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A New Halogen-Free Parylene for High Performance and Reliability of Microelectronics in Harsh Environments

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Abstract—**The rapid growth and adoption of microelectronics around the world has resulted in an increased awareness of potential environmental issues related to their use and disposal. Halogens, which have had various uses in microelectronics over the years, are known to emit toxic and corrosive gases during the disposal of electronic waste. Many organizations have applied pressure to the electronics industry to eliminate halogens completely (e.g., fluorine, chlorine, and bromine) from their products. Among the various efforts toward environmentally friendly products, making electronics completely halogen-free has gained significant attention, particularly in Asia and Europe. This initiative even impacts conformal coatings worldwide, on which most electronics rely for their long-term protection, reliability, and high performance against water and other corrosive harsh environments. Among the various coating options, the parylene family of conformal coatings offers beneficial properties to the microelectronics, improved over many properties offered by common epoxies, acrylics, urethanes, and silicones. Although parylene N is the only commercially available parylene that does not contain any halogens, its barrier performance against moisture and other corrosive chemicals is not quite as robust as the other parylenes. To meet the industry's current and future requirements, a new halogen-free parylene, ParyFree®, has been developed. This study introduces a new parylene type to the microelectronics industry and shares the characterization and qualification results of ParyFree® parylene conformal coating for the protection, reliability, and robust performance of microelectronics. Testing on the new coating includes IPX water resistance, corrosion resistance, and qualification per IPC-CC-830B.**

Keywords—**ParyFree, protection, reliability, halogen-free, green electronics**

Introduction

As demand for small and less expensive electronic devices grows, the use of microelectronics continues to expand. Some of the microelectronics components which include transistors, capacitors, inductors, resistors, and diodes are playing significant roles in the advancement of consumer electronics. The dependence on consumer electronics is changing our day-to-day lifestyle incredibly. Although such advancement is welcome, it has resulted in increased concerns and awareness of potential environmental issues related to their disposal. There are many governmental and nongovernmental agencies continuing their efforts to reduce or eliminate such concerns through research and education on using environment-friendly materials and processes for both critical and consumer electronics.

Among various materials used in electronics, the use of halogens in electronics over the years is known to emit toxic and corrosive gases during the disposal of electronic waste. Nongovernment organizations (NGOs) first highlighted environmental concerns and, therefore, have applied pressure to the electronics industry to eliminate halogens (e.g., fluorine, chlorine, bromine, and iodine) from their products. As a result, the International Electromechanical Commission (IEC) moved to define "halogen-free" as ≤900 ppm for chlorine, ≤900 ppm for bromine, and ≤1,500 ppm total for both combined. Because of the pressure applied by NGOs and the guidance set forth by the IEC, many consumer electronic companies have committed to eliminating halogens from their products [1-5].

There are various methods of making consumer electronics more reliable and protecting them from detrimental effects of physical and operational environments. Manufacturers of consumer electronics are looking to protective coating materials, commonly in the form of thin film coatings with improved processing characteristics and greater electrical insulation, while ensuring that their products are halogen-free. Among the various options, polymeric coatings/materials such as such epoxies, acrylics, urethanes, and silicones are being used for packaging, protection, and reliability enhancement and have achieved acceptance up to a certain level. However, their effectiveness in various operating environments is, at times, less than desired because of their very low thermal stability, coating imperfections, presence of pinholes, and their poor barrier properties. In recent years, organic polymers, particularly those deposited through vapor-phase polymerization, have found an increasing role in the conformal insulation of electronics by enhancing their overall reliability [6-9].

The paraxylylene (parylenes) family of vapor-phase polymers offers unique characteristics, not available by other polymeric materials, for harsh environment applications. Examples of parylenes' use in electronics applications include flex circuits, printed circuit boards, sensors, medical electronics, MEMS (micro-electromechanical system) wafers, probes/pin, components (metal, brackets, and cables), rotors/stators, ferrite cores and telecommunication devices, nanoelectronics, automotive components, and engine electronics. Although parylene N is the only commercially available parylene that does not

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contain any halogens, its barrier performance against moisture and other corrosive chemicals is not quite as robust as the other parylenes.

In support of the global initiatives that continue to drive toward the elimination of halogens in electronics and taking into consideration the need for a completely halogen-free environmentally friendly conformal coating, yet one that is suitable for various operating environments, this study introduces and describes the attributes and suitability of a new halogen-free variant of parylene—ParyFree. This material has been tested for IPX water resistance, corrosion resistance, and the most common industry qualification testing per IPC-CC-830B and has been shown to improve the reliability of various electronics that are exposed to water, corrosive, and other harsh environmental conditions. Some of the key characteristics of this material include excellent barrier properties, electrical and mechanical properties, chemical inertness, long-term contamination and corrosion control, dry-film lubrication, RoHS & REACH compliance.

What Is Halogen-Free ParyFree?

ParyFree®, the newest and a unique member of parylene family, replaces one or more hydrogen atoms of the p-xylylene polymer with nonhalogenated substituents. This halogen-free variant offers the advanced barrier properties of parylene C and adds improved mechanical and electrical properties compared with other commercially available parylenes. ParyFree optimizes the critical combination of barrier, electrical and mechanical properties to provide robust protection against moisture, water, corrosive solvents and gases, while complying with halogen-free requirements of select industries worldwide.

Parylene refers to a polymer series based on paraxylylene. Parylenes (xylylene polymers) have been classified as thermoplastic polymers that are formed on substrate surfaces using vacuum deposition polymerization. They are polycrystalline and linear in nature and possess useful dielectric and barrier properties per unit thickness. They are chemically inert and form thin layer coatings without pinholes.

Parylenes are applied to substrates in a vacuum chamber and have certain similarities with vacuum metallizing. Unlike vacuum metallization, however, which is conducted at pressures of 10^{-5} torr or below, parylenes are formed at around .1 torr. Under these conditions, the mean free path of the gas molecules in the deposition chamber is in the order of .1 cm. Thus, all sides of an object to be coated are uniformly impinged by the gaseous monomer, providing a high degree of conformability [10-12]. Vacuum deposition polymerization begins with the vaporization of a parylene dimer. The dimer vapor is pyrolytically cleaved to form a reactive monomer vapor. The reactive monomer vapor is then transferred to a deposition chamber where the substrates are located. In the deposition chamber, the reactive monomer vapor spontaneously condenses onto the substrates to form a parylene coating. There is no liquid phase in the deposition process, and substrate temperatures remain near ambient.

ParyFree coating complies with the biological requirements of ISO 10993. Testing included cytotoxicity, irritation and skin sensitization, hemocompatibility (hemolysis and partial thromboplastin time, and muscle implantation (12 w and 26 w). ParyFree is also certified to comply with the biological testing requirements for USP (United States Pharmacopeia) Class VI Plastics.

Like other commercially available parylene variants, ParyFree undergoes a vapor deposition process that results in an ultrathin, uniform, pinhole-free conformal coating. The thin film forms at a molecular level to fully encapsulate components and devices, offering complete protection and increased reliability of intricate, complex electronic devices [11, 12].

Halogen-Free Test

To verify its efficacy as a halogen-free material, ParyFree coatings were tested in accordance with BS EN 14582:2007 at SGS North America, Inc. The results, which are displayed in Table I, show that there are no detectable levels of chlorine, bromine, fluorine, or iodine in ParyFree coatings, validating the coating's use in halogen-free applications.

Performance and Reliability Evaluation

The evaluation for high performance and reliability of electronics coated with 25-μm (±10%)-thick ParyFree (a halogen-free parylene coating, available from Specialty Coating Systems, Inc.) was carried out under the following four test categories, where SCS AdPro Poly was used as an adhesion promoting agent:

1. water immersion (IPX designations),
2. barrier and electrical,
3. salt fog exposure, and
4. qualification per IPC-CC-830B

A. Water Immersion Test (IPX Designations)

ParyFree-coated LED (light-emitting diode) electronic boards, as shown in Fig. 1, were tested in accordance with IEC 60529, test conditions 14.2.7 and 14.2.8 for IPX7 and IPX8 designations, which demonstrates protection from harmful effects due to the ingress of water. Testing was carried out at an atmospheric pressure of 28 ± 2.5 in Hg, a temperature of 75 ± 15°F, and a relative humidity of 50 ± 30% RH.

The testing criterion is defined as "ingress of water in quantities causing harmful effects shall not be possible when the enclosure is temporarily immersed in water under standardized conditions of pressure and time." The uncoated (control) electronics functionally failed during the test, but all ParyFree-coated electronics (12 LED boards, 100%) passed both test conditions, functioning normally both during and after testing.

Table I
Halogen Testing, Detection Limit of 50 ppm

Halogen	CAS	Halogen in ParyFree
Fluorine (F)	7726-95-6	Not detected
Chlorine (Cl)	7782-50-5	Not detected
Bromine (Br)	7782-41-4	Not detected
Iodine (I)	7553-56-2	Not detected

These tests demonstrate that ParyFree conformal coating is suitable to protect electronics and other devices against water splash and water immersion for more than 30 min at a depth of 1 m (IPX7) and 1.5 m (IPX8), Fig. 2.

B. Barrier and Electrical Tests

The water vapor transmission rate (WVTR) is defined as the amount of water vapor that flows between two parallel surfaces under steady-state conditions per unit area and is a common measure of the barrier performance of thin films against water vapor.

Samples are exposed to water vapor under controlled environmental conditions until a steady state is reached, which is the point where the amount of water absorbed by the film is in equilibrium with the flux of water vapor passing through the film. Several factors can affect the WVTR of a polymeric material, including environmental (temperature, humidity, and pressure) and physical (molecular weight, pendant groups, chain mobility, degree of crosslinking, crystallinity, etc.) considerations. Several samples of ParyFree were tested for WVTR at 37°C/100% RH, per ASTM F1249, using a MOCON Permatran-W Water Vapor Permeability Instrument. The result of this testing is shown in Table II and compared with other parylenes and conformal coatings.

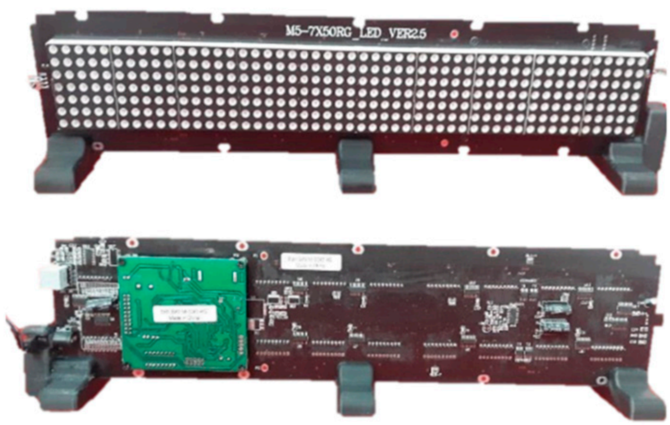

Fig. 1. ParyFree-coated LED electronic board (top: front side; bottom: back side with various electronic components).

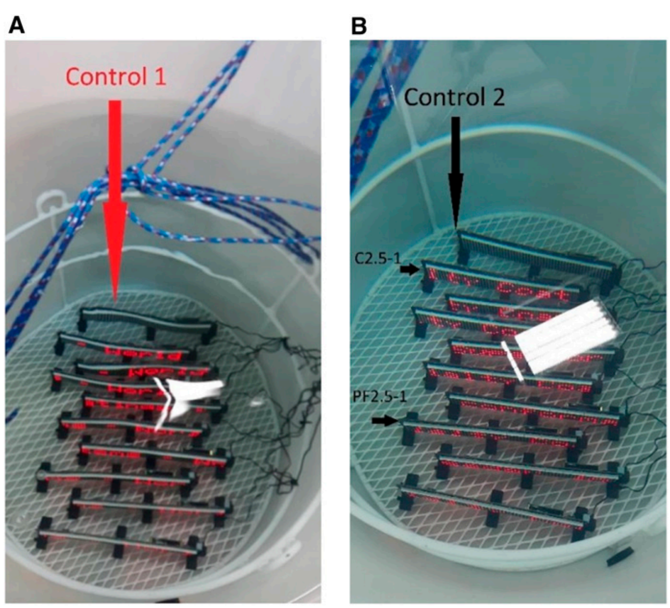

Fig. 2. IPX testing of ParyFree-coated LED electronic boards (left image: IPX7 and right image: IPX8).

Dielectric strength is the measure of the maximum voltage per unit thickness a given material can withstand before physical breakdown occurs. Units of volts per mil (V/mil) are typically used in the coatings industry for dielectric strength; this value is calculated from the measured voltage breakdown (VBD) value of the material in volts and the thickness of the film tested in mils. The preferred film thickness target for testing is 1 mil because, at this thickness, the VBD and dielectric strength values will be equal. Dielectric strength testing of ParyFree films was performed per ASTM D149 at room temperature. Polished stainless steel plates (4- × 4-in.^{2}) were coated with ParyFree. Samples were submerged in dielectric oil during testing to prevent arcing.

The dielectric constant and dissipation factor of ParyFree are very low and unaffected by moisture absorption. The bulk resistivities are advantageously high because of the purity of the parylenes, their low moisture absorption, and, in particular, their freedom from trace ionic impurities. The low dielectric constant for parylene in the gigahertz frequency range is often of great interest to designers of high-frequency devices.

Exhibiting the lowest dielectric constant among halogen-free conformal coatings, ParyFree is particularly suited for these high-frequency applications. The dielectric strength value (an average of measurements taken from 10 locations) and other electrical properties of ParyFree are shown in the Table III in comparison with other parylene coatings.

C. Salt Fog Exposure Test

Salt fog testing is designed to evaluate the corrosion resistance of a surface after exposure to a controlled, harsh saltwater environment for a specified amount of time. Coating thickness and exposure time are the main variables that affect the level of surface protection in a corrosive environment. Exposed test samples are rated on a visual appearance scale based on a subjective estimation of the percent surface area affected by corrosion and the pattern of corrosion.

Table II
WVTRs

Conformal coating	WVTR at 100% RH, 37°C (g-mm/m^2·d)
ParyFree	.09
Parylene N	.59
Parylene C	.08
Parylene HT	.22
Acrylic (AR)	13.9
Epoxy (ER)	.94
Silicone (SR)	1.7-47.5
Polyurethane (UR)	.93-3.4

Table III
Electrical Property of ParyFree (Tested at 25-µm-Thick Film) Compared with Other Parylenes

	Parylene N	ParyFree	Parylene C	Parylene D	Parylene HT
Dielectric strength (V/mil)	7,000	6,900	5,600	5,500	5,400
Volume resistivity (Ω·cm), 23°C, 50% RH	1.4×10^{17}	2.8×10^{16}	8.8×10^{16}	1.2×10^{17}	2.0×10^{17}
Surface resistivity (Ω), 23°C, 50% RH	1.0×10^{13}	2.4×10^{15}	1.0×10^{14}	1.0×10^{16}	5.0×10^{15}
Dielectric constant					
60 Hz	2.65	2.38	3.15	2.84	2.21
1 KHz	2.65	2.37	3.10	2.82	2.20
1 MHz	2.65	2.35	2.95	2.80	2.17
Dissipation factor					
60 Hz	.0002	.00001	.020	.004	<.0002
1 KHz	.0002	.0009	.019	.003	.0020
1 MHz	.0006	.0007	.013	.002	.0010

A set of ParyFree-coated 4- × 6-in.^{2} steel Q-panels were exposed to salt spray (fog) testing for 168 h per ASTM B117-16. The panels were photographed and visually evaluated per ASTM D610 after 24, 48, 72, and 168 h of exposure. Visual ratings were reported on a scale of 0-10, with 10 being the best appearance (based on percentage of the surface area rusted to identify rust grade). All samples passed the test with ratings of 9 after 168 h. In addition to Q-panels, several circuit boards coated with ParyFree were salt fog tested by an independent facility. As shown in Fig. 3, the coated boards exhibited no corrosion, salt, or heavy iron oxide deposits after 144 h of exposure in accordance with ASTM B117-(16).

D. Qualification per IPC-CC-830B

Qualification testing is aimed to assess the properties of a conformal coating product on industry-established standardized test vehicles using standardized test procedures [13].

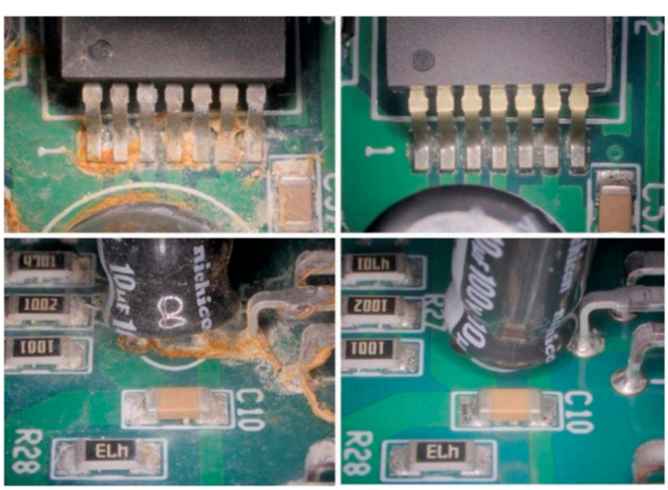

Fig. 3. ParyFree-coated circuit board. Left: Images showing corrosion due to salt spray on uncoated board areas. Right: Images showing ParyFree-coated board areas unaffected by salt spray.

1) Dielectric Withstanding Voltage

Five ParyFree-coated IPC-B-25A "C" pattern test specimens were subjected to dielectric withstanding voltage testing in accordance with IPC-TM-650, method 2.5.7.1 using an applied voltage of 1,500 VAC for a period of 60 s. The requirements include no disruptive discharge evidenced by flashover, spark over, or breakdown and the leakage current not exceeding 10 µA. Test results are shown in Table IV.

2) Moisture and Insulation Resistance

Four ParyFree-coated IPC-B-25A "D" comb pattern samples and one uncoated control test sample were subjected to moisture and insulation resistance testing in accordance with IPC-TM-650, method 2.6.3.4.

On completion of the temperature and humidity cycling, the samples were visually examined in accordance with paragraph 3.5.2 and subjected to dielectric withstanding voltage testing in accordance with paragraph 3.6.1.

The requirement for this test is to maintain 5,000 MΩ during humidity cycle and one to 2 h at reference conditions (25°C and 50% RH for 24 h), and after 24 h at reference conditions. Moisture-insulation resistance test results are shown in Fig. 4. Visual examination after completion of the moisture and insulation resistance test indicates no evidence of deleterious substances, bubbles, pinholes, whitish spots, blistering, wrinkling, cracking, or peeling. The coating was smooth, homogenous, transparent, and tack-free when observed at ambient

Table IV
Dielectric Withstanding Voltage Test Results

Specimen	Voltage applied (VAC)	Application time (s)	Resistance (K-Ω)	Measured voltage (mV)	Leakage current (µA)	Results
1	1,500	60	51.1	68	1.3	Pass
2	1,500	60	51.1	73	1.4	Pass
3	1,500	60	51.1	75	1.5	Pass
4	1,500	60	51.1	71	1.4	Pass
5	1,500	60	51.1	70	1.4	Pass

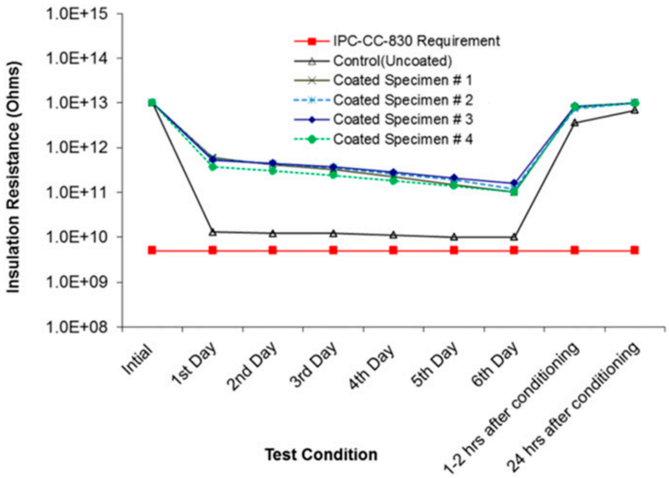

Fig. 4. Moisture-insulation test results per IPC-TM-650, method 2.6.3.4.

conditions. There was no evidence of blisters, reversion of the conformal coating, or corrosion caused by the conformal coating.

3) Thermal Shock

Five ParyFree-coated IPC-B-25A, "D" comb pattern, samples were subjected to thermal shock testing in accordance with IPC-TM-650, test method 2.6.7.1 (100 cycles of −65°C to +125°C, 15-min dwell time at each temperature extreme).

On completion of the thermal shock test, the test samples were subjected to dielectric withstanding voltage testing in accordance with paragraph 3.6.1 and visually examined in accordance with paragraphs 3.5.2 using a 3-diopter magnifying lamp and a Nikon ×10 magnification illuminated microscope. No defects were found during visual examination. Dielectric withstanding voltage test results, after thermal shock testing, are shown in Table V.

Table V
Dielectric Withstanding Voltage Test Results, After Thermal Shock Testing

Specimen	Voltage applied (VAC)	Application time (s)	Resistance (K-Ω)	Measured voltage (mV)	Leakage current (μA)	Results
1	1,500	60	51.1	84	1.6	Pass
2	1,500	60	51.1	88	1.7	Pass
3	1,500	60	51.1	84	1.6	Pass
4	1,500	60	51.1	87	1.7	Pass
5	1,500	60	51.1	89	1.7	Pass

Table VI
Flammability Test Results

Specimen	Thickness (in.)	Time of application (s)	Damaged length (mm)	Elapsed time for combustion (s)	Burning rate (mm/min)	Results
1	.061	30	0	0	0	Pass
2	.059	30	0	0	0	Pass
3	.060	30	0	0	0	Pass

4) Temperature and Humidity Aging

Four ParyFree-coated "Y" pattern samples (FR4 boards) and one uncoated control sample were subjected to thermal humidity aging in accordance with IPC-TM-650, method 2.6.11.1 for a total of 120 d of temperature (85 ± 2°C) and relative humidity (95 ± 4%) cycling. The test samples were visually examined for any changes after 38 d and every 28 d thereafter. Final visual examination was performed after 7 d of removal of the samples from the chamber. On completion of the cycling, there was no evidence of softening, chalking, blistering, surface tack, cracking, loss of adhesion, or reversion to a liquid state. All tested samples met the specified requirements of the test.

5) Flammability

Three ParyFree-coated laminate strip samples (.5 × 5.0 in.^{2}) were subjected to flammability testing in accordance with UL 94, horizontal burn method. Flammability test results are shown in Table VI. The pass criterion was to not have a burning rate more than 75 mm/min.

Conclusions

Based on the evaluation results described in this article, ParyFree offers a halogen-free conformal coating solution that can meet the challenges of protection, high performance, and reliability of various types of electronics and provide a splash and waterproof coating option meeting the requirements of both IPX7 and IPX8 designations of the coated devices. In addition, its high dielectric strength, low dielectric constant, and low dissipation factor properties make it suitable for an excellent electrical insulation of harsh environment electronics and high-frequency next-generation devices as well.

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