

I. INTRODUCTION

Parylene is the generic name for members of a unique polymer series. The basic member of the series, called Parylene N, is poly-paraxylylene, a completely linear, highly crystalline material.

Parylene C, the second commercially available member of the series, 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.

Parylene D, the third member of the series, is produced from the same monomer modified by the substitution of the chlorine atom for two of the aromatic hydrogens. Parylene D is similar in properties to Parylene C with the added ability to withstand higher use temperatures.

Parylene N is a primary dielectric, exhibiting a very low dissipation factor, high dielectric strength, and a dielectric constant invariant with frequency. This form has the highest penetrating power of all the Parylenes. 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 coating 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 micrometer to as thick as several mils.



Figure 1. Parylene N, C, & D Chemical Structures

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 coating.

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



Figure 2. Parylene Deposition Process

The first step is vaporization of the solid dimer at approximately 150 °C. The second step is the quantitative cleavage (pyrolysis) of the dimer at the two methy-lenemethylene bonds at about 680 °C to yield the stable monomeric diradical, para-xylylene. Finally, the monomer enters the room temperature deposition chamber where it simultaneously adsorbs 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 modified to meet the requirements or configuration of the items to be coated. Present coating chambers vary in size from 23 cm in diameter and 31 cm long to a 85 cm high hemi-cylindrical unit. One particular configuration, 45 cm in diameter and 60 cm high, was designed specifically for circuit boards and can accommodate up to two hundred 12 cm wide by 16 cm long 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 0.2 mils/hr. 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, C and D are discussed below. These properties are compared to those reported for other conformal coating materials such as epoxides, silicones, and urethanes.

A. Electrical Properties

The electrical properties of Parylene N, C, and D are shown in Table 1.

1. Thin Film Dielectric Properties One of the features of the Parylenes is that they can be formed in extremely thin layers. The breakdown dc 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 micrometers (0.0002 in). These data show that both Parylenes have excellent dielectric withstanding voltages even below the 1 micrometer thickness range, and the voltage breakdown per unit thickness generally increases with decreasing thickness.

Table 1. Parylene Electrical Properties						
Properties (1)	Parylene N	Parylene C	Parylene D	Epoxides (2)	Silicones (2)	Urethanes (2)
Dielectric Strength, dc volts/mil short time, 1 mil filmsª	7,000	5,600	5,500	-	-	-
corrected to 1/8 in	630	500	490	400-500	550	450-500
Volume Resistivity, ohm-cm, 23 °C, 50% RH ^b	1.4X10 ¹⁷	8.8X10 ¹⁶	1.2X10 ¹⁷	10 ¹² -10 ¹⁷	1015	10 ¹¹ -10 ¹⁵
Surface Resistivity, ohms, 23 °C, 50% RH ^b	1013	1014	10 ¹⁶	10 ¹³	1013	10 ¹⁴
Dielectric Constant ^c 2.65 3.15 60 Hz 2.65 3.10 1 1 KHz 2.65 3.10 1 1 MHz 2.65 2.95 1		2.84 2.82 2.80	3.5-5.0 3.5-4.5 3.3-4.0	2.7-3.1 2.6-2.7 2.6-2.7	5.3-7.8 5.4-7.6 4.2-5.2	
Dissipation Factor ^c 60 Hz 1 KHz 1 MHz	0.0002 0.0002 0.0006	0.020 0.019 0.013	0.004 0.003 0.002	0.002-0.01 0.002-0.02 0.03-0.05	0.001-0.007 0.001-0.005 0.001-0.002	0.015-0.05 0.04-0.06 0.05-0.07

^a ASTM D 149

^b ASTM D 257, 1 in² mercury electrodes

^c ASTM D 150, 1 in² mercury electrodes

(1) Properties measured on Parylene films, 0.001 in thick.

(2) Properties and methods as reported in *Modern Plastics Enclyclopedia*, issue for 1968, Vol. 45/No. 1A, McGraw Hill, New York, 1967.

(International Conversion Chart, Page 12)

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)



Figure 3. Breakdown Voltage of Parylene C and N vs Polymer Film Thickness

and subject them to insulation resistance measurements during a temperaturehumidity cycle (MIL-STD-202, methods 106 and 302).

In brief, this test consists of ten cycles (one cycle per day), with each cycle consisting of seven steps. The seven steps range from low temperature, low humidity ($25 \degree C$, 50% RH) to more severe conditions ($65 \degree C$, 90% RH). Resistance readings are taken initially and at the $65 \degree C$, 90% RH step for each cycle of the ten day test.

Results are shown in Table 2 for Parylene C coating thicknesses from 0.002 in to 0.0001 in. It is interesting to note that even for the very thin coatings (0.0001 in), the insulation resistance values are about one order of magnitude above the prescribed specification.

Parylene C Thickness (in)	Initial Measurement	Precycle	Step 5 Cycle 3	Step 5 Cycle 7	Step 5 Cycle 10	Step 7 Cycle 10
	23 °C, 50% RH	23 °C, 90% RH	65 °C, 90% RH	65 °C, 90% RH	65 °C, 90% RH	25 °C, 90% R⊦
0.002	2.0X10 ¹⁴	1.8X10 ¹³	2.3X10 ¹²	2.5X10 ¹¹	1.4X10 ¹¹	7.5X10 ¹²
0.0015	5.0X10 ¹⁴	2.4X10 ¹³	8.6X10 ¹¹	1.9X10 ¹¹	1.1X10 ¹¹	5.2X10 ¹²
0.001	2.0X10 ¹⁴	9.2X10 ¹²	8.1X10 ¹¹	3.4X10 ¹¹	1.3X10 ¹¹	6.3X10 ¹²
0.0005	5.0X10 ¹⁴	2.3X10 ¹³	4.1X10 ¹²	2.4X10 ¹¹	1.1X10 ¹¹	4.7X10 ¹²
0.0003	5.0X10 ¹⁴	2.7X10 ¹³	4.4X10 ¹²	9.0X10 ¹⁰	4.7X10 ¹⁰	2.9X1012
0.0001	5.0X10 ¹⁴	3.2X10 ¹⁰	1.3X10 ¹¹	1.1X10 ¹¹	6.4X10 ¹⁰	2.3X10 ¹²

B. Physical and Mechanical Properties

Physical and mechanical properties of the Parylenes are summarized in Table 3. Because of their high molecular weight (~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 °C, is so low that they cannot be formed by casting.

Properties (1)	Method	Parylene N (2)	Parylene C	Parylene D	Epoxides (3)	Silicones (3)	Urethanes (3)
- Secant (Young's Modulus (psi)) 1	350,000	400,000	380,000	350,000	900	1,000-10,000
- Tensile Strength (psi)	2	6,000-11,000	10,000	11,000	4,000-13,000	800-1,000	175-10,000
- Yield Strength (psi)	2	6,100	8,000	9,000	-	-	-
- Elongation to Break (%)	2	20-250	200	10	3-6	100	100-1,000
- Yield - Elongation (%)	2	2.5	2.9	3.0	-	-	-
- Density (g/cm³)	3	1.10-1.12	1.289	1.418	1.11-1.40	1.05-1.23	1.10-2.50
- Index of Refraction (n _D ²³)	4	1.661	1.639	1.669	1.55-1.61	1.43	1.50-1.60
- Water Absorption (% after 24 hrs)	5	⊢ Le	ess than 0.1 -		0.08-0.15	0.12 (7 days)	0.02-1.50
- Rockwell Hardness	6	R85	R80	R80	M80-M110	40-45 (Shore A)	10A-25D (Shore)
Coefficient of Friction Static Dynamic	7	0.25 0.25	0.29 0.29	0.33 0.31	-	-	-
Test Methods: 1. ASTM D 882 at 1% strain 2. ASTM D 882 at 10% strain, min. 3. ASTM D 1505 4. Abbe Refractometer 5. ASTM D 570 6. ASTM D 785			 Properties measured on Parylene films, 0.001-0.003 in thick except where specified. Properties depend somewhat on deposition conditions. Properties and methods as reported in <i>Modern Plastics Encyclopedia</i>, issue for 1968, Vol. 45/No. 1A, McGraw Hill, New York, 1967. Modulus values are for tensile modulus. 				

Table 3. Parylene Physical and Mechanical Properties

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

Wear index values (measured on a Taber Abraser machine using CS-17 "Calibrase" wheel with 1000 gram weight) were 22.5 for Parylene C and 8.8 for Parylene N. By comparison, polytetrafluoroethylene (Teflon®) is 8.4, high impact polyvinylchloride is 24.4, epoxide is 41.9 and urethane is 59.5.

C. Thermal, Cryogenic, and Vacuum Properties

1. Thermal

Based on an Arrhenius extrapolation of test data, Parylene C is expected to survive continuous exposure to air at 100 °C for ten years (100,000 hours). In oxygen free

atmospheres, or in the vacuum of space, the Parylenes are expected to serve similarly on continuous exposure to 220 °C. In all cases, higher temperature shortens use life. If the requirements for your application are near or exceed this time-temperature-atmospheric conditions envelope, it is recommended that you test the complete structure under conditions more closely resembling the actual conditions of intended use.

Parylene may be annealed to increase cutthrough resistance, increase hardness, and improve abrasion resistance. This is the result of a density and crystallinity increase.

General thermal properties are summarized in Table 4.

Properties	Method	Parylene N	Parylene C	Parylene D	Epoxides (1)	Silicones (1)	Urethanes (1)
Melting Point (°C)	1	420	290	380	cured	cured	~170
T5 Point (°C) (modulus = (10 ⁵ psi)	1	160	125	125	110	~125	~30
T4 Point (°C) (modulus = (10 ⁴ psi	1)	>300	240	240	120	~80	0
Linear Coef. of Expan. at 25 °C (x10 ⁵ , (°C) ⁻¹)	-	6.9	3.5	3-8	4.5-6.5	25-30	10-20
Thermal Conductivity at 25 ° (10 ⁻⁴ cal/(cm•s• °C))	2 C	3.0	2.0	-	4-5	3.5-7.5	5.0
Specific Heat at 20 °C (cal/g• °C)	-	0.20	0.17	-	0.25	-	0.42

2. ASTM C 177

(1) Properties and methods as reported in *Modern Plastics Enclyclopedia*, issue for 1968, Vol. 45/No. 1A, McGraw Hill, New York, 1967.

(International Conversion Chart, Page 12)

Gas Permeab	oility at 25	°C, (cm ³ (STP) ∙mil)/(1 00 i			
Polymer	N ₂	O ₂	CO2	H ₂	Moisture Vapor Transmission at 90% RH, 37 °C (g·mil/100 in²·d)**	
Parylene N	7.7	39	214	540	1.5	
Parylene C	1.0	7.2	7.7	110	0.21	
Parylene D	4.5	32	13(a)	240	0.25	
Epoxides	4	5-10	8	110	1.79-2.38(a)	
Silicones	-	50,000	300,000	45,000	4.4 - 7.9(a)	
Urethanes	80	200	3,000	-	2.4 - 8.7(a)	

Table 5. Parylene Barrier Properties

* ASTM D 1434

** ASTM E 96

2. Cryogenic

Steel panels coated with Parylene C and chilled in liquid nitrogen at -160 °C withstood impacts of more than 100 in-lb in a modified Gardner falling ball impact test. This compares with values of about 250 in-lb at room temperature.

Unsupported 0.002 in films of Parylene C can be flexed 180° six times at -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 °K (-271 °C) to room temperature.

3. Vacuum Stability Vacuum tests conducted at the let Propulsion Laboratory show that total weight loss at 121 °F and 10⁻⁶ torr were 0.12% for Parylene C and 0.30% for Parylene N. Volatile collectible, condensible material

values were less than 0.01% (the limit of sensitivity of the test) for both polymers.

(International Conversion Chart, Page 12)

D. Barrier Properties and Chemical Resistance 1. Barrier

The barrier properties of the Parylenes are given in Table 5. The moisture vapor transmission rates are again compared with those of other conformal coating materials. The rate for Parylene C is superior to almost all polymeric materials.

Moisture vapor permeability values have been measured at thicknesses below 0.1 micrometer. Normalized to equivalent thickness, the values are the same for all thicknesses.

2. Chemical Resistance The Parvlenes resist room temperature chemical attack and are insoluble in all organic solvents up to 150 °C. Parylene C can be dissolved in chloro-napthalene at 175 °C, and Parylene N is soluble at the solvent's

boiling point (265 °C). Both polymers are resistant to permeation by most solvents. They also are unaffected by stress-cracking agents such as Hostepal[®], Igepal[®], and lemon oil.

E. Optical Properties, Radiation, and Weathering Resistance

1. Optical Properties

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

The infrared spectra for 1 mil films are shown in Figures 5, 6, and 7.



Figure 4. Ultraviolet Absorption Spectra of Parylene N and C



Figure 5. Infrared Transmission Spectra of Parylene C



Figure 6. Infrared Transmission Spectra of Parylene N



Figure 7. Infrared Transmission Spectra of Parylene D

2. Radiation and Weathering Resistance Parylene N, C and D 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 Mr/h. Exposure in air leads to rapid embrittlement.

Although stable indoors, the Parylenes are not recommended for long term 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 simple treatment with a dilute solution of an organic silane prior to Parylene coating. Two silanes, vinyl trichlorosilane in either xylene, isopropyl alcohol, or Freon® and gamma-methacryloxypropyltrimethoxysilane 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. Silanes can also be vapor phase applied if non-liquid application is preferable. Generalized procedures for using these silanes are available upon request.

V. PRODUCT SAFETY

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VI. APPLICATIONS

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

The ability to deposit Parylene as a truly conformal, thin, continuous, uniform adherent coating permits its application as a protective PCB coating.

A number of printed circuit assemblies and conductor patterns have been crosssectioned and polished after coating with Parylene. Figure 8 is a representation of a photomicrograph taken of a 0.025 in wire on a phenolic laminate, drawn to scale at 50X magnification.



Figure 8. Scale drawing of 0.025 in wire coated with 0.001 in of Parylene (50X)

The Parylene C coating was 0.001 in thick. The Parylene polymer penetrated and coated uniformly even in the 0.002 in gap between the wire and board.

Figure 9 shows photomicrograph of a conductor pattern on an epoxy glass

laminate coated with 0.002 in. of Parylene C. Replication of the step-edge is particularly impressive.

B. Surface Passivation and Environmental Protection of Semiconductor Devices

Parylene at thicknesses from 0.1 micrometer to 0.002 in. has been found useful in this application. 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 micrometer 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 epoxide compounds their performance is equivalent to hermetically sealed units in accelerated aging tests (pressure cooker).



Figure 9. Cross section of Conductor Pattern on Glass-Epoxy Laminate (50X)

C. Conformal Coating of Biomedical Devices for Environmental Protection and Electrical Insulation Requirements

Thin Parylene films can be deposited on virtually any biomedical substrate. Parylene coated devices are stable, exhibit little or no change in response characteristics, and are electrically and chemically isolated from the body.

D. Parylene has found acceptance in a myriad of industrial, aerospace, chemical, automotive, consumer, pharmaceutical, and defense applications

Figure 10. International Conversions

 $g/cm^3 \times 1,000 = Kg/m^3$ $psi \div 145 = MPa$ $cal/(g \cdot K) \times 4.184 = J/(g \cdot K)$ $cal/(s \cdot cm \cdot K) \times 418.4 = W/(m \cdot K)$ g·mil/(100 in²·d) at 90% RH, 37 °C ÷ 1240 = ng/(Pa·s·m) (cm³(STP)·mil)/(100 in²/d·atm) ÷ 0.498 = amol/(Pa·s·m) volts/mil at 1 mil ÷ 25.4 = Mvolts/m at 25 μ m Ω -cm ÷ 100 = Ω -m



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