrate temperature never rises more than a few degrees above ambient. A necessary fourth component in this system is the mechanical vacuum pump and associated protective traps.

The equipment can be widely modified to meet the requirements or configurations of the items to be coated. Presently used coating chambers vary in size from six inches in diameter and fourteen inches long to a five foot high hemicylindrical unit. One particular configuration, one foot in diameter and thirty inches in length was designed specifically for circuit boards and can accommodate up to one hundred  $4\text{-}3/4'' \times 6\text{-}1/2''$  boards. The process is inherently simple and can be conducted with a minimum of supervision.

Compared with vacuum metallizing, deposition rates are fast, especially for parylene C which is normally deposited at about 0.5 microns per minute. The deposition rate of parylene N is somewhat slower. Kinetic studies have established that this rate is directly proportional to the square of the monomer concentration and inversely proportional to the absolute temperature.

### III. Properties

The electrical, mechanical, thermal, barrier, optical and other properties of parylene N and C are discussed below. These properties are compared to those reported for other conformal coating materials such as epoxies, urethanes and silicones.

#### A. Electrical Properties

The electrical properties of parylenes N and C are shown in Table I.

TABLE I

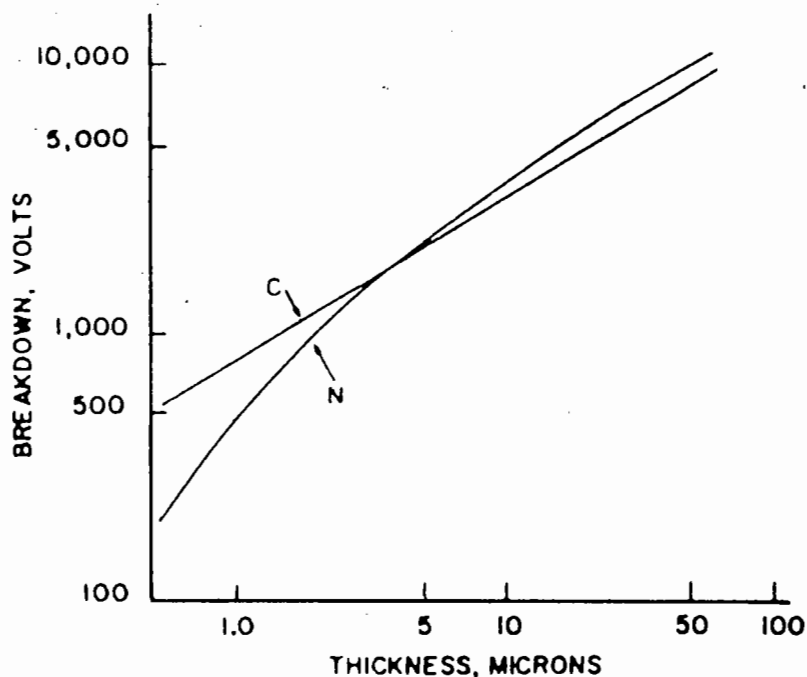
<u>ELECTRICAL PROPERTIES</u>			
<u>Properties</u> <sup>(1)</sup>	<u>Method or Conditions</u>	<u>Parylene C</u>	<u>Parylene N</u>
Dielectric Strength, volts/mil short time 1 mil films	ASTM D149-64	5,600	7,000
corr. to 1/8"	ASTM D149-64	590	700
step-by-step 1 mil films	ASTM D149-64	4,700	6,000
corr. to 1/8"	ASTM D149-64	550	550
Volume Resistivity, ohms 23° C, 50% RH	ASTM D257-61 (1 in. <sup>2</sup> mercury electrodes)	8.8 x 10 <sup>16</sup>	1.4 x 10 <sup>17</sup>
Surface Resistivity, ohms 23° C, 50% RH	ASTM D257-61 (1 in. <sup>2</sup> mercury electrodes)	10 <sup>14</sup>	10 <sup>13</sup>
Dielectric Constant 60 Hz	ASTM D150-65T (1 in. <sup>2</sup> mercury electrodes)	3.15	2.65
10 <sup>3</sup> Hz		3.10	2.65
10 <sup>6</sup> Hz		2.95	2.65
Dissipation Factor 60 Hz	ASTM D150-65T (1 in. <sup>2</sup> mercury electrodes)	0.020	0.0002
10 <sup>3</sup> Hz		0.019	0.0002
10 <sup>6</sup> Hz		0.013	0.0006

(1) Properties measured on parylene films, 0.001 inch thick.

### 1. Thin Film Dielectric Properties

One of the features of the parylenes is that they can be formed in extremely thin layers. The D.C. breakdown voltages of both parylene C and N films have been determined as a function of polymer thickness, a plot of which is shown in Figure 3. Parylene C is superior to N in this respect for films under 5 microns (0.0002 inch). These data show that both parylenes have respectable dielectric withstanding voltages even below the 1 micron thickness range and the voltage breakdown per unit thickness generally increases with decreasing thickness.

FIGURE 3  
BREAKDOWN VOLTAGE OF PARYLENE C AND N  
VS POLYMER FILM THICKNESS



## 2. Circuit Board Insulation Resistance

A critical test of the protection afforded by the parylene coating is to coat circuit board test patterns (as described in MIL-I-46058C) and subject them to insulation resistance measurements during a temperature-humidity cycle (MIL-STD-202, Methods 106 and 302). In brief, this test consists of ten cycles (one cycle per day), each cycle being in seven steps. The seven steps range from low temperature, low humidity (25°C, 50% RH) to more severe conditions (65°C, 90% RH). Resistance readings are taken initially and at periodic times at 65°C, 90% RH during the ten-day cycle.

Results are shown in Table II for parylene C coatings 0.0001 inch to 0.002 inch in thickness. It is interesting to note that even for the very thin coating (.0001 inch), the insulation resistance values are about one order of magnitude above the prescribed specification.

**TABLE II**  
**PARYLENE C**  
**CIRCUIT BOARD SCREENING**

Insulation Resistance (ohms) Mil-Std 202 Method 302

<u>Parylene C Thickness, (Inches)</u>	<u>Initial Measurement Temp. 23° C Humidity 50%</u>	<u>Precycle Temp. 23° C Humidity 90%</u>	<u>Step 5 Cycle 3 Temp. 65° C Humidity 90%</u>	<u>Step 5 Cycle 7 Temp. 65° C Humidity 90%</u>	<u>Step 5 Cycle 10 Temp. 65° C Humidity 90%</u>	<u>Step 7 Cycle 10 Temp. 25° C Humidity 90%</u>
0.002	$2.0 \times 10^{14}$	$1.8 \times 10^{13}$	$2.3 \times 10^{12}$	$2.5 \times 10^{11}$	$1.4 \times 10^{11}$	$7.5 \times 10^{12}$
0.0015	$5.0 \times 10^{14}$	$2.4 \times 10^{13}$	$8.6 \times 10^{11}$	$1.9 \times 10^{11}$	$1.1 \times 10^{11}$	$5.2 \times 10^{12}$
0.001	$2.0 \times 10^{14}$	$9.2 \times 10^{12}$	$8.1 \times 10^{11}$	$3.4 \times 10^{11}$	$1.3 \times 10^{11}$	$6.3 \times 10^{12}$
0.0005	$5.0 \times 10^{14}$	$2.3 \times 10^{13}$	$4.1 \times 10^{12}$	$2.4 \times 10^{11}$	$1.1 \times 10^{11}$	$4.7 \times 10^{12}$
0.0003	$5.0 \times 10^{14}$	$2.7 \times 10^{13}$	$4.4 \times 10^{12}$	$9.0 \times 10^{10}$	$4.7 \times 10^{10}$	$2.9 \times 10^{12}$
0.0001	$5.0 \times 10^{14}$	$3.2 \times 10^{10}$	$1.3 \times 10^{11}$	$1.1 \times 10^{11}$	$6.4 \times 10^{10}$	$2.3 \times 10^{12}$

### B. Physical and Mechanical Properties

Physical and mechanical properties of the parylenes are summarized in Table III. Because of their high molecular weight ( $\sim 500,000$ ) and because the melting temperatures and crystallinity are high, the parylenes cannot be formed by conventional methods such as extrusion or molding. Solubility in organic or other media, except at temperatures above  $175^{\circ}\text{C}$ , is so low that they cannot be formed by casting.



TABLE III  
PHYSICAL AND MECHANICAL PROPERTIES

<u>Properties</u> <sup>1</sup>	<u>Method of Conditions</u>	<u>Parylene N</u>	<u>Parylene C</u>	<u>Epoxies</u> <sup>2</sup>	<u>Silicones</u> <sup>2</sup>	<u>Urethanes</u> <sup>2</sup>
Secant modulus, p.s.i.	ASTM D882-56T @ 1% strain	350,000	400,000	350,000	900	1,000-10,000
Tensile strength, p.s.i.	ASTM D882-56T @ 10% strain/min.	9,000	13,000	4,000-13,000	800-1,000	175-10,000
Yield strength, p.s.i.	ASTM D882-56T @ 10% strain/min.	6,100	8,000	-	-	-
Elongation to break, %	ASTM D882-56T @ 10% strain/min.	20-200	200	3-6	100	100 -1,000
Yield Elongation, %	ASTM D882-56T @ 10% strain/min.	2.5	2.9	-	-	-
Density, gm/cc	ASTM D1505-57T	1.103-1.120	1.289	1.11 - 1.40 1.55 - 1.61	1.05 - 1.23 1.43	1.10 - 2.5 1.50 - 1.60
Index of refraction, $N_D^{23}$	Abbe Refractometer	1.661	1.639			
Water absorption, 24 hr.	ASTM D570-57T	0.01 (19 mils)	0.06 (29 mils)	0.08-0.15	0.12 (7 da.)	0.02 - 1.5
Rockwell hardness	ASTM D785-65	R85 (19 mils)	R80 (29 mils)	M80-M110	40-45 (Shore A)	10A-25D (Shore)
Coefficient of friction						
Static		0.25	0.29			
Dynamic		0.25	0.29			

1-Properties measured on parylene films 2 mils thick, except where specified.

2-Properties and methods as reported in Modern Plastics Encyclopedia, 45 1A (Sept. 1968).  
Modulus values are for tensile modulus.

Impact resistance is high when the parylene polymers are supported on test panels. Gardiner falling ball impact tests on 0.001 inch thick parylene C coated steel "Q" panels are in the 250 inch-pound range.

Wear index values (measured on a Tabor Abraser machine using CS-17 Calibraser wheels and 1000 gram weights) were 22.5 for parylene C and 8.8 for parylene N. By comparison, polytetrafluoroethylene ("Teflon") is 8.4, high impact PVC is 24.4, epoxy is 41.9 and urethane is 59.5.

### C. Thermal, Cryogenic and Vacuum Properties

#### 1. Thermal

Based on extrapolation of Arrhenius plot data, parylene C may be exposed continuously at 130° C (100,000 hours) without undergoing more than 20% loss in dielectric strength. In inert atmospheres parylenes C and N can be used continuously at temperatures in excess of 220° C.

Parylenes may be annealed to increase cut-through resistance, increase hardness and improve abrasion resistance. This is the result of a density and crystallinity increase.

General thermal data is summarized in Table IV.

TABLE IV  
THERMAL PROPERTIES

<u>Properties</u>	<u>Methods or Conditions</u>	<u>Parylene C</u>	<u>Parylene N</u>
T (melting), °C	Taken from secant modulus-temperature curve (1)	280	405
T (glass transition), °C	Taken from secant modulus-temperature curve (1)	80-100	60-70
T <sub>5</sub> (where modulus = 10 <sup>5</sup> ), °C	Taken from secant modulus temperature curve (1)	125	160
T <sub>4</sub> (where modulus = 10 <sup>4</sup> ), °C	Taken from secant modulus-temperature curve (1)	240	>300
Linear Coef. of Expansion (10 <sup>-5</sup> /°C)	ASTM D696-44 (61)	3.5	6.9
Volume Coef. of Expansion (10 <sup>-4</sup> cc/g/°C)	-	-	4.3
Thermal Conductivity (10 <sup>-4</sup> cal/sec/cm <sup>2</sup> -°C/cm)	ASTM C177	-	3
Specific Heat @ 20°C cal/g/°C	-	0.17	0.20

## 2. Cryogenic

Steel panels coated with parylene C and chilled in liquid nitrogen at minus 160° C withstood impacts of more than 100 in.-lbs. in a modified Gardiner falling ball impact test. This compares with values of over 200 in.-lbs. at room temperature.

Unsupported 0.002 inch films of parylene C can be flexed 180° six times at minus 165° C before failure occurs. Comparable films of polyethylene, polyethylene terephthalate and polytetrafluoroethylene fail at three, two and one flexes, respectively.

Neither electrical nor physical properties are affected by cycling from 2° Kelvin (about minus 270° C) to room temperature.

## 3. Vacuum Stability

Vacuum tests conducted at Jet Propulsion Laboratories show that total weight loss at 250° F and 10<sup>-6</sup> torr were 0.12% for parylene C and 0.30% for parylene N. Volatile condensable material values were less than 0.01% (the limit of sensitivity of the test) for both polymers.

### D. Barrier Properties and Chemical Resistance

#### 1. Barrier

The barrier properties of the parylenes are given in Table V. This rate for parylene C is superior to almost all polymeric materials.

TABLE V  
BARRIER PROPERTIES OF PARYLENES C AND N

<u>Polymer</u>	<u>Gas Permeability</u>				<u>Moisture Vapor Transmission</u>
	<u>N<sub>2</sub></u>	<u>O<sub>2</sub></u>	<u>CO<sub>2</sub></u>	<u>H<sub>2</sub></u>	<u>gm-mil/100 in. - 24 hours**</u>
Parylene C	.6	5	14	110	1
Parylene D	4.5	32	13 <sup>(a)</sup>	240	5
Parylene N	15	55	420	540	15

(a) Licari, J.J. and Brands, E.R., Machine Design, May 25, 1967, page 192.

\* ASTM D1434-63T

\*\* ASTM E96-63T

Moisture vapor permeability values have been measured at thicknesses below 0.1 micron. Normalized to equivalent thickness, the values are the same for all thicknesses. Assuming that parylene C at 0.001 inch is pinhole free, then parylene C films at 0.1 micron ( $4 \times 10^{-6}$  inch) are also pinhole free.

## 2. Chemical Resistance

The parylenes resist attack and are insoluble in all organic solvents up to 150° C. Parylene C can be dissolved in chloro-naphthalene at 175° C and parylene N is soluble at the solvent boiling, 265° C. Both polymers are resistant to permeation by most solvents with the exception of aromatic hydrocarbons. They also are unaffected by stress-cracking agents such as "Hostepal", "Igepal" and lemon oil.

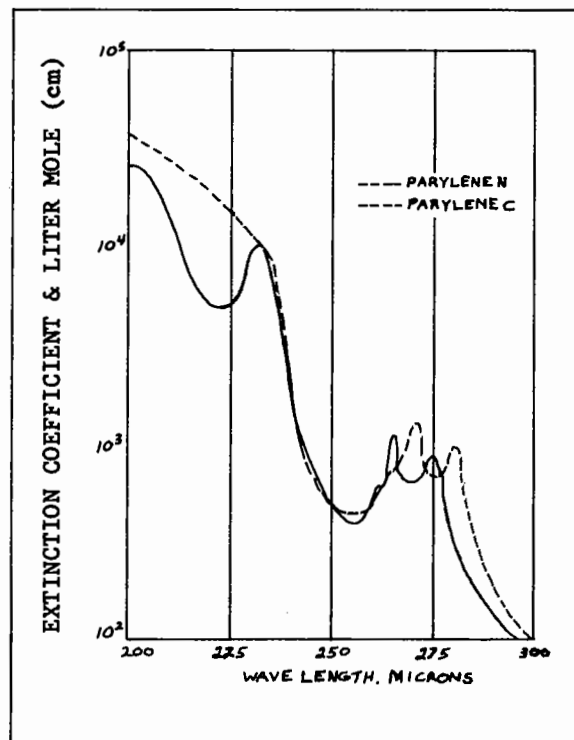
E. Optical Properties, Weathering and Radiation Resistance

1. Opticals

Parylene exhibits very little absorption in the visible region and is, therefore, transparent and colorless. Below about 280 $\mu$  both N and C absorb strongly as shown in Figure 4.

FIGURE 4

ULTRAVIOLET SPECTRA OF PARYLENE C AND N



Both parylenes are relatively featureless to at least 50 micron wavelengths (except for a few characteristic peaks), especially in thin film form ( $< 1\mu$ ). The IR spectra for 1 mil films are shown in Figures 5 and 6.

FIGURE 5  
INFRARED SPECTRUM OF PARYLENE C

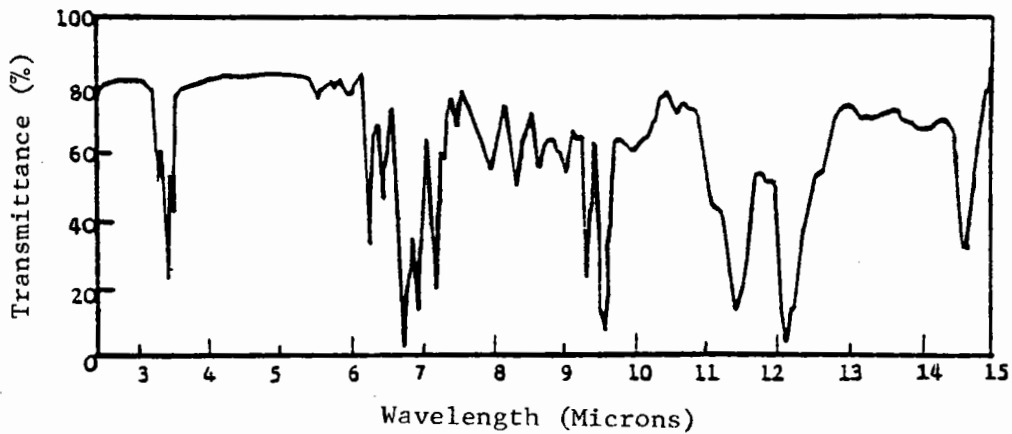
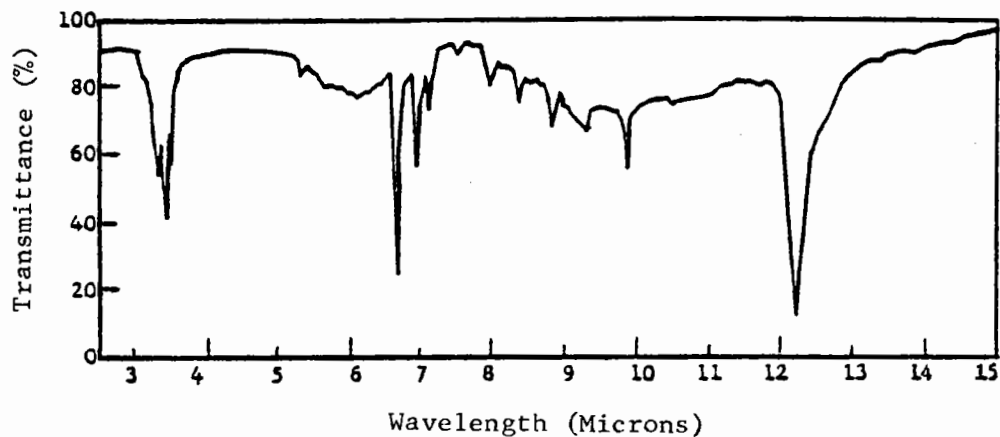


FIGURE 6  
INFRARED SPECTRUM OF PARYLENE N



## 2. Radiation and Weathering Resistance

Parylene C and N films show a high degree of resistance to degradation by gamma rays in vacuum. Tensile and electrical properties were unchanged after 100 Mr dosage at a dose rate of 1.6 megarads per hour. Exposure in air leads to rapid embrittlement.

Although stable indoors, the parylenes are not recommended for use outdoors when exposed to direct sunlight.

### IV. Adhesion

Good to excellent adhesion of parylene to a wide variety of substrates can be achieved by the use of a simply applied pre-coating treatment with a dilute solution of an organic silane. Two silanes, vinyl trichlorosilane in either xylene, isopropyl alcohol or UCON (or Freon) and  $\gamma$ -methacryloxypropyltrimethoxy silane in a methanol-water solvent have been successfully used. The techniques were developed primarily for electronic components and assemblies and do not affect any of the substrate or coating properties.

Generalized procedures for using these silanes are available upon request.

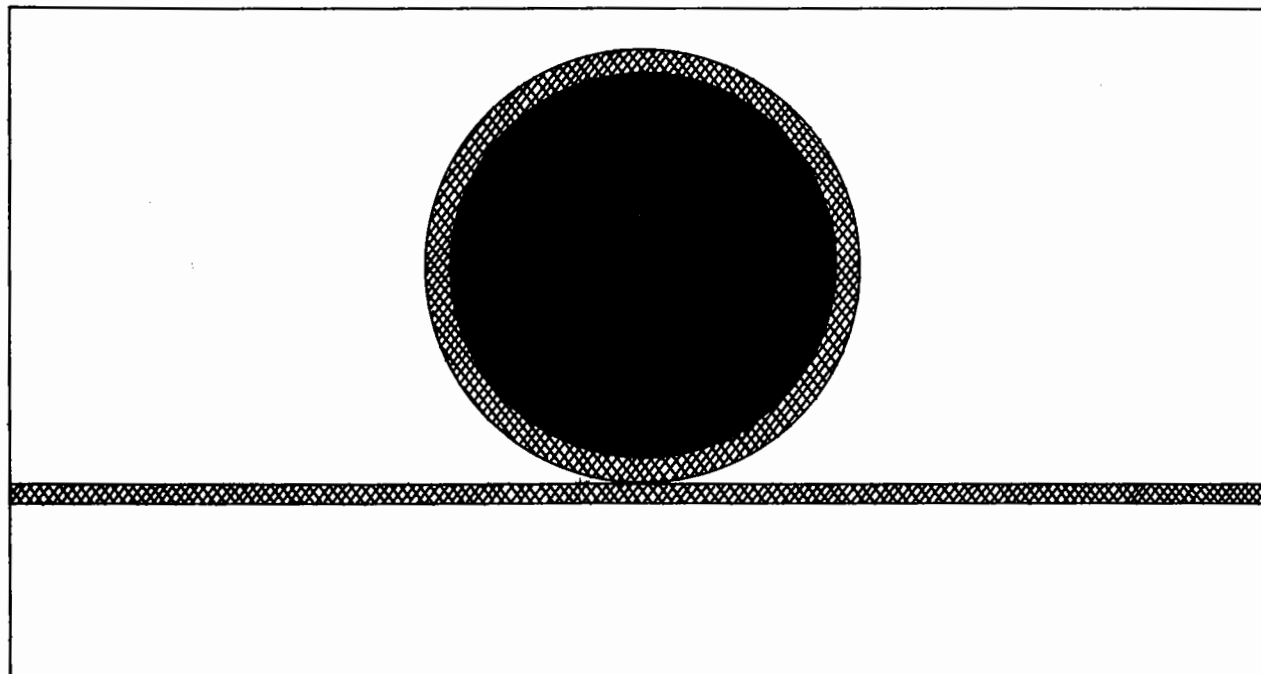
### V. Applications

#### A. Conformal Insulation of Printed Circuit Boards for Protection Against Moisture and Corrosive Environments

The ability to deposit parylene as a truly conforming, thin, continuous, uniform, adherent coating highly recommends its use in this application.

A number of printed circuit assemblies and conductor patterns have been cross-sectioned after coating with parylene. A potting compound was used to permit adequate polishing of each specimen. Figure 7 is a photomicrograph of a .025 inch wire on a board, in this case, a phenolic laminate.

FIGURE 7  
CROSS-SECTION OF COATED WIRE  
ON PHENOLIC LAMINATE (50X)



The coating is 0.001 inch of parylene C. The polymer will penetrate and coat uniformly even in the 0.002 inch space between the wire and the board.



B. Surface Passivation and Environmental Protection of Semiconductor Devices

Parylene at thicknesses from 0.1 micron to 0.0002 inch has been found useful in these applications. Again, the truly conformal nature of the coating allows bonded wires and evaporated conductor patterns to be coated at the same thickness as the silicon or other semiconductor surfaces. Parylene at thicknesses down to at least 0.4 micron is pinhole free as shown by HF and Chlorine Etch techniques.

Thorough evaluation proves that parylene does not alter the electronic parameters of devices. Furthermore, when parylene-coated devices, integrated and hybrid circuits are encapsulated by transfer molded epoxy compounds, their performance is equivalent to hermetically sealed units in accelerated aging tests (pressure cooker).