# Parylene HT®: A High Temperature Vapor Phase Polymer for Electronics Applications

**Rakesh Kumar**
Specialty Coating Systems
7645 Woodland Drive, Indianapolis, IN 46278, USA
Phone: (317) 244-1200; Email: rkumar@scscoatings.com

## Abstract

*A development in the area of high temperature polymers, which offers solutions to many existing packaging and reliability challenges of electronics industry, is described. Packaging, protection and reliability of various electronic devices and components that include PCB's, MEM's, optoelectronic devices, fuel cell components and nano-electronic parts are becoming more challenging due to their long-term performance requirements. Parylene HT offers solutions to many existing packaging and reliability issues of electronics industry in part because of its excellent electrical & mechanical properties, chemical inertness and long-term thermal stability at high temperature exposure to over 350°C (short - term at 450 °C). Experimental results and trial runs demonstrate the ability of Parylene HT coating to meet the growing requirements of higher dielectric capabilities, higher temperature integrity and mechanical processing etc. of dynamic electronic industry. In addition, Parylene HT polymer coating truly conforms to the parts due to its molecular level deposition characteristics. Its suitability and biocompatibilty encourage researchers to explore Parylene HT's role in sensors and in active electronic devices for various industries, which include enhancing high temperature application/technologies.*

**Keywords –** Parylene HT, Electronics, Protection, reliability and packaging.

## Introduction

The demands on the electronics industry, where organic materials have been used for decades, continue to evolve. With the increasing trend for better and safer products, protection and reliability of various electronic components (pressure and temperature sensors, PCB's, MEM's, optoelectronic devices, fuel cell components and nanoelectronic parts etc.) used in electronics industry are critical as they are becoming smaller, more complex. The challenge is to find a suitable thin organic coating that could provide much needed protection from harsh environments for advanced parts and be thermally stable at higher temperatures.

The components of electronics such as integrated circuits, sensors, batteries, semiconductor devices, and other passive devices are packaged into smaller sizes with better performance and minimal weight. Overall system reliability and efficiency of the electronics depend on the quality of materials, packaging and how these devices are used. Packaging of these devices involves technology of material, fabrication process, thermal management and optimization of layout related to various performances of the devices. Hence, the desire for more reliable components and appropriate packaging is becoming more apparent, as fewer field failures save the manufacturer money [1-6].

There are several methods of making electronic components and devices more reliable and protecting them from detrimental effects of both physical and operational environments. Among the several desired areas of improvements, manufacturers of electronics are looking at the protective materials, preferably in the form of thin film coatings with improved processing characteristics (e.g. hardness, lubricity), higher temperature integrity for potting, and even better dielectric strength.

For the past thirty years, Parylene (Para-xylylene) polymers are known to the electronic industry as extremely thin coatings for various electronic components due to their desirable physical and electrical properties. Because Parylene coatings are applied in very thin layers, heat tends to dissipate rapidly from the underlying components. Thus, the coated components cool down quickly and are less prone to temperature related degradation than similar components bearing other types of coatings.

Parylene coatings are known for their inertness, gas phase deposition, pinhole free, and excellent barrier properties. Parylenes available to the current market so far have been found to be useful up to 130°C. The demand, however, is growing for a more stable Parylene at higher temperatures with excellent electrical properties that can be deposited easily on various substrates.

This paper describes the attributes of Parylene HT, a fluorinated variant of Parylene that provides thermal stability up to 450°C, improved properties such as low dielectric constant, low coefficient of friction etc., greatly surpassing that of other Parylenes. In addition, it demonstrates the suitability of Parylene HT for a variety of electronics applications through characterization of its thermal, electrical and other physical and chemical properties. Physical property data is presented through comparison with other commercially existing Parylenes.

## Experimental

### *Vapor Phase Deposition Polymerization (VDP)*

Following the vapor phase polymerization process [Fig 1], several 1 mil film samples of Parylene HT were prepared using both metallic and non metallic substrates for physical and chemical characterization.

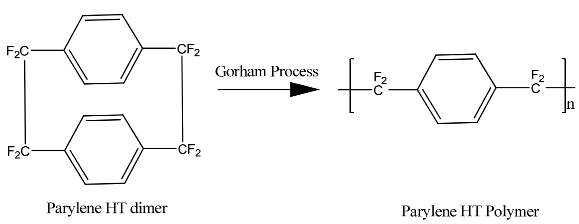


**Figure 1**. Parylene Polymerization Scheme

### *Characterization and Qualifications*

Dielectric Strength, Tensile Strength, Water Vapor Transmission Rate, Thermal Stability, Outgassing, Volume Resistivity, Surface Resistivity, Coefficient of Friction, Coefficient of linear thermal expansion, Specific Heat, Hardness, Dielectric Constant, UV Stability, Thermal Conductivity, Water Absorption, and Gas Permeabilities of Parylene HT were characterized using standard ASTM test methods [7-11].

Parylene HT coating has also been tested using various industry standards and in compliance with the following qualifications/standards and electronics industry's requirements.

- ISO 10993
- USP Class VI
- IPC-CC-830
- MIL-I-46058C (listed on the QPL )
- European Union's RoHS Directive 2002/95/EC
- Halogen free per IEC 60754-2

## Results and Discussion

### *Physical and Mechanical Properties*

The physical and mechanical properties of Parylene HT are summarized in Table 1

**Table 1.** Physical and Mechanical Properties of Parylene HT

| Properties | Unit | Parylene HT |
|---|---|---|
| Dielectric Strength | volts/mil | 5,400 |
| Dielectric Constant 60Hz | | 2.21 |
| 1kHz | | 2.2 |
| 1MHz | | 2.17 |
| Dissipation Factor 60Hz | | 0.0002 |
| 1kHz | | 0.0020 |
| 1MHz | | 0.0010 |
| Volume Resistivity | ohm-cm | $1.9 \times 10^{17}$ |
| Surface Resistivity | ohms | $5.0 \times 10^{15}$ |
| Tensile Strength | psi | 7,500 |
| Modulus | psi | 370,000 |
| T4 | | >450°C |
| T5 | | 377°C |
| Elongation to Break | | 10% |
| Hardness Rockwell | | R122 |
| Knoop | | 19-20 |
| Coefficient of Friction -Static | | 0.145 |
| Coefficient of Friction -Dynamic | | 0.130 |
| CTE | µm/m°C | 36 |
| Specific Heat | j/g°K | 1.04 |
| Thermal Stability | | 450°C |
| Thermal Conductivity | w/m°K | 0.096 |
| Outgassing TML, total mass loss | % | 0.03 |
| CVCM, | % | 0.04 |
| WVR, water vapor regain | % | 0.03 |
| Water Absorption | % | <0.01 |
| WVTR | g-mm/m$^2$-day | 0.22 |
| Gas Permeabilities $N_2$ | cc-mm/m$^2$-day-atm | 4.8 |
| $O_2$ | cc-mm/m$^2$-day-atm | 23.5 |
| $CO_2$ | cc-mm/m$^2$-day-atm | 95.4 |
| UV Stability | hrs | >2000 |

Figure 2 demonstrates higher thermal stability of Parylene HT. This TGA data indicates that Parylene HT would not be degraded by thermal levels encountered during the manufacturing of electronics at temperatures up to 450°C.

### *Useful Attributes for Reliability Enhancement*

The most common attributes that impact electronics applications include superior chemical, electrical and moisture barrier, chemical inertness, corrosion and UV resistance. Each property has its own significance for specific applications.

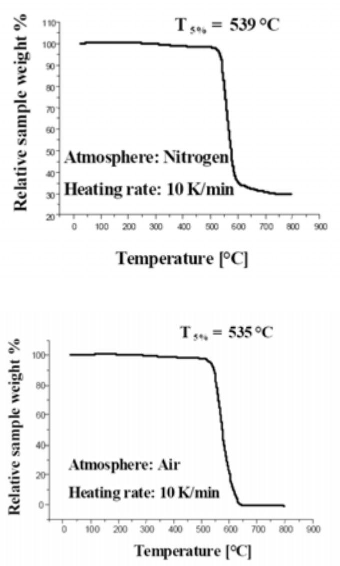


**Figure 2.** TGA of Parylene HT

*Barrier Properties and Chemical Resistance*

The bulk barrier properties of Parylenes are among the best of organic polymer coatings. Their excellent moisture and chemical barrier attributes are well suited for electronic devices and electronic components. Generally applied much thinner than alternate liquid coatings, Parylene HT provides a pinhole-free barrier to protect against various fluids as well as moisture, chemicals and common gases. Figure 3 compares water vapor transmission rate data of Parylene HT with other Parylenes and polymers.

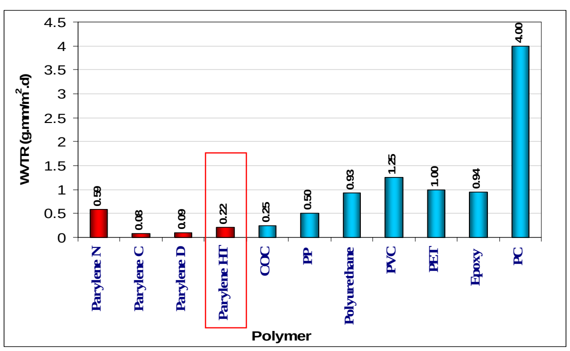


**Figure 3**. Water Vapor Transmission Rates

The chemical resistance testing consisted of measuring the thickness of a free film before and after exposure to various Chemicals. The thicknesses of all the films tested were 16 – 20 microns. The exposure time for each sample was 120 minutes. The annealing process for Parylene HT consisted of heating the film to approximately 250°C for one hour in air. FTIR readings were taken of the film before and after exposure of the chemical in order to obtain a thickness reading. The thickness of the Parylene HT film was recorded and the difference and % swelling was then captured. Of all the chemicals tested, there was not a significant change in the films' thickness. As shown in Table 2, all of the films had a % swelling of 3% or less at RT.

**Table 2**. Chemical Resistance of Parylene HT

| | Parylene HT Swelling % | Parylene HT annealed Swelling % |
|---|---|---|
| 10% Nitric Acid, RT | 0.0 | 1.2 |
| 10% Nitric Acid, 75°C | 0.0 | 1.2 |
| 70% Nitric Acid, RT | 0.0 | 0.0 |
| 70% Nitric Acid, 75°C | 0.0 | 0.6 |
| 10% Sulfuric Acid, RT | 0.0 | 0.0 |
| 10% Sulfuric Acid, 75°C | 0.0 | 0.0 |
| 95-98% Sulfuric Acid, RT | 0.6 | 1.2 |
| 95-98% Sulfuric Acid, 75°C | 0.0 | 0.0 |

*Corrosion Resistance*

Parylene HT successfully resists corrosion of many electronic assemblies and substrates in a variety of application conditions. Since the actual corrosive environment changes from day to day (or faster), most testing experiments are designed to expose samples to various environmental stresses that promotes corrosion.

A test commonly used in the electronics industry to determine the effectiveness of material finishes and protective coatings on materials and the effects of salt deposits on the electrical functions of electronic assemblies is the salt fog test. The salt fog test is an accelerated corrosion test in which specimens are exposed to a fine mist of a solution usually containing sodium chloride (typically 5 %). Several PCB boards coated with Parylene HT along with controls were subjected to 144 hours of salt fog exposure in accordance with ASTM B117-(03). After exposure, the boards were visually examined.

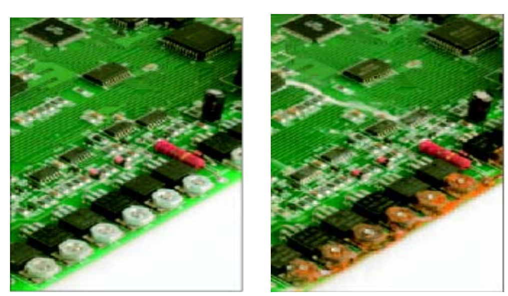

**Figure 4.** Close up view of Parylene HT coated (left side) and corroded uncoated PCB board (right side) after salt fog test.

Parylene HT coated boards did not show any evidence of corrosion while the uncoated boards had salt and corrosion residue running vertically down the PCB. Salt deposits were noticed on connector pins.

Heavy iron oxide deposits were on and around schottky diode heat sinks. Examples of such corrosion and effectiveness of Parylene HT are shown in Figure 4. Parylene HT provided complete protection from corrosion under saline conditions.

*Electrical Resistance*

Parylene HT is an excellent candidate for use in electronics because of its bulk electrical properties. The dielectric constant and dielectric losses are very low and unaffected by moisture absorption. The bulk resistivities are advantageously high because of the purity of the Parylene HT, its low moisture absorption, and in particular its freedom from trace ionic impurities. The typical electrical properties of Parylene HT are compared with other Parylenes in Table 3.

**Table 3.** Typical Electrical properties of Parylenes

| Properties | Parylene N | Parylene C | Parylene HT® |
|---|---|---|---|
| Dielectric Strength, V/mil | 7000 | 5600 | 5400 |
| Dielectric Constant, 60Hz | 2.65 | 3.15 | 2.21 |
| 1 KHz | 2.65 | 3.10 | 2.20 |
| 1 MHz | 2.65 | 2.95 | 2.17 |
| Dissipation Factor, 60 Hz | 0.0002 | 0.0200 | 0.0002 |
| 1 KHz | 0.0002 | 0.0190 | 0.0020 |
| 1 MHz | 0.0002 | 0.0130 | 0.0010 |

The low dielectric constant for Parylene HT in the gigahertz frequency range is often of great interest to designers of high frequency devices. Exhibiting the lowest dielectric constant among Parylenes, Parylene HT is particularly suited for these applications. Many electronics and components are used in critical areas with great demand on reliability. Generally for electronics applications, moisture-insulation resistance tests are carried out in an accelerated manner to evaluate the resistance of conformal coatings to the deleterious effects of high temperature/humidity conditions.

Insulation resistance of Parylene HT coated Y-test pattern boards were tested in accordance with Mil-STD 202, Method 302, test conditions of Temp: $23^0$C, RH: 50% and Method 106 with test conditions of Temp: $65^0$C and 90-95%. This Mil standard is also recognized as meeting the requirements of IPC-CC-830B. Insulation resistance measurements were taken using a megohms bridge at 500 volts DC, with an electrification time of one minute during the $1^{st}$, $4^{th}$, $7^{th}$ and $10^{th}$ cycles at high temperature and humidity. The test consists of 10 cycles (one cycle per day), with each cycle consisting of seven steps. The seven steps range from low temperature, low humidity ($23^0$C, 50% RH) to more severe conditions ($65^0$C, RH: 95% RH). The insulation was again measured upon completion of the moisture resistance test, after a 24-hour stabilization period. Insulation resistance value of Parylene HT is compared with other Parylenes in Figure 5. Parylene HT is about one to two orders of magnitude better than the IPC or Mil requirements.

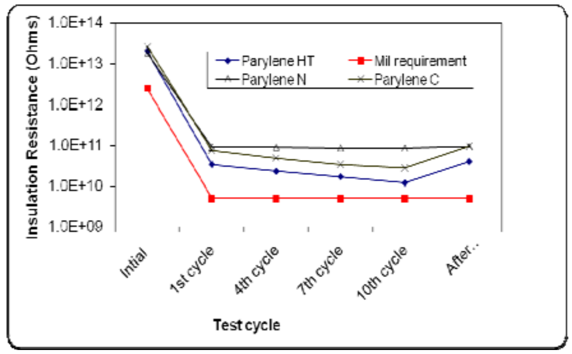


**Figure 5.** Insulation resistance of Parylenes

For moisture resistance-dielectric withstanding voltage test, several samples (Y-test patterns) coated with Parylene HT were tested (upon completion of moisture resistance testing) in accordance with Mil-Std-202, method 301, using 1500 Vrms at 60 hertz. Duration of voltage application was 60 seconds. After the moisture resistance test cycle (humidity and temperature cycle as described for insulation resistance test), samples were visually examined using 10X magnification. All samples were free from bubbles, pinholes, whitish spots, blistering, wrinkling, cracking and peeling. The coating did not mask or obliterate the identification markings. No evidence of corrosion was noticed. Leakage current results from dielectric withstanding voltage tests are described in Figure 6. Per test requirements, there shall be no disruptive discharge evidenced by flashover, sparkover or breakdown. The leakage rate shall not exceed 10 microamperes.

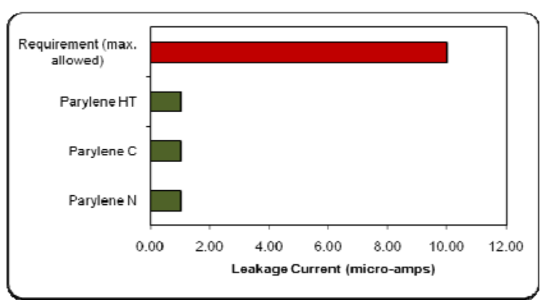


**Figure 6.** Leakage current (micro-amps)

*Thermal Stability and Resistance to Oxidation*

The Parylenes exhibit changes in mechanical properties with changes in temperature much as do other materials. The oxidative chain scission is the most important mode of degradation for Parylenes. Freestanding films of Parylenes were exposed to constant elevated temperature in air-circulating ovens for period of weeks to months and after exposure physical properties of the film were analyzed. The failure criterion was a 50% loss in tensile strength. In the degradation of many polymers, tensile strength is maintained until chain scission has reduced the molecular weight to the point at which entanglement is no longer a factor in determining physical properties. Despite the large variance in tensile strength measurements, the 50% loss criterion allows a reasonably precise location of end of useful life on a log time scale. Figure 7 describes the expected short-term and continuous service temperature of Parylenes in air.

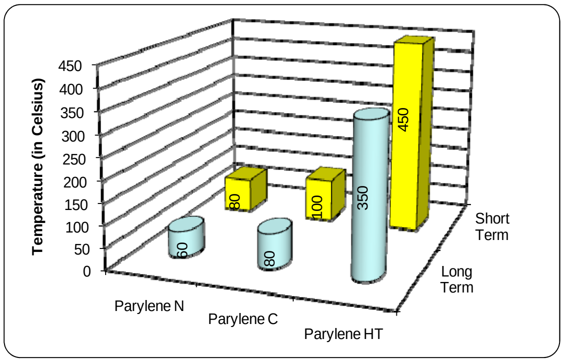


**Figure 7.** Oxidative stability of Parylenes

In oxygen-free atmospheres or in the vacuum of space, the continuous service temperature projections exceed 200°C for both Parylene N and C. On the other hand, Parylene HT has ability to resist thermal oxidation up to 450°C both in oxygen and oxygen-free atmospheres. Parylene HT has shown to survive continuous exposure to 350°C in air without any adverse property change for more than 1000 hours. The excellent thermal oxidative stability of Parylene HT in both air and inert environments is due to the stable carbon-fluorine bond in the polymer chain.

Another factor in oxidative degradation is ultraviolet radiation exposure. While the oxidation of Parylene N and C appears to be enhanced by exposure to ultraviolet radiation, Parylene HT has much higher resistance. When exposed to an accelerated UV stability testing per ASTM G154, Parylene N and C film survived less than 100 hours before yellowing or discoloration of the films occurred. However, Parylene HT film was stable without any change in appearance or other visual properties for more than 2000 hours as shown in figure 8. Test results demonstrate that the thermal stability of Parylene HT is up to 450 °C (short term exposure).

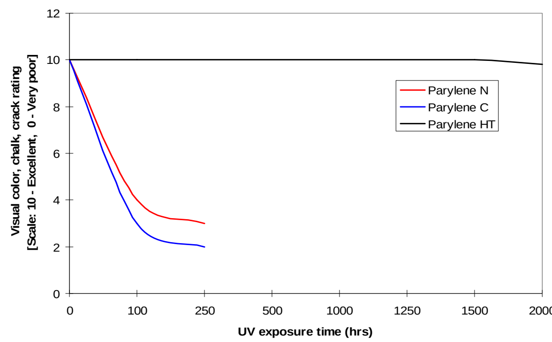


**Figure 8.** UV exposure results of Parylene N, C and Parylene HT

*Thermal Humidity Aging Resistance*

Y-pattern test samples coated with Parylene HT were subjected to 120 days of 85°C and 95% RH. The samples were visually examined after the 28th day, 56th day, and 84th day at 25°C and 50% RH. After each examination, the samples were returned to the chamber for continuation of conditioning. After completion of the aging period, the samples were removed from the chamber and allowed to stabilize at 25°C and 50% RH for a period of seven days. The aged samples were visually examined and compared with the control sample (not aged). The samples were tested for tackiness in accordance with per FED-STD-141, Method 4061(Referenced in Mil-I-46058C). All aged samples showed no evidence of softening, chalking, blistering, cracking, tacking, loss of adhesion or liquification.

*Fungus Resistance*

Glass panels were coated with Parylene HT were subjected to fungus resistance test in accordance with ASTM G-21 (Referenced in Mil-I-46058C). The glass panels were placed on the surface of solidified agar. The surface and test panels were inoculated by spraying the mixed fungus spore suspension from a sterilized atomizer so that the entire surface was moistened with the spore suspension. The inoculated test panels were covered and incubated at 28-30°C, with a relative humidity of not less than 85%. The panels remained in incubation for a total of 28 days. The growth was recorded each week. The observation results are described in Table 4.

Table 4. Fungus resistance of Parylenes

| Test Samples | Days | | | |
|---|---|---|---|---|
| | 7 | 14 | 21 | 28 |
| Parylene N | 0 | 0 | 0 | 0 |
| Parylene C | 0 | 0 | 0 | 0 |
| Parylene HT® | 0 | 0 | 0 | 0 |
| Filter | 4 | 4 | 4 | 4 |
| Cotton Duck | 4 | 4 | 4 | 4 |

Ratings used for the test are 0- None, 1-Traces of growth (less than 10%), 2-Light growth (10-30%), 3-Medium growth (30-60%) and 4-Heavy growth (60% to complete coverage).

*Improvement in Wire Lead and Bond Strength*

As demonstrated with Parylene C, Parylene HT can also provide an improvement in hybrid wire lead and bond strength compared to uncoated circuits.

*Low Coefficient of Friction*

The dry-film lubricity of any coating is generally indicated by its coefficient of friction. A lower coefficient of friction indicates that the surfaces are slicker. In other words, there is less resistance to sliding motion. Parylenes possess excellent dry-film lubricity. The coefficient of friction values (static) for Parylene N, C and Parylene HT, per ASTM D 1894 are 0.25, 0.29 and 0.15, respectively. Although Parylene N and C are suitable for many electronics applications, Parylene HT offers unique advantage of having a very low coefficient of friction value.

*Outgassing*

The outgassing of Parylene HT was tested per ASTM E595. The percentage of Total Mass Loss (%TML) and Collected Volatile Condensable Materials (% CVCM) were 0.03 and 0.04 respectively.

*RoHS and Halogen-Free Compliance*

Parylene HT samples were tested in accordance with the European restriction on use of hazardous substances in electrical and electronic equipment directive 2002/95/EC using ASTM D5839. Per test results, Parylene Parylene HT is RoHS compliant. Parylene HT is also halogen free per IEC-60754-2.

*Conclusion*

The data provided in this paper indicates that Parylene HT is an excellent coating material for meeting the growing requirements of protection and reliability of advanced electronics and components. With the commercial availability of Parylene HT, manufacturers of electronics have an option of an advanced protective coating that can enhance product reliability without hermeticity under many high temperature application conditions. Parylene HT is well suited for electrical and environmental protection of various micro and nano electrical components, biosensors, printed circuit boards and other electronic components. Parylene HT is also suitable for contamination and corrosion control, dry lubrication and protection of high density and high-speed integrated circuits.

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