# Parylene as a Suppressant for Tin Whiskers Growth on Printed Circuit Boards

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## Abstract

With the implementation of RoHS directives, pure tin plating is replacing lead in the tin-alloy used in the printed circuit boards and other worldwide electronics. Although use of tin provides a safer environment for electronic manufacturers and helps meet the regulatory requirements, it is known to form tin whiskers, odd shape eruptions and dendrites that cause printed circuit boards or devices to fail. Research has been ongoing for decades in an attempt to understand and control the whisker formation with limited successes to date. Because of the RoHS requirements, efforts to find an appropriate solution to the tin whisker problem have increased significantly in the past couple of years. This paper reviews various options and presents a practical solution utilizing Parylene coating technology for suppressing the formation of metallic whiskers, OSEs and dendrites.

Parylenes are solvent and catalyst-free thin organic coatings that offer solutions to many existing protective, packaging and reliability challenges of electronic industry in part because of their excellent electrical, mechanical and barrier properties and chemical inertness. In addition, Parylenes truly conform to the parts due to their molecular level deposition characteristics. It has been observed that Parylene conformal coatings are more suitable for suppressing metallic whiskers than other conformal coatings or other proposed solutions.

This paper also highlights some key attributes of a recently commercialized Parylene HT that help mitigate the risk of metallic whiskers even further, particularly for electronics or PCBs used at higher temperature and high frequencies. Parylene HT offers long-term thermal stability at temperature exposures in excess of 350$^{o}$C.

## Introduction

For the past several decades, scientists and engineers (from government agencies, academic institutions and industries) involved in electronic assemblies have been working to understand the mechanisms of tin whiskers growth and their control [1-10], on which agreement has not yet been achieved. Experiments over the years have resulted in extensive publications providing some understanding of the phenomenon of tin whiskers growth. Various factors, including dislocation mechanism, stress, grain growth and crystalline structure, substrate temperature and humidity have been related to tin whisker formation [1,2,3,4]. Due to continued interest in tin based plating and solder, efforts continue in an attempt to understand the growth fundaments and find suitable industrial solutions. Many mitigation /control strategies have been proposed, including avoiding of tin plated parts, stripping and re-plating, solder dipping the plated surfaces sufficiently using tin-lead solder, selecting a matte or low stress tin finish, selecting under-plating (barrier layer) to reduce intermetallic formation, varying the thickness of the plating, reflowing of pure tin plated surfaces, annealing, avoiding compressive loads on plated surfaces, and applying a conformal coat. Although these strategies have been tried, depending upon the suitability of the applications, addition of lead in tin alloys has been a common practice to eliminate or reduce the whiskers growth for many printed circuit boards and other electronic applications.

The RoHS directives, legislation enacted in Europe in July 2006 restricts the use of certain hazardous materials, including lead, in electrical and electronic equipment. RoHS has forced manufacturers to rethink their strategies and look for solutions for tin whiskers issue either by eliminating the use of tin or by controlling the tin whiskers formation. Since electroplated pure tin finishes on components are one of the options for new lead-free electronics and tin seems to be unavoidable material, focus is now shifting to finding a suitable mitigation or control method for tin whiskers that can be easily adopted by electronic component manufacturers and sub-system assemblers. The trend toward miniaturization of electrical and electronic assemblies will further complicate the issue of tin whiskers due to dimensional restrictions.

Although no perfect solution has yet been found to eliminate tin whiskers, the use of conformal coating seems to have significant beneficial impact among the various mitigation strategies. There have been efforts, recently, to evaluate conformal coatings for mitigation of tin whiskers problems. This paper provides a critical review of the earlier work done on conformal coatings and develops a basis for their extended use as a solution to tin whiskers, enhancing the reliability of electronic components and assemblies. Further, based on an understanding of the issues, this paper analyzes the use of Parylene (p- xylylenes) technology to mitigate the risk on printed circuit boards and other electronic assembles.

## Tin Whiskers and Associated Problems

Several descriptions of tin whiskers have been published and accepted by many researchers and engineers [1, 2, 3,4,5,6], but work continues in an effort to understand their nature further as we move toward addressing the issue on printed circuit boards and electronic assemblies after the implantation of RoHS. The current description of tin whiskers can be summarized as follows.

- Spontaneous filamentary growth of single tin crystals from tin plated surfaces (0.5 to 50 µm thick metal films).
- Electrically conductive, crystalline structures.
- Can grow without electrical field or moisture and independent of atmospheric pressure.
- Extremely thin with typical diameters of 1-3 microns, typical lengths of 1-500 microns.
- Grow as straight, kinked, spiraled, hooked, or forked single crystals of tin, usually with striated outer surfaces.
- Able to reach lengths of 10 mm
- Grow at room temperature to 75º C.

In addition, another type of tin growth or eruption has been observed on tin plated surfaces which are quite different from tin whiskers. These anomalies have generally been referred to in the literature as odd shaped eruptions and in many cases as dendrites, flowers, extrusions, volcanoes, etc., and have drawn less attention compared to single crystalline filamentary tin whisker growth.

Failures attributed to tin whiskers are widely known and well documented[10, 11], and several theories[3] on the damage mechanisms have been proposed. The details of the reliability risks and examples are extensively described in the literature [3,10,18,19]. For electronic components and assemblies, there are two major reliability problems, as mentioned below, that are associated with tin whiskers growth.

- Mechanical Failures
    - Debris/Contamination
- Electrical Shorts
    - Stable short circuits
    - Transient short circuits
    - Plasma arching in vacuum

As we continue the miniaturization of electronics, the adverse impact of tin whiskers has increased considerably. Also, the use of low voltage and current levels in modern circuits does not provide enough energy to melt the tin whiskers that create a short. This problem was less evident in earlier technologies where the use of high voltage and current levels would generally destroy or vaporize any tin whiskers and devices would not be damaged due to short circuits.

Tin whiskers pose serious problems for manufacturers who now prefer using tin in place of lead/tin alloys for interconnections. As worldwide regulations are forcing electronics manufacturers to make electronic interconnections lead-free, one of the economical options is to use pure tin soldering and coating alternatives instead of traditional tin-lead alloys. This approach has resulted in a renewed interest in understanding the impact of and finding a solution for tin whiskers issues.

### How Do Tin Whiskers Occur?

For the past several decades, extensive research has been done to understand the mechanisms for tin whisker formation and growth [1, 2, 3,9,10]. Although still the subject of much investigation and uncertainty, several theories have been proposed to explain tin whiskers growth [3,10,18,20]. The reasons for tin whisker growths have been attributed broadly to the following factors.

- Plating chemistry and process
- Re-crystallization & crystalline structures
- Stress (e.g., internal and external, compressive stresses, etc.)
- Diffusion of substrate elements into tin layer
- Intermetallic formation
- Thermal expansion mismatch
- Corrosion of the substrates
- Externally applied forces (e.g., bending or stretching, lead forming, etc.)
- Scratches or nicks
- Dislocation
- Surface tin oxide
- Environmental factors (e.g., thermal cycling, power cycling, temperature, humidity, etc.)

Efforts to understand and verify the basic mechanisms that are involved in tin whiskers growth continue[10]. Further details on the all factors involved in the growth of tin whiskers are beyond the scope of this paper.

### Tin Whiskers Mitigation Methods

Despite extensive research performed by government agencies, industry and academia, effective methods to completely eliminate or control tin whiskers have not been found [2,3,10,11,12,13,14,15]. However, this has not stopped manufacturers completely from using tin in their electronic assemblies. The continued use of tin is partly because of uncertainties associated with tin whiskers formation, which make it difficult to predict when tin whiskers will form and start affecting the reliability of components or devices. The matter is further complicated by not having any industry-accepted accelerated test methods to evaluate the propensity to form tin whiskers on printed circuit boards and other electronic assemblies. A number of organizations are trying to develop methods to test and evaluate the effects. Such efforts will take some time, but the industry is facing immediate challenges in dealing with tin finishes in electronic components and devices. To address the issue, mitigation seems to be the best approach until a solution is found to eliminate the formation of tin whiskers completely. Several mitigation approaches have been developed, each with its own limitations. The most commonly discussed mitigation methods in literature are:

- Avoid tin plated parts
- Strip and replate
- Solder dip the plated surfaces sufficiently using a tin-lead solder
- Select a matte or low stress tin finish
- Select underplating (barrier layer) to reduce intermetallic formation
- Vary thickness of tin plating
- Reflow of pure tin plated surfaces
- Annealing
- Avoid compressive loads on plated surfaces
- Apply a conformal coat

A review of all the methods above is beyond the scope of this paper, and only the application of conformal coating will be analyzed here.

### Conformal Coatings for Minimizing Tin Whiskers

The use of conformal coatings to mitigate the risk of tin whiskers growth has been considered for some time [3, 11]. However, there have not been significant efforts to look into this possibility until recently. While it is assumed that conformal coatings can provide good protection, including retardation of tin whiskers, a thorough analysis of the materials and their impacts has not been completed, perhaps due to the lack of evaluation efforts and standard industry accepted methods to do so. Nonetheless, based on the potential benefits, conformal coatings appear to be the most practical and easily controlled method for retarding the growth of tin whiskers. Previously, it was not possible to provide any significant evidence in favor of conformal coatings due to the lack of experimental data. However, recent publications[14, 15] do indicate the fact that using particular types of conformal coatings might be a solution for mitigating the risk of tin whiskers in many applications.

In 1998, NASA GSFC started experiments[11, 12, 13] to evaluate the effectiveness of a particular type of conformal coating, named Uralane 5750 (a polyurethane conformal coating widely used by NASA at that time for general protection purposes) to address the issue of tin whiskers growth. Published results after two and half years demonstrate that the material does not prevent tin whisker formation, but shortens the incubation period of whisker formation. Experiments also demonstrate that, although tin whiskers initiate more rapidly under the coating, the coating also retards their growth rate. Whiskers are capable of growing from beneath a ¼ mil thick coating. Tin whiskers also can bend under forces of electrostatic attraction, thus increasing the probability of shortening. This work claims to be continuing, but no further data has been available. This effort was a significant one, particularly in its initial approach, but lacked some comparative details (including further analysis on the factors that might have impact on results) with which to draw any more meaningful conclusions.

More recent publications[14, 15] on the evaluation of conformal coatings as tin whisker mitigators filled several gaps in earlier efforts, and presented evidence that could have positive impact on mitigation of tin whisker problems. In 2005, the first phase of the study[14] included the evaluation of six types of conformal coatings. All coatings had different physical properties and the authors assumed that some properties such as Young modulus, hardness, tensile strength, oxygen permeability and water vapor transmission could have an impact on suppressing the formation and growth of tin whiskers. The assumptions seemed reasonable considering the current knowledge of tin whiskers and some key factors that affect the propensity for formation. The experimental approach included test coupons coated with bright tin over brass, applying six conformal coatings and then subjecting the coated coupons to aging in two stages; 1) 278 days at ambient conditions, which resulted in the formation of nodules, but no significant whisker growth and 2) exposure to 50ºC/50%RH for 419 days. The coatings included in the tests were; Urethane-Acrylic (three different combinations), Acrylic, Silicone and Parylene C (poly -2-chloro-p xylylene). It is important to note that except for silicone and Parylene C, all coatings were applied in two thicknesses; 1 mil thick on one end of the coupon and 4-6 mils thick on the opposite end. The thicknesses of Silicone and Parylene C were 1.5 mils and 0.8-1.0 mil respectively.

The results of the study[14] demonstrated that the formation of tin whiskers and odd shaped eruptions can be suppressed by the use of conformal coatings. On the other hand, with time, tin whiskers grow under the coatings and once whiskers growth started, most coatings, particularly thinner the ones were penetrated. The authors did not try to establish any relationship between any of the coatings' properties and their ability to suppress or retard tin whiskers growth. The observations of this study concluded that Parylene C was the best and acrylic was the least effective for suppressing tin whisker and odd shaped eruptions. In addition, it was also concluded that Parylene C will completely and uniformly coat component leads unlike other liquid type coatings.

The second phase of the study[15] by the same authors, which is still ongoing, subjected six conformally coated coupons to slightly different set of conditions. Test coupons were allowed to sit for 401 days at ambient temperature and humidity and then subjected to 25ºC and 97% RH for 347 days. Compared to first phase of the study, coating thickness varied. Except in case of Parylene C, all test coupons were coated with 1 mil thick coating at one end and approximately 3 mils thick coating on the apposite end, leaving middle of the coupons uncoated. The Parylene C coating was applied with 0.4-0.5 mil thick on the entire surface. Based on their observations, the authors concluded that all conformal coatings suppressed the formation of tin whiskers. However, they noticed that one of the urethane acrylic combinations was the best among all coatings and once again acrylic coating was the worst for tin whiskers suppression. The performance of Parylene C in the second phase may be related to its effective thickness, which is half of the first phase thickness. It was also evident that all coatings were eventually penetrated indicating that these coatings are not reliable as a foolproof mitigation strategy.

Based upon the observations above of the first and second phases of the study, it seems that conformal coatings have potential to help extend the reliability of the electronic components and assemblies by reducing the growth of tin whiskers. It is the matter of how long and under what circumstances. Although the above studies[11, 12,13,14,15] are encouraging and have thrown some light on the mitigation strategy using conformal coating, more work is required to understand the effectiveness of various coatings in relation to application methods, inherent physical and chemical properties, adhesion to the substrates, nature of the polymeric material themselves, stresses related to coatings application and cure, effective thicknesses, and their conformability.

### Why Parylene as a Suppressant for Tin Whiskers Growth?

With the current regulations for lead-free electronics and worldwide interests in using environmentally friendly conformal coatings, Parylene has been getting more attention due the nature of its chemistry, which offers many attributes that are very attractive. Work has also begun to evaluate different Parylenes for the mitigation of the tin whiskers problems. It has been observed that Parylene conformal coatings are more suitable for suppressing metallic whiskers than other conformal coatings or other proposed options [14]. Although no data is presented here on Parylene evaluations for reducing the tin whisker growth (results to be shared in the near future), this paper does provide an analysis on the key properties indicating that Parylene could potentially be suitable for the mitigation of tin whiskers problems in many applications.

### What is Parylene?

Parylene is the generic name for members of a unique polymer series. The Parylenes (xylylene polymers) have been classified as thermoplastic polymers that are formed on substrate surfaces using vacuum deposition polymerization (VDP). They are polycrystalline and linear in nature, and possess useful dielectric and barrier properties per unit thickness. They are also chemically inert and form thin layer coatings without pinholes. In addition, Parylenes truly conform to parts due to their molecular level deposition characteristics.

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, 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 0.1cm. As a result, all surfaces of an object to be coated are uniformly impinged by the gaseous monomer, providing a high degree of conformability[21, 22].

Vacuum deposition polymerization begins with the vaporization of a Parylene dimer. The dimer vapor is pyrolytically cleaved at temperatures of 400ºC to 750ºC to form a reactive monomer vapor. The reactive monomer vapor is then transferred to a deposition chamber where the substrates are located. In the room temperature deposition chamber, the reactive monomer vapor spontaneously condenses onto the substrates to form a Parylene coating. The entire Parylene process is carried out in a closed system under constant negative pressure. The closed system incorporates separate chambers for the vaporization, pyrolysis, and deposition steps of the process. There is no liquid phase in the deposition process, and substrate temperatures remain near ambient.

Although Parylene research and development efforts during the past four decades have resulted in several Parylene types, only three of them, Parylene N, C, and D have found wide commercial application to date. Properties of Parylene N, C and D are described extensively in the literature[22, 23, and 24]. The recent commercial availability of Parylene HT has now added many additional advantages for electronics applications. Parylene HT possesses unique properties[25, 26] compared to all existing Parylenes and other vapor phase coatings and is able to meet the growing requirements of better dielectric capabilities, higher temperature integrity and mechanical processing of dynamic medical electronics devices. The chemical structures of Parylene N, C, D and Parylene HT are shown in Figure. 1

**Parylene N** **Parylene C**

**Parylene D** **Parylene HT®**

**Figure 1 - Commercially Available Parylene Variants**

Parylene HT can easily be applied on PCB's, MEM's, a variety of micro, medical and optoelectronic devices, stators, capacitors, inductors, power supply electronics, batteries, nano-electronic parts and ceramics for high performance and reliability. It provides excellent corrosion, solvent, acid, moisture and UV resistance. Its very low dielectric constant, low coefficient of friction and high dielectric strength make it ideal for protecting parts that are exposed to high temperature, saline and corrosive environments. This coating is not limited to electronic applications, but also protects silicone, glass, composites, plastics, ceramic and ferrite cores. In addition to enhancing components' overall reliability, it is also suitable for contamination control, dry film lubrication and as an interlayer dielectric in manufacturing high density and high-speed integrated circuits.

## Key Properties

The most important characteristic of Parylenes that dominates the decision of their use in any specific situation is the vapor phase deposition polymerization process. Vapor phase polymerization provides the room temperature coating process and results in a polymer coating that is uniform in thickness, truly conformal and of high purity. The key properties of Parylenes that might be effective in suppressing tin whiskers growth are described below.

## Crystallinity

There are many conformal coatings that may possess crystalline structure, but may not be pure in terms of their chemical nature. On the other hand, Parylenes are polycrystalline in nature and are chemically pure compared to any liquid conformal coatings. The crystallinity of the Parylenes determines two of their most important practical characteristics; mechanical strength and solvent resistance. The crystallinity of Parylenes is confined to small sub-micrometer domains that are randomly dispersed throughout an amorphous phase. Because a given Parylene polymer chain is long enough to participate successively in several crystallites, these crystallites function as cross-links to strengthen the bulk polymer. The crystallinity of freshly deposited Parylenes increases with aging or annealing, affecting the modulus of the coating. In addition, crystalline domains are much more resistant to permeation than the amorphous phase, and because their structural roles remain the same even in the presence of permeates in the amorphous phase, Parylenes show great resistance to solvent attack.

Parylene prepared by VDP is a linear high-purity polymer whose crystalline transitions were characterized by X-Ray and electron diffraction, mechanical creep studies and differential thermal analysis. Two of the three endotherms observed can be related to alpha and beta polymorphs of poly-p-xylylene [27,28,29,33]. Parylene N possesses a singularly complex crystalline morphology in which two distinct crystalline modifications are recognized. When deposited in the usual VDP fashion, the crystallites tend to be mostly of the $\alpha$ modification. On annealing at a temperature of about 220ºC, the $\alpha$ form is converted to the $\beta$ modification. This transition was originally thought to be irreversible, but studies have demonstrated that it can be made reversible [30]. The crystalline phase undergoes further modifications at higher temperatures before reaching its melting point of 420ºC. The detailed crystal structures of the $\alpha$ ($a$ = 592 pm, $b$ = 1060 pm, $c$ = 655 pm, $\beta$ = 134.7º, for two monomer repeat units per cell) [31] and $\beta$ ($a = b$ = 2052 pm, $c$ = 655 pm, $\gamma$ = 120º, for 16 monomer repeat units per cell) modifications have been determined[32]. In Parylene C, the single crystalline form observed is very similar to the $\alpha$ form of Parylene N. Its detailed crystal structure has been determined ($a$ = 596 pm, $b$ = 1269 pm, $c$ (chain axis) = 666 pm, $\beta$ = 135.2º)[29]. The crystalline nature of Parylene D and HT is expected to have similar characteristics.

As indicated above, when applied as thin layer, Parylenes do have a very high modulus due to crystallinity compared to any other conformal coatings. The modulus of Parylenes can be further increased by heat or aging to provide a very high modulus coating to suppress tin whisker formation. In addition, this characteristic provides excellent resistance to various chemical and solvents enhancing corrosion resistance.

## Cryogenicity

Parylene C coated on steel plates chilled in liquid nitrogen at -160ºC withstood impacts of more than 11.3 Nm in a modified Gardener falling ball impact test. This compares with the values of about 28.2 Nm at room temperature. Unsupported 0.002 in films of Parylene C can be flexed 180º six times at -165ºC before failure occurs. Comparable films of polyethylene, polyethylene terphtahlate and polytetrafluoroethylene fail at three, two and one flexes respectively. Neither electrical nor physical properties of Parylene are affected by cycling from -271ºC to room temperature. Such properties of Parylene C and other Parylenes demonstrate that Parylenes are well suited to provide protection on electronic components in cryogenic conditions without compromising on their bulk properties[34].

## Tensile Strength and Modulus

Many of the mechanical properties of the Parylenes are similar to other conventional plastics, but are considerably better when compared with other conformal coatings at normal Parylene thickness. Due the crystalline nature of the Parylenes, they have high modulus values compared to liquid conformal coatings available for electronic applications. As indicated earlier, an increase in crystallinity with aging and annealing results in lowering of elongation to break and an increase in modulus and strength. Both tensile strength and modulus values, along with other properties, for Parylenes and other conformal coatings are compared in the Table 1.

In an accelerated testing, Parylene HT has shown remarkable thermal and oxidative stability at elevated temperatures. Useful physical and chemical properties are retained after aging for 3000 hrs at 250ºC in air. When heated, Parylenes anneal and increase in density. Along with the increase in density, due undoubtedly to increased crystallinity, the modulus increases. The initial decrease in elongation is also the result of increase crystallinity. Tensile strength of Parylenes also increases after heat aging. The values for each Parylenes are different with respect to their thermal stabilities. Thermal aging data for Parylene HT, showing increase in modulus and tensile strength, is shown in Fig. 2.

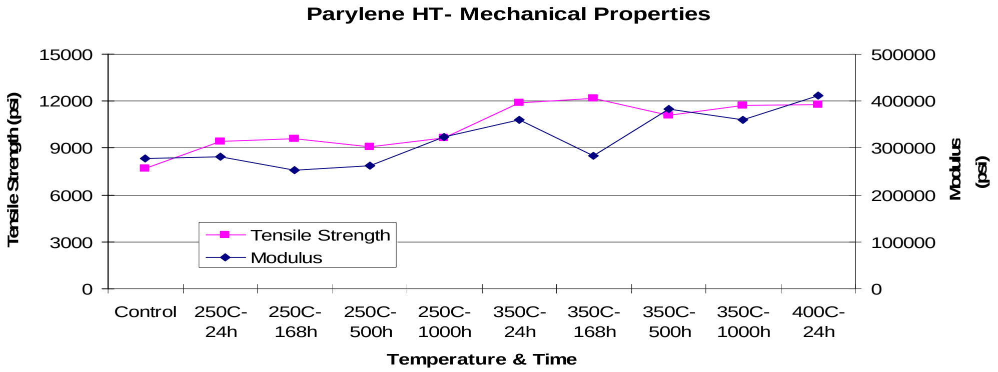


**Figure 2 - Tensile Strength and Modulus of Parylene HT after Annealing**

**Table 1 - Key Properties of Parylenes Compared with Other Conformal Coatings**

| **Properties**[34, 38, 39] | **Parylene N** | **Parylene C** | **Parylene D** | **Parylene HT** | **Acrylics (AR)** | **Epoxy (ER)** | **Silicones (SR)** | **Polyurethanes (UR)** |
|---|---|---|---|---|---|---|---|---|
| Young's Modulus (psi) | 350,000 | 400,000 | 380,000 | 370,000 | 2,000-10,000 | 350,000 | 900 | 1,000 – 100,000 |
| Tensile Strength (psi) | 6,000 – 11,000 | 10,000 | 11,000 | 7,500 | 7,000-11,000 | 4,000 – 13,000 | 350 - 1,000 | 175 – 10,000 |
| Dielectric Strength V/mil | 7,000 | 5,600 | 5,500 | 5,400 | 3,500 | 2200 | 2000 | 3500 |
| Elongation to Break (%) | 20 – 250 | 20 – 200 | 10 | 10 | 2 - 5.5 | 3 – 6 | 100 -210 | >14 |
| Density (g/cm$^3$) | 1.10 – 1.12 | 1.289 | 1.418 | 1.506 | 1.19 | 1.11 – 1.40 | 1.05 – 1.23 | 1.10 – 2.50 |
| Water Absorption (% after 24 hrs) | < 0.1 | < 0.1 | <0.1 | < 0.01 | 0.3 | 0.5 -1.0 | 0.1 | 0.6 – 0.8 |
| Rockwell Hardness | R85 | R80 | R80 | R122 | M68-105 | M80 – 110 | 40A – 45A (Shore) | 68A -80D (Shore) |
| LCTE at 25º C (ppm) | 69 | 35 | 30 – 80 | 36 | 55-205 | 45-65 | 250-300 | 100-200 |
| Gas Permeability at 25º C, (cc • mm)/(m$^2$•d)a | | | | | | | | |
| $N_2$ | 3.00 | 0.40 | 1.80 | 4.80 | No data | 1.60 | No data | 31.50 |
| $O_2$ | 15.40 | 2.80 | 12.60 | 23.50 | No data | 2.0 - 3.9 | 19,685 | 78.70 |
| $CO_2$ | 84.30 | 3.00 | 5.10 | 95.40 | No data | 3.10 | 118,110 | 1,181 |
| WVTR at 37$^{o}$C,100%RH, (cc-mm)/(m$^2$-day) | 0.59 | 0.08 | 0.09 | 0.22 | 13.9 | 0.94 | 1747 | 0.93 -3.4 |

Parylenes mechanical properties enhancement due to annealing can be exploited for suppression of tin whiskers formation. Annealing of tin plating is also one of many suggested methods to reduce or suppress the formation of tin whiskers

### Stress

Another property which may be very important, when considering tin whiskers mitigation strategy, is the total stress applied by coatings on the tin surfaces. The stress values for Parylene N were found to be compressive in nature while polyimide exhibits stresses in the tensile mode [36]. Parylene N, which can achieve a 10 µm thickness in one layer, offers reduction in stress of 54% and 50% compared to two and four layered polyimide films, respectively. For a 10 µm thick Parylene N film, an average inherent stress value is 1.8±0.2 X 10$^{-8}$ dynes/cm$^2$. Generally, the total stress of a thin film or coating can be defined as sum of three stress components; applied external stress, thermal or cure stress and intrinsic stress. When comparing Parylenes with other conformal coatings, it must be noted that stress for Parylenes result largely from intrinsic stress while others have contributions from both thermal (or other curing methods) and intrinsic stress. As shown above, Parylenes offer perhaps the lowest possible stress on any surfaces when applied as a coating. Although still a matter of debate as to whether stress is a main reason for tin whiskers growth, it is important to remember that stress applied by any conformal coatings on tin plated surfaces must be low. Conformal coating application methods may contribute to stress.

### Barrier Properties

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 components and assemblies. Generally applied much thinner than alternate liquid coatings, Parylene provides a pinhole-free barrier to protect against moisture, chemicals and common gases. Several coatings were evaluated, including Parylene C, to protect pacemaker electronic modules[26]. The coated modules were immersed in 0.9 percent saline solution at 37$^{o}$C. On the first day of testing, units were removed from the saline bath every four hours, washed in deionized water and dried in air for 30 min at 55$^{o}$C. The test parameters (pulse width, current drain, pulse interval etc.) were then measured and modules were returned to immersion for continued testing. After the first 24 hours, parameters were measured daily until units failed completely. The test unit coated with Parylene C performed extremely well over a period of 30 days compared to the second best, which lasted for 58 hrs only. All other coatings failed within 8 hours. Other coatings that were evaluated included epoxies, polyurethanes, silicones and polytetrafluoroethylene. Parylene C has been found suitable for protection of non-hermetically packaged integrated circuits. Evaluation of Parylene C has shown that it can withstand immersion in saline solution for over 320 days under continuous bias of 3V, and still protect the current carrying conductors on the surface of the IC device it coats[35].

Water vapor transmission is one of the key properties of protective coating impacting the function of electronic devices. Parylenes are best among the organic coatings for having low water vapor transmission rate. The water vapor transmission rates and water absorption of Parylenes are compared with other common conformal coating materials in Table 1. Water absorption (% after 24 hours) and permeability values of oxygen, nitrogen and carbon dioxide for Parylenes are also very low compared to other conformal coatings. These attributes indicate that Parylenes will provide protection from detrimental effects on the coated surfaces that might occur due to water or water vapor transmission and offer a potential to reduce tin whiskers formation.

### Adhesion

For any conformal coatings to perform satisfactorily, their adherence to the substrate on which they are applied is imperative. It is well known that there are several modes of adhesion, including mechanical, chemical, dispersive, electrostatic and diffusive. When any conformal coating is applied on a substrate, either several modes combined or one single mode contributes towards the adherence between the two surfaces. Achieving good adhesion is a function of surface wettability, relative surface energies, and the kinetics of wetting. However, adhesion gets complicated when surfaces have contamination or surface energies are not compatible to provide proper adhesion. Although a never ending challenge, there have been extensive discussions in the literature regarding adhesion, adhesion failures, surface contamination and preparation of surfaces for good adhesion, etc. A most important aspect for this discussion is to have excellent adhesion of the conformal coating to tin plated surfaces when attempting to suppress tin whiskers growth. Results of coatings evaluation for tin whiskers growth retardation can be misleading if the adhesion aspects are not considered carefully at the beginning of the experiments or on the actual parts. This is true for other attributes of conformal coating and its effectiveness. When the coating is highly adherent, the tin surface may experience less stress from of conformal coating, which in turn can help retard the growth of tin whiskers.

Although Parylenes adhere well on many surfaces, several coupling technologies are currently available to enhance adhesion on difficult substrates. Since Parylenes are deposited using vapor phase polymerization process, adhesion can be improved more effectively on various types and complicated substrates compared to many liquid conformal coatings applications.

### Conformability

It is important that any conformal coating applied on tin plated or coated substrates for the purpose of tin whiskers suppression also provides complete protection from moisture ingress and other contamination. Liquid coatings generally have the undesired effect of meniscus forming, bridging, pooling and edge pull-backs depending on the surface profile of the electronic substrates. Parylene avoids all of those issues by virtue of its vapor phase polymerization. The ability to deposit Parylene as a truly pinhole-free, conformal, thin, continuous and uniform adherent coating enhances its application as protective barrier coating for all types of devices.

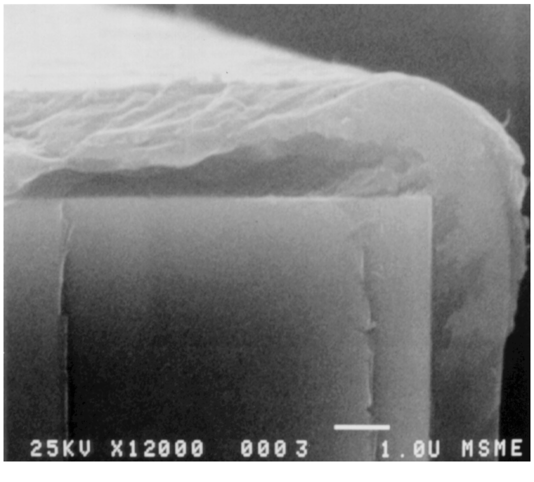


**Figure 3 - SEM photograph of 1.5 µm of Parylene C on a silicon device. Photo courtesy: E.E. Hui & TRF Research Foundation**

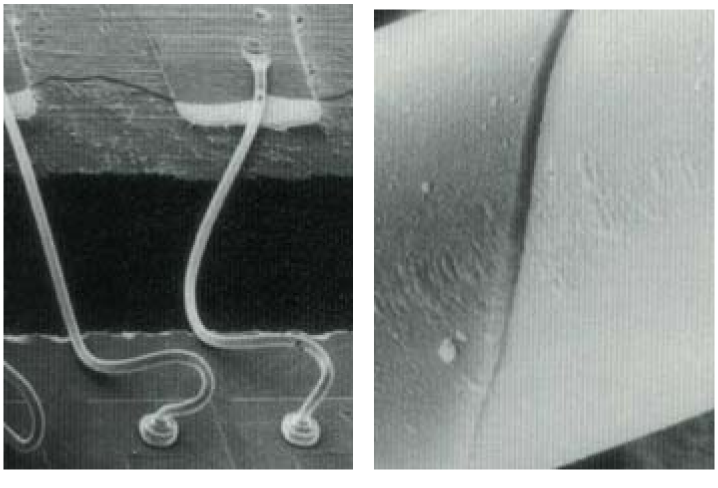


**Figure 4 - Left side photo: Shows gold wire bond coated with 1.5µm thick Parylene. Right side photo: Parylene has been selectively removed from this one mil gold wire bond to reveal the thin, conformal nature of the coating.**

As shown in the Figure 3 (an SEM photograph of a one and a half micron film of Parylene C on a silicon device), the conformal nature of the coating is validated by the radius of curvature that is formed. Figure 4 is another demonstration of Parylene's true conformal nature where a portion of coating has been removed to show surface imperfections and how well Parylene has conformed over the micro imperfections. This property of Parylenes can have significantly impact in the encapsulation of electronic components and assemblies, thereby contributing to the suppression of tin whiskers growth by preventing some of the factors that accelerate tin whiskers growth.

**Corrosion Resistance**

Parylenes successfully control corrosion of electronic assemblies and substrates in a variety of application conditions. Since the actual corrosive environment changes continuously, most testing experiments are designed to expose samples to various environmental stresses that promote 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 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 C and 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 examined. Both Parylene C and Parylene HT coated boards showed no evidence of corrosion while the uncoated boards had salt and corrosion residue running down the PCB. Salt deposits were observed on connector pins. Heavy iron oxide deposits were on and around schottky diode heat sinks. Both Parylene C and Parylene HT provided complete protection from corrosion under these saline conditions.

**Oxidation Resistance**

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. In oxygen-free atmospheres or in the vacuum of space, the continuous service temperature projections exceed 200$^{o}$C for both Parylene N and C. On the other hand, Parylene HT has ability to resist thermal oxidation up to 450$^{o}$C both in oxygen and oxygen-free atmospheres. Parylene HT has survived continuous exposure to 350$^{o}$C for more than 1000 hours in air without any adverse property change. 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. However, Parylene HT film was stable without any change in appearance or other visual properties for more than 2000 hours. The accelerated test was designed for 2000 hours, which is indicative of about twenty years of UV stability in normal outdoor environment.

**Electrical Resistance**

Parylenes are excellent candidates for use in electronics because of their 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 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 Parylenes, Parylene HT is particularly suited for these applications. The typical electrical properties of Parylenes and other polymers are compared in Table 1.

For electronics applications, moisture-insulation resistance tests are generally 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 N, C and 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 megohm bridge at 500 volts DC, with an electrification time of one minute during the 1st, 4th, 7th and 10th 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 property was again measured upon completion of the moisture resistance test, after a 24-hour stabilization period. The results demonstrate that insulation resistance values of Parylene N, C and Parylene HT are about one to two orders of magnitude better than the IPC or Mil requirements.

For moisture resistance-dielectric withstanding voltage tests, several Y-test pattern samples coated with Parylene N, C and 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 less than one microampere for Parylenes. The leakage rate shall not exceed 10 microamperes.

The above tests indicate that Parylenes are capable of providing excellent electrical insulation in adverse conditions. Parylene C coating with a thickness of 0.05 mm on PCBs was capable of maintaining electrical insulation properties during immersion in PBS solution (phosphate buffer saline, P-3813) at temperatures of 40-80°C for six months[37].

Although no direct relationship between tin whiskers growth and electrical insulation properties has been demonstrated, excellent electrical insulation helps mitigate the risk of short circuit failures and does protect electronics from any external electrical energy ingress which may help cause corrosion and or contribute to the growth of tin whiskers formation.

## Coating Thickness

The thickness of typical liquid conformal coatings is in the range of 3 to 8 mil (0.003 to 0.008 in). However, the range for vapor phase deposited Parylene films is generally from 0.1 to 1 mil (0.0001 to 0.001 in). With the advancement of microelectronics, there is growing demand for thin and ultra-thin coatings for reduction of weight, size and materials consumption. The thickness at which a coating is considered to be an encapsulating instead of merely a conformal coating has not been well defined. For most printed circuit boards and other electronic components, Parylene thickness range from 0.5 to 1.0 mil has shown to be effective for protection purposes. This thickness range may also be suitable for suppression of tin whiskers formation. However, experiments would be required to verify this. Parylene coating thickness varies with the required performance capabilities.

## Other Attributes of Parylenes

In addition to the attributes of Parylenes mentioned above that may have impact on retardation of tin whiskers formation, there are other characteristics of Parylenes particularly suitable for protection of printed circuit boards, wafers or other electronic components. The details of such properties are available at www.scscoatings.com. Parylenes are most often used to protect PCBs, electronic components, medical devices from body and environmental contamination, dust, dirt, moisture, corrosion, thermal or mechanical shock, vibration, harsh chemicals and solvents etc., any one of which can degrade the performance or reliability of the component, device or system.

## Conclusion

It is apparent that worldwide movement to lead-free electronics and the RoHS directives have caused the tin whiskers threat to reemerge, and industry has responded by starting to look for appropriate solutions. Numerous studies have provided information on this issue and have been able to identify several strategies to mitigate tin whiskers risks until a method is found to completely eliminate the problem. One of the mitigation strategies that is getting more attention recently is the application of conformal coatings. Although the list of conformal coatings is very long, not all of them have the potential to mitigate the risk of tin whiskers formation. The information provided in this paper clearly indicates, in light of the factors responsible for tin whiskers growth, that Parylenes are suitable, particularly Parylene C and Parylene HT, for suppressing the growth of tin whiskers. Since Parylenes are truly conformal, they offer better coverage on components to be coated compared to any liquid coating applied either by dip or spray methods. Parylenes can be annealed after coating (subject to Parylene types and parts thermal stability) and have the potential to provide good adhesion that can further enhance the effectiveness of the coating. With the commercial availability of Parylene HT, manufacturers of electronics may have an option of an advanced protective coating that can enhance electronics reliability without hermeticity under many harsh application conditions. Parylene HT is well suited for electrical and environmental protection of electronics, various micro and nano electrical components, sensors, printed circuit boards and other components. It is also suitable for contamination and corrosion control, dry lubrication and protection of high density and high-speed integrated circuits and electronics.

## Acknowledgments

The author would like to thank both technical and marketing team members of Specialty Coating Systems, Inc. for their support and advice.

## References

1. G. Galyon, "A History of Tin Whisker Theory: 1946 to 2004", *SMTAI International conference*, September 26-30, 2004(Chicago, IL)

2. C. Xu, C. Fan, Y. Zhang, J. Abys, "Whisker Prevention", *Proceedings of the Technical Conference*, APEX 2003, Anaheim, CA, April 2003
3. M. Osterman, "Mitigation Strategies for Tin Whiskers", *University of Maryland, CALCE Consortium*, July 3, 2002.
4. G. Galyon, "Annotated Tin Whisker Bibliography and Anthology", *NEMI Publication*, pp. 1-22, March 2004.
5. B. D. Dunn, “A Laboratory Study of Tin Whisker Growth”, *European Space Research and Technology Center*, Noordwijk, The Netherlands, September 1987.
6. P. Lavery, “Strategies to Mitigate the Tin Whisker Phenomenon”, Rev 1.1, *Vicar Corporation*, February, 2006.
7. G. Galyon, R. Gedney, "Avoiding Tin Whisker Reliability Problems", *Circuits Assembly*, pp. 26-31, August 2004.
8. “BMPCOE Strives to Mitigate Tin Whiskers” *Test & Screening”, Latent Defects: Ticking Timebombs, COTS Journal,* September 2003.
9. M. Dittes, P. Oberndorf, P. Crema, V. Schroeder, "Tin Whisker Formation in Thermal Cycling Conditions", *IEEE Electronics Packaging and Technology Conference*, pp. 183-188, 2003.
10. J. Brusse, G. Ewell, and J. Siplon, "Tin Whiskers: Attributes and Mitigation", *Capacitor and Resistor Technology Symposium (CARTS)*, pp. 67-80 March 25-29, 2002.
11. J. S. Kadesch, and J. Brusse, "The Continuing Dangers of Tin Whiskers and Attempts to Control them with Conformal Coat", *NASA's EEE Links Newsletter,* July 2001.
12. H. Leidecker, and J.S. Kadesch, "Effects of Conformal Coat on Tin Whisker Growth", *Proceedings of IMAPS Nordic, The 37th IMAPS Nordic Annual Conference*, pp. 108-116, September, 10-13, 2000.
13. J. Kadesch, "Effects of Conformal Coat on Tin Whisker Growth", *NASA's EEE Links Newsletter*, March 2000.
14. T. Woodrow, "Evaluation of Conformal Coatings as a Tin Whisker Mitigation Strategy", *IPC/JEDEC 8th International Conference on Pb-Free Electronic Components and Assemblies*, San Jose, CA, April 18-20, 2005.
15. T. Woodrow, "Evaluation of Conformal Coatings as a Tin Whisker Mitigation Strategy, Part 2", *SMTAI*, Sept. 2006
16. T. Woodrow, "Tracer Diffusion in Whisker-Prone Tin Platings", *SMTAI*, Sept. 2006.
17. “Current Tin Whiskers Theory and Mitigation Practices Guidelines” *JDEC/IPC Joint Publication*, March 2006.
18. M. Barsoum, et al, "Driving Force and Mechanism for Spontaneous Metal Whisker Formation", *Physical Review Letters 93*, pp.206104-1 to 206104-4, November 10, 2004.
19. J. Brusse, "Tin Whisker Observations on Pure Tin-Plated Ceramic Chip Capacitors", Proceedings of the American Electroplaters and Surface Finishers (AESF) SUR/FIN Conference, pp. 45-61, June 24-28, 2002.
20. G. T. Galyon and L. Palmer, “The Structure and Kinetics of Tin Whisker Formation and Growth on High Tin Content Finishes,” Handbook of Lead - free Solder Technology for Microelectronic Assemblies-Marcel Dekker, Inc., N.Y., ed. Karl J. Puttlitz and Kathaleen A. Stalter, pp 851-914, 2004.
21. W. F. Gorham, “Para-Xylylene Polymers” US patent No. 3,342754, 1967.
22. W. F. Gorham, “A New, General Synthetic Method for the Preparation of Linear Poly-P-Xylylenes", J. Polym. Sci, Vol. 4, pp 3027-3039, 1966.
23. W. F. Beach, C. Lee, D. R. Bassett, T. M. Austin, and R.A. Olson, “ Xylylene Polymers”, Encyclopedia of Polymer Science and Technology, vol. 17, 2nd ed., John Wiley, New York, , pp 990-1025, 1989.
24. R. Olson, “Careful PCB Design Enhances Conformal Coating Performance”, Electronic Packaging and Production, pp 79, 1987.
25. W. R. Dolbier Jr., J. Duan and A.J. Roche, “Parylene AF4 synthesis”, US patent No. 5,841,005, 1998.
26. R. Kumar, D. Molin, L. Young, and F.Ke, “New High Temperature Thin Coatings for Power Electronics”, Proceedings, APEC-Nineteenth Annual IEEE Applied Power Electronics Conference and Exposition, California, USA, pp1247-1249, 2004.
27. W. D. Niegisch, “Morphology of Poly-p-Xylylene” *Polymer Letters*, Vol. 4, pp. 531-536, 1966.
28. W. D. Niegisch, “Crystallography of Poly-p-Xylylenes”, *J. of Applied Physics*, Vol. 37, Number 11, October 1966.

29. S. Isoda, T. Ichida, A. Kawaguchi, and K. Katayama, Crystal Structure of Poly (2-chloro-p-xylylene)", *Bull. Inst. Chem. Res. Kyoto Univ.* **61**(3), 222, 1983.
30. D. E. Kirkpatrick and B. Wunderlich, "On the Reversibility of the Crystalline Phase Transitions of Poly(p-xylylene)", J. Polymer Science, Polymer Physics 24, pp 931-933, 1986
31. R. Iwamoto and B. Wunderlich "Crystal Structure of Poly (p-xylylene). I. Alpha Form", J. Polymer Science, Polymer Phys. Ed. 11 (12), 2403-2411, 1973
32. S. Isoda, M. Tsuji, M. Ohara, A. Kawaguchi, and K. Katayama, "Structural Analysis of B-form Poly (p-Xylylene) Starting from a High-resolution Image", *Polymer* **24**, pp1155, 1983
33. K. A. Mailyan, S. N. Chavalun, A. V. Pebalk, I. E. Kardash, " X-Ray Study of Crystalline Structure of Poly-p-Xylylene Films", Polymer Science, Vol 34, No. 9, pp 761-765, 1992.
34. SCS Parylene Specifications and Properties, Specialty Coating Systems, Indianapolis, 2006.
35. Charlson, E. J., R. Sabeti, E.M. Charlson, and K. K. Yasuda, "Protective Coating of Integrated Circuits for Operation in Corrosive environments", Proceedings of Mat. Res. Soc. Symp., 1989, Vol. 154, pp.91-96.
36. B. J. Bachman, "Poly-p-xylylene as a Dielectric Material": SAMPE Proc.1st.Int. Electronics Conf. June 23-25, pp 431-440, 1987.
37. M. T. F. Reitman and J. McPeak, "Protective Coatings for Implantable Medical Devices", Proceedings of ANTEC, pp. 3120-3124, 2005.
38. Handbook of Plastics, Elastomers, and Composites, Chapter 6- Plastics in Coatings and Finishes, Fourth Edition, McGraw Hill, Inc., New York, 2002.
39. Properties and method as reported in "Coatings Materials for Electronic Applications", James J. Licari, 2003, ISBN: 0-8155-1492-1

SPECIALTY COATING SYSTEMS™

# Parylene as a suppressant for Tin Whiskers Growth on Printed Circuit Boards

**Rakesh Kumar**

**February 22, 2007**

IPC Printed Circuit Expo®, APEX® and the Designers Summit

# Agenda

- Introduction
- Tin Whiskers Mitigation Methods
- Why Parylene as a Suppressant
- Conclusion

# What Are Tin Whiskers?

- Spontaneous filamentary growth from plated tin surfaces
- Electrically conductive, crystalline structures
- Can grow without electrical field in vacuum and tin atmosphere
- Extremely thin, Diameters: 1-2 microns, lengths: >1.5 mm
- Grow as straight, kinked or spiraled single crystals of tin
- Able to reach length of 10 mm
- Grows at room temperature to 75°C

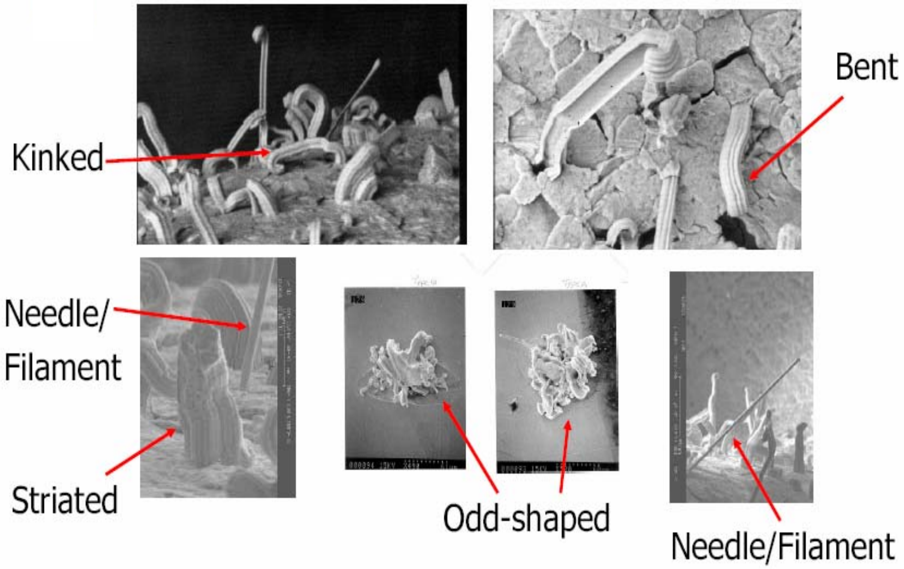
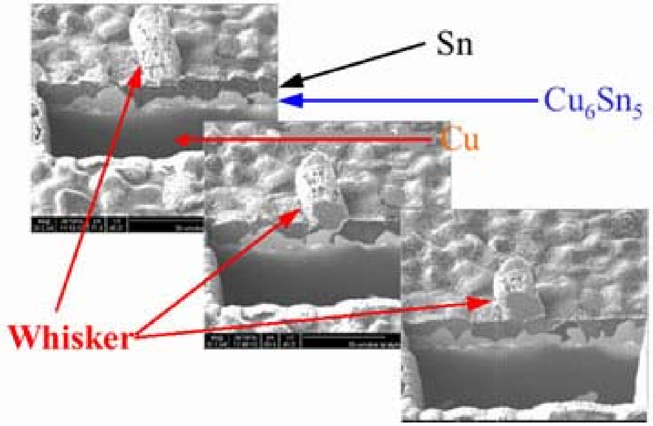


**Photo courtesy by NASA EEE Parts and Packaging Program (NEPP)**

# How Do They Occur?

## Still subject of much investigation & uncertainty

- Plating chemistry and process
- Re-crystallization and crystalline structures
- Stress (e.g. Internal and external, Compressive stresses, etc.)
- Diffusion of substrate elements into tin layer
- Intermetallic formation
- Thermal expansion mismatch
- Corrosion of the substrates
- Externally applied forces (e.g.Bending or stretching, lead forming etc.)
- Scratches or nicks



Focused ion beam (FIB) images taken at various stages of cutting through a matt tin whisker on a copper substrate

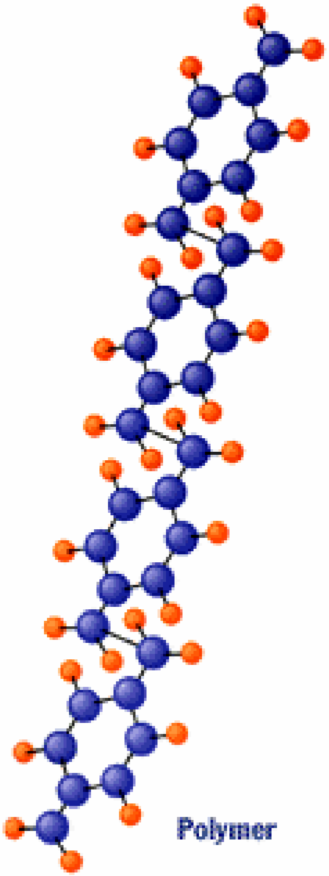
(Source-John Lau)

# Tin Whiskers Mitigation Methods

- Avoid tin plated parts
- Strip and replate
- Solder dip the plated surfaces sufficiently using a tin-lead solder
- Select a matte or low stress tin finish
- Select underplating (barrier layer) to reduce intermetallic formation
- Vary thickness of tin plating
- Reflow of pure tin plated surfaces
- Annealing
- Avoid compressive loads on plated surfaces
- **Apply a conformal coat**

# Conformal Coatings for Minimizing Tin Whiskers

- Urelane 5750
- Urethane-Acrylic
- Acrylic
- Silicone
- Parylene C



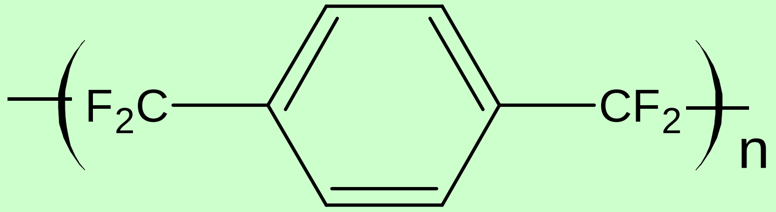
# Why Parylene as a Suppressant ?

- Crystallinity
- Cryogenicity
- Tensile Strength and Modulus
- Low Stress
- Barrier Properties
- Adhesion
- Conformability
- Corrosion Resistance
- Oxidation Resistance
- Electrical Resistance
- Controlled Coating Thickness
- RoHS Compliant

**Generally Known for :**

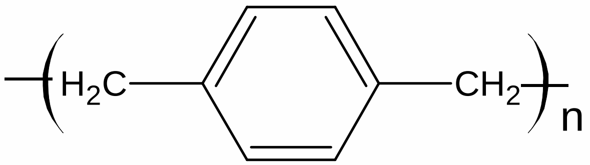
- Chemical barrier
- Moisture barrier
- Dielectric barrier
- Complete encapsulation
- Pinhole/defect-free
- Extremely thin
- Dry lubricity
- Biologically inert
- Chemical Inertness
- Environmentally friendly

# Parylene Types

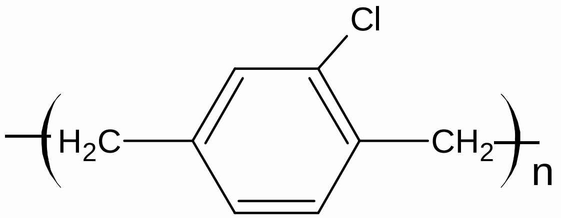


**Parylene HT®**

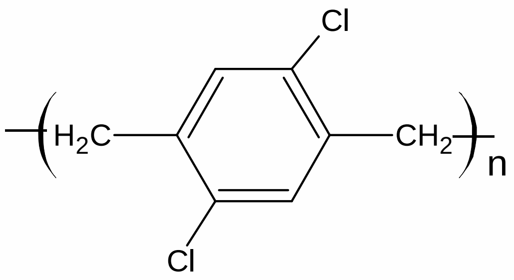
A New Generation High Performance Coating



**Parylene N**



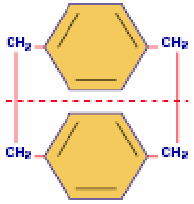
**Parylene C**



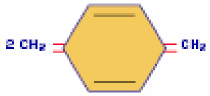
**Parylene D**

# Parylene Deposition Process

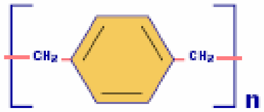
[2,2]Paracyclophane
(Dimer)



Para-xylylene
(Monomer)



Poly(para-xylylene)
(Polymer)



VAPORIZATION:
DIMER
DI-PARA-XYLYLENE
150°C, 1 TORR

PYROLYSIS:
MONOMER
PARA-XYLYLENE
680°C, 0.5 TORR

DEPOSITION:
POLYMER
POLY-PARA-XYLYLENE
25°C, 0.1 TORR

Dimer is vaporized

Vapor is pyrolized

Monomer molecules combine to form conformal polymer coating

THE BALANCE OF PARAMETERS THROUGHOUT THE ENTIRE SYSTEM IS CRITICAL FOR PRODUCING GOOD POLYMER FILM.

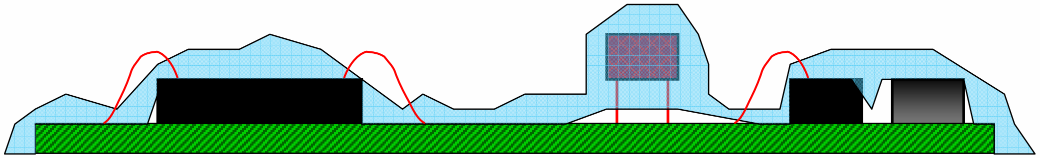
# Unique Process Features

- Gas phase deposition (VDP)
- No liquid phase ever isolated
- Gas phase is highly reactive
- Controllable thickness
- No cure cycle
- No volatile component
- High purity polymer
- Clean, self-contained process
- Room temperature deposition
- Spontaneous formation
- No cure stresses
- Low mass thin films

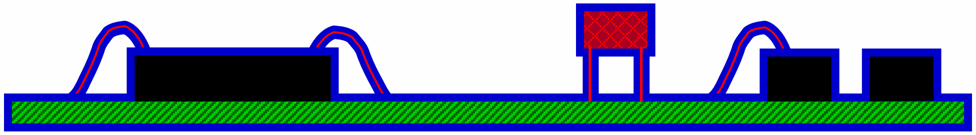
# Liquid vs. Parylene Coating

## Circuit Board Comparison

**Liquid Coating**



**Parylene Coating**

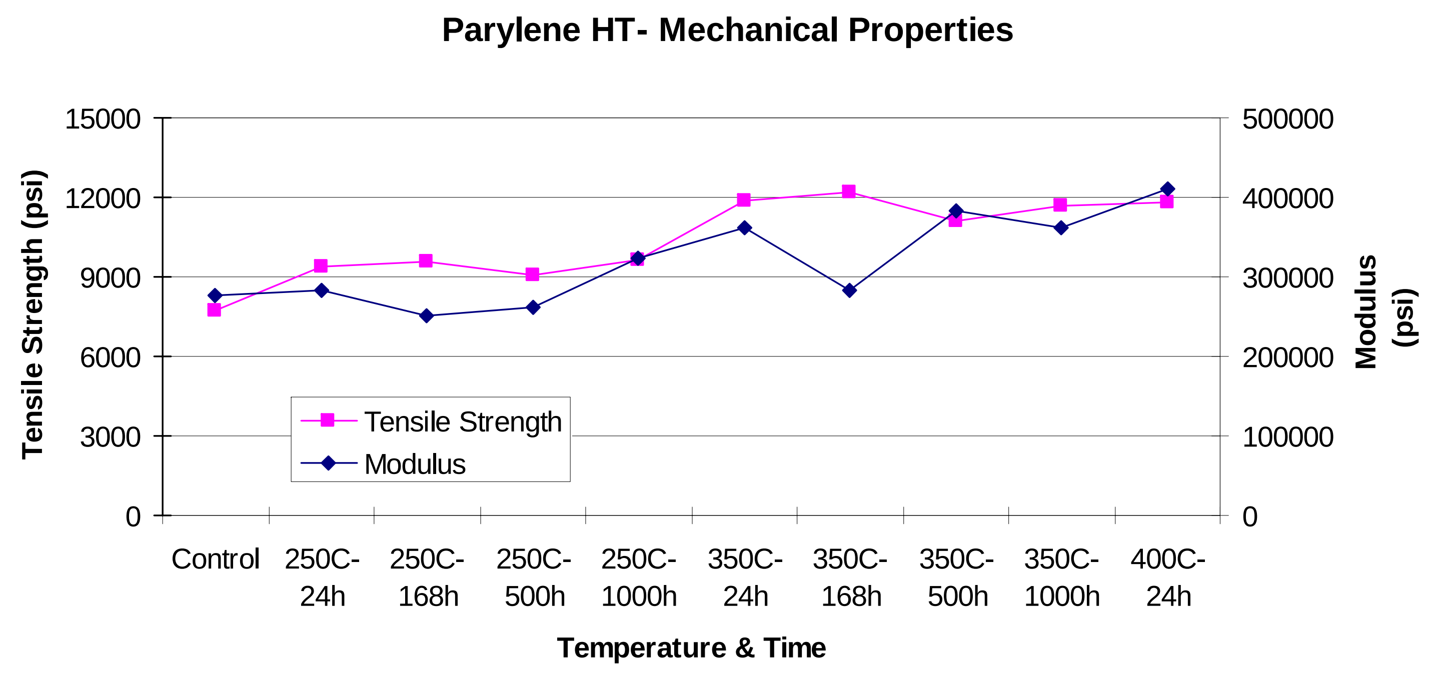


# Why Parylene as a Suppressant ?

- Crystallinity
  - Mechanical strength
  - Solvent resistance
  - Increase with aging or annealing
- Cryogenicity
  - Cycling from -271$^0$C to RT

# Tensile Strength & Modulus

| Properties[34, 38, 39] | Parylene N | Parylene C | Parylene D | Parylene HT | Acrylics (AR) | Epoxy (ER) | Silicones (SR) | Polyurethanes (UR) |
|---|---|---|---|---|---|---|---|---|
| Young's Modulus (psi) | 350,000 | 400,000 | 380,000 | 370,000 | 2,000-10,000 | 350,000 | 900 | 1,000 – 100,000 |
| Tensile Strength (psi) | 6,000 – 11,000 | 10,000 | 11,000 | 7,500 | 7,000-11,000 | 4,000 – 13,000 | 350 - 1,000 | 175 – 10,000 |



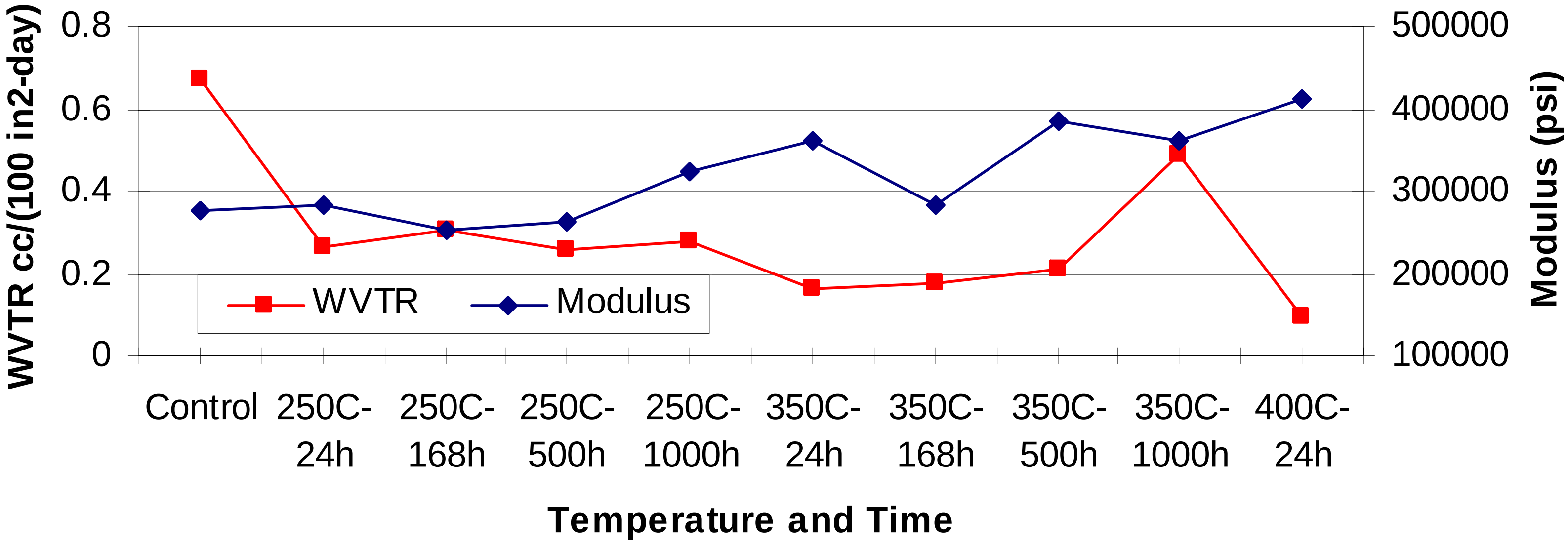
# Why Parylene as a Suppressant ?

- Stress
  - Compressive in nature
  - 10 um thick film offers 50-54% reduction
  - Average  stress value is 1.8 X $10^{-8}$ dynes/$cm^2$
  - Intrinsic stress only
- Barrier Properties

| Parylene Thickness (μm) | Calcium (ppm) | Aluminum (ppm) | Zinc (ppm) |
|---|---|---|---|
| 0.0 | 0.17 | 4.2 | 50 |
| 0.1 | 0.15 | 1.8 | 35 |
| 0.5 | 0.03 | 0.1 | 12 |
| 1.0 | <0.002 | <0.05 | 0.2 |
| 2.0 | <0.002 | <0.05 | <0.05 |

# Why Parylene as a Suppressant ?

## Water Vapor Transmission Rate (WVTR) and Modulus

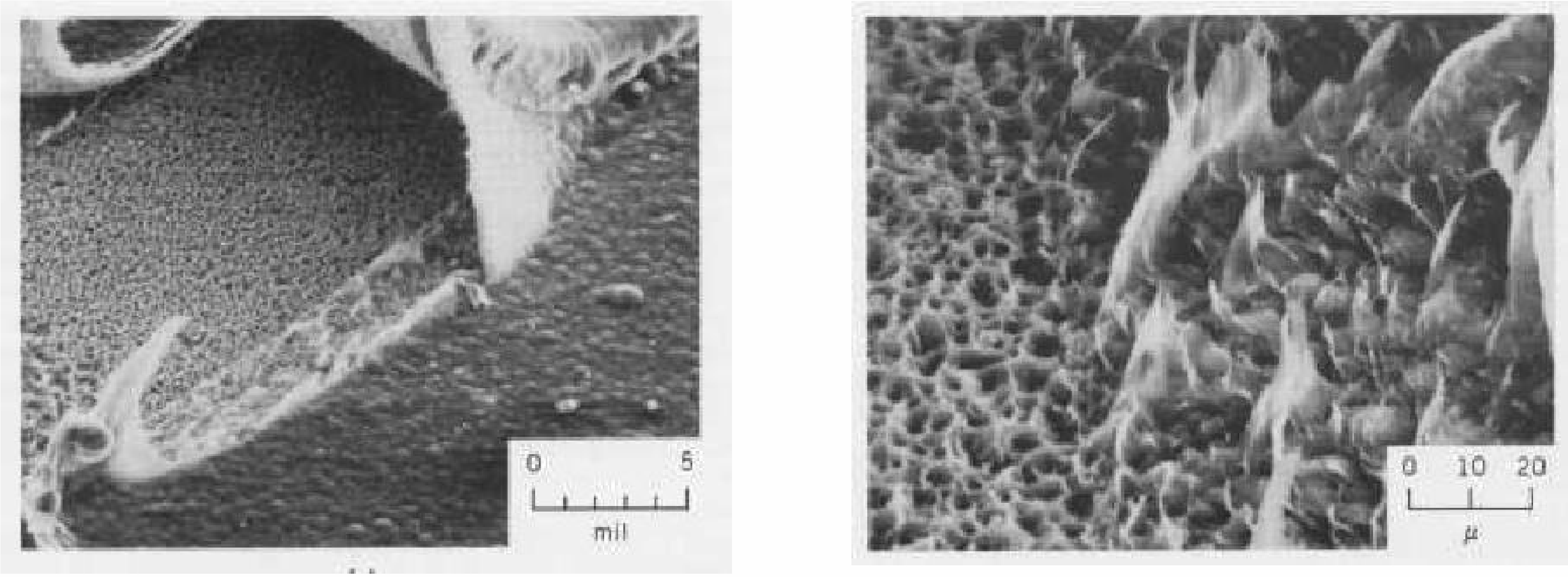


# Key Properties of Parylenes Compared to Other Conformal Coatings

| **Properties**[34, 38, 39] | **Parylene N** | **Parylene C** | **Parylene D** | **Parylene HT** | **Acrylics (AR)** | **Epoxy (ER)** | **Silicones (SR)** | **Polyurethanes (UR)** |
|---|---|---|---|---|---|---|---|---|
| Young's Modulus (psi) | 350,000 | 400,000 | 380,000 | 370,000 | 2,000-10,000 | 350,000 | 900 | 1,000 – 100,000 |
| Tensile Strength (psi) | 6,000 – 11,000 | 10,000 | 11,000 | 7,500 | 7,000-11,000 | 4,000 – 13,000 | 350 - 1,000 | 175 – 10,000 |
| Dielectric Strength V/mil | 7,000 | 5,600 | 5,500 | 5,400 | 3,500 | 2200 | 2000 | 3500 |
| Elongation to Break (%) | 20 – 250 | 20 – 200 | 10 | 10 | 2 - 5.5 | 3 – 6 | 100 -210 | >14 |
| Density ($\text{g/cm}^3$) | 1.10 – 1.12 | 1.289 | 1.418 | 1.506 | 1.19 | 1.11 – 1.40 | 1.05 – 1.23 | 1.10 – 2.50 |
| Water Absorption (% after 24 hrs) | < 0.1 | < 0.1 | <0.1 | < 0.01 | 0.3 | 0.5 -1.0 | 0.1 | 0.6 – 0.8 |
| Rockwell Hardness | R85 | R80 | R80 | R122 | M68-105 | M80 – M110 | 40A – 45A (Shore) | 68A -80D (Shore) |
| LCTE at 25° C (ppm) | 69 | 35 | 30 – 80 | 36 | 55-205 | 45-65 | 250-300 | 100-200 |
| Gas Permeability at 25° C, (cc • mm)/($\text{m}^2$•d)a | | | | | | | | |
| $N_2$ | 3.00 | 0.40 | 1.80 | 4.80 | No data | 1.60 | No data | 31.50 |
| $O_2$ | 15.40 | 2.80 | 12.60 | 23.50 | No data | 2.0 - 3.9 | 19,685 | 78.70 |
| $CO_2$ | 84.30 | 3.00 | 5.10 | 95.40 | No data | 3.10 | 118,110 | 1,181 |
| WVTR at $37^{o}$C,100%RH, (cc-mm)/($\text{m}^2$-day) | 0.59 | 0.08 | 0.09 | 0.22 | 13.9 | 0.94 | 1.7 48 | 0.93 -3.4 |

# Why Parylene as a Suppressant ?

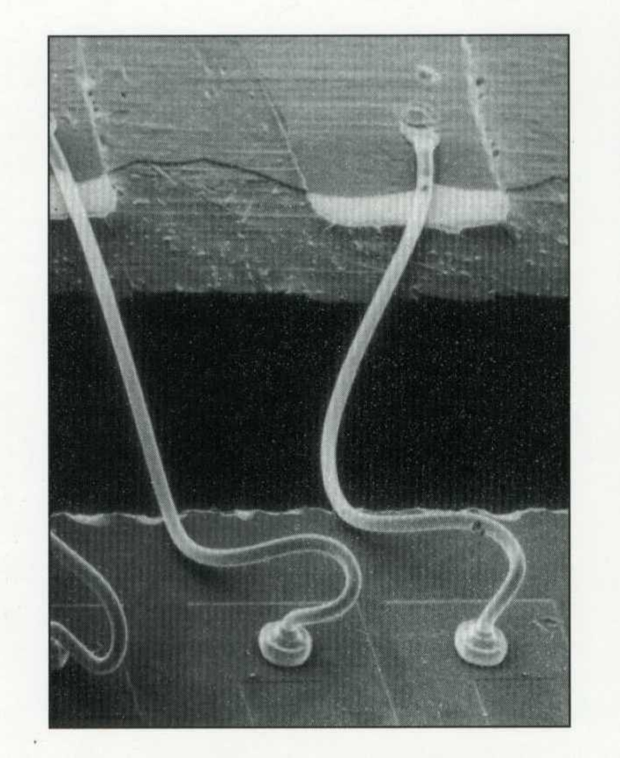
- Adhesion

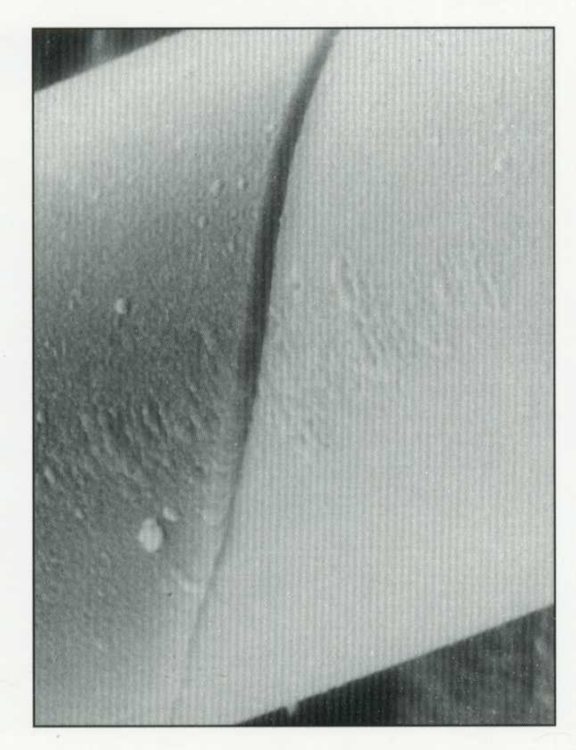


Cohesion-Adhesion on Printed Circuit Board

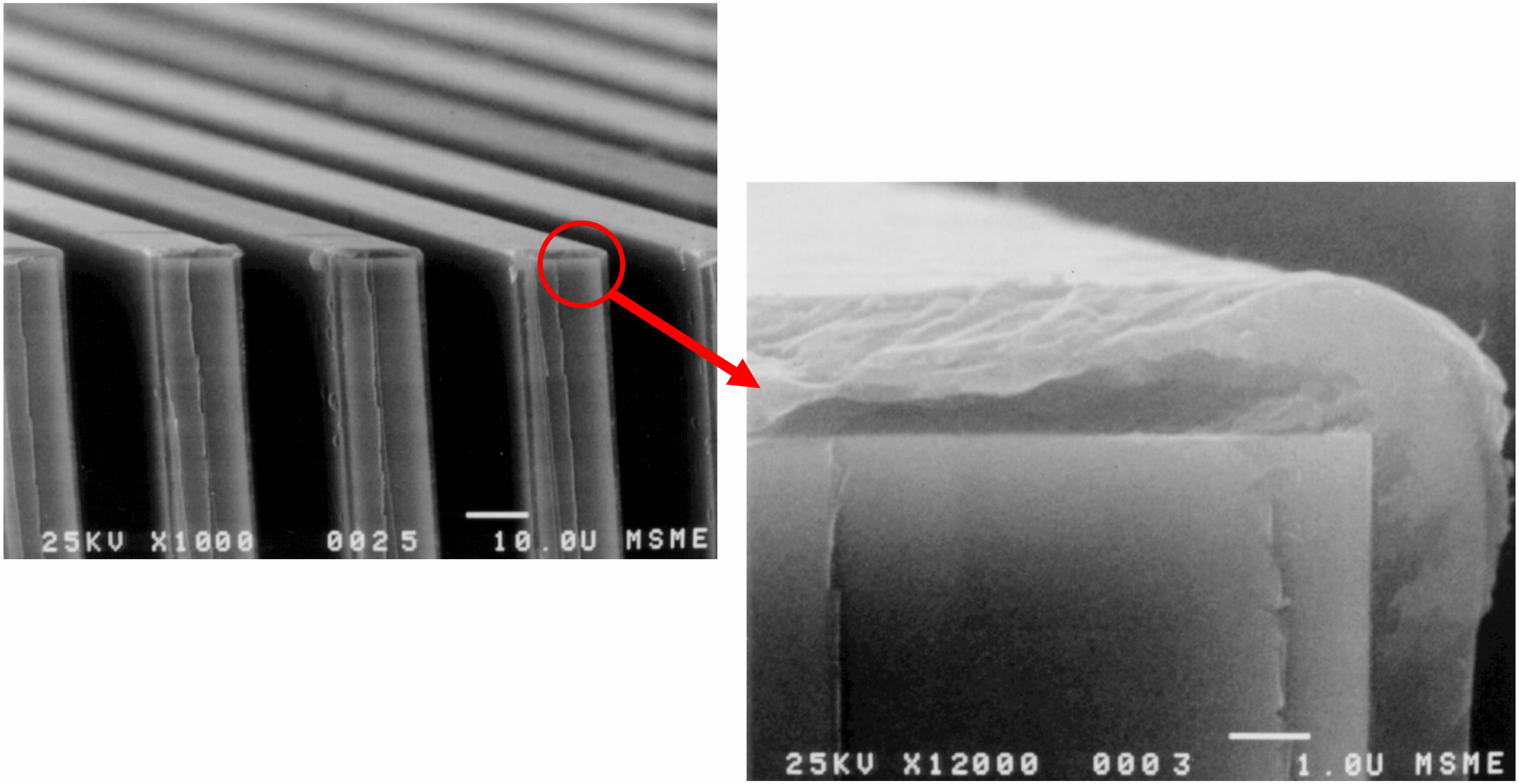
# Conformability

0.001" (1 mil) gold wire ... with a 1.5$\mu$m coating





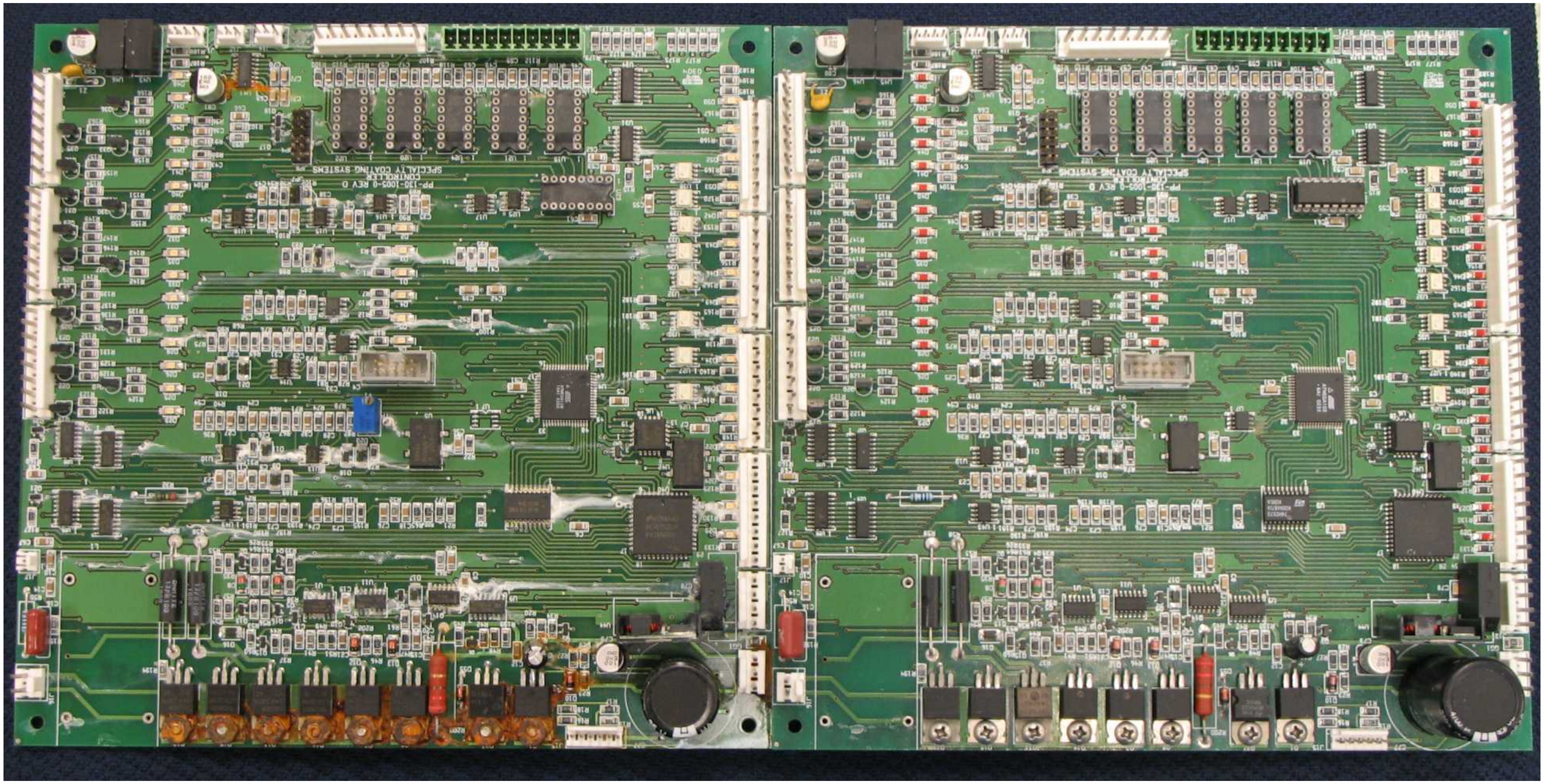
# Conformability



**Parylene C; As deposited**

E.E. Hui, UC Berkeley

# Corrosion Resistance



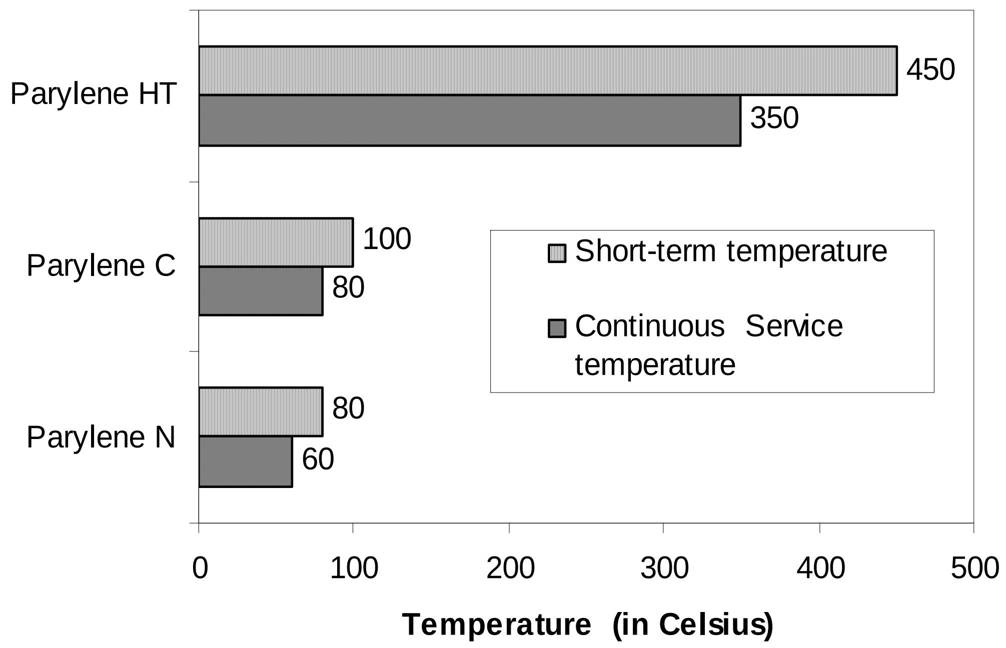
# Chemical Resistance of Parylene HT

## Corrosive chemicals

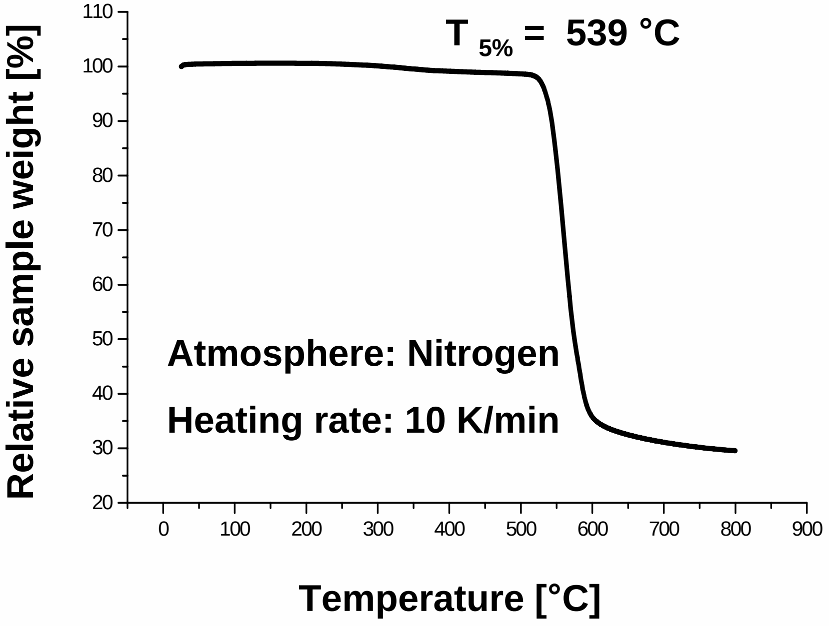
| | **Parylene HT Swelling %** | **Parylene HT annealed Swelling %** |
|---|---|---|
| 10% Nitric Acid, RT | 0.0 | 1.2 |
| 10% Nitric Acid, 75$^{o}$C | 0.0 | 1.2 |
| 70% Nitric Acid, RT | 0.0 | 0.0 |
| 70% Nitric Acid, 75$^{o}$C | 0.0 | 0.6 |
| 10% Sulfuric Acid, RT | 0.0 | 0.0 |
| 10% Sulfuric Acid, 75$^{o}$C | 0.0 | 0.0 |
| 95-98% Sulfuric Acid, RT | 0.6 | 1.2 |
| 95-98% Sulfuric Acid, 75$^{o}$C | 0.0 | 0.0 |

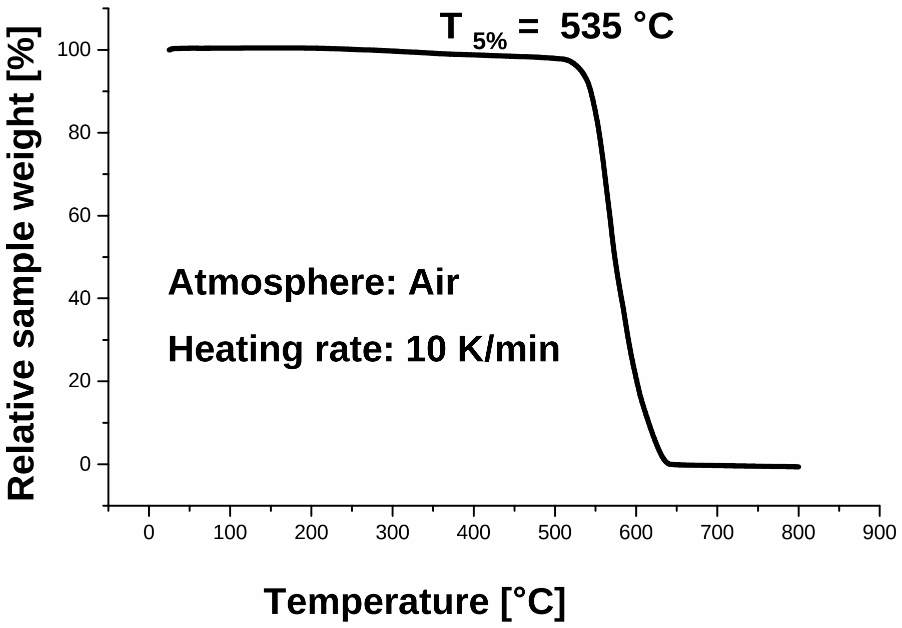
# Resistance to Oxidation

Thermal-oxidative stability of Parylenes

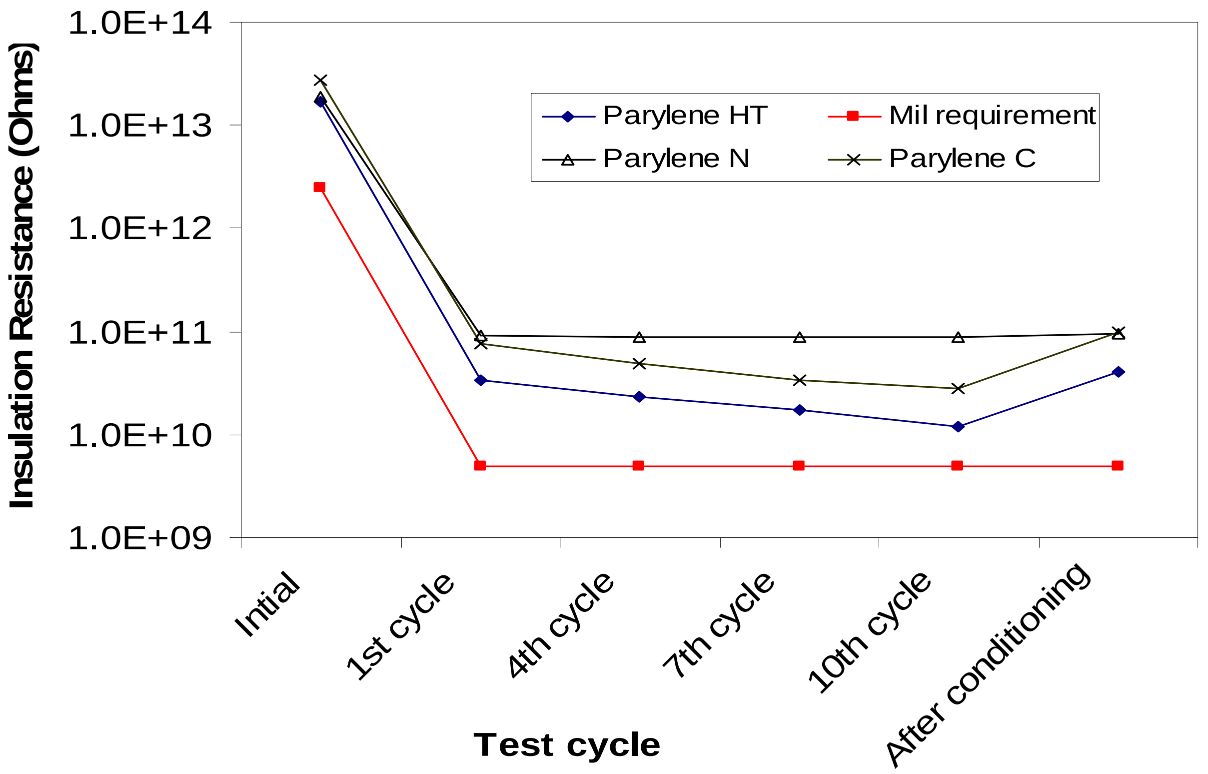


# TGA of Parylene HT



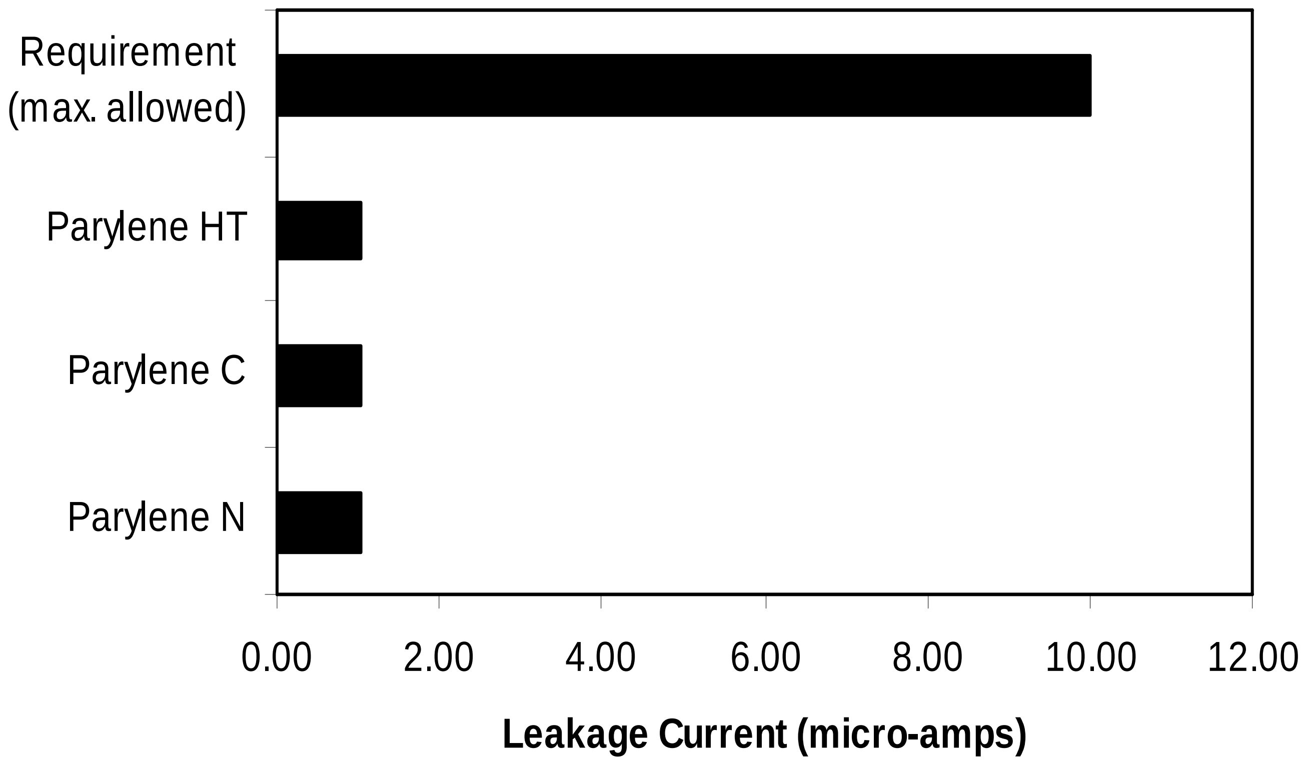


# Electrical Resistance



**Tested in accordance with Mil-STD 202, Method 302, test condition B (Temp: 65$^0$C, RH: 90-96%)**

# Electrical Resistance



**For moisture resistance-dielectric withstanding voltage test, several samples (Y-test patterns) coated with Parylene N, C and 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.**

# Fungus Resistance

| 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 |

**Rating:**

0 = none
1= Traces of growth (less than 10%0
2= Light growth (10-30%)
3= Medium growth (30-60%)
4= Heavy growth (60% to complete coverage)

**Test Method: ASTM G-21**

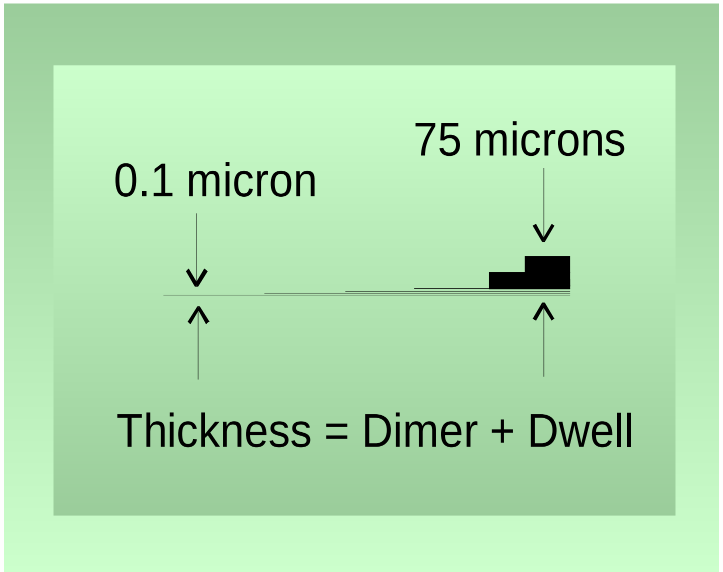
# Thermal-Humidity Aging

## (Parylene C and Parylene HT)

- Test conditions
  - Temp: 85$^0$C
  - RH: 95%
  - Control sample kept at Temp: 25$^0$C, RH: 50%)
- **Samples were examined at following intervals**
  - After 28th day (after 2 hr stabilization @ 25$^0$C/RH: 50%
  - After 56th day (after 2 hr stabilization @ 25$^0$C/RH: 50%
  - After 84th day (after 2 hr stabilization @ 25$^0$C/RH: 50%
  - After 120th day (after 7 days stabilization @ 25$^0$C/RH: 50%
- **Results** (visual examination compared to control sample)
  - No evidence of softening, chalking, blistering, cracking, loss of adhesion or liquifications. All markings and color underneath the coating were legible and distinguishable

# Coating Thickness

- **Thickness is Controllable**
- **Based on Dimer and Time in Chamber**



# Conclusion

- Due to RoHS directive, conformal coatings are getting more attention for suppressing the formation of tin whiskers.
- Parylene C and Parylene HT are suitable for suppressing the growth of tin whiskers growth.
  - Parylenes are truly conformal
  - Low stress coating
  - Chemically inert
  - High modulus and tensile strength
- Annealing of Parylenes can help enhance the performance
- Parylene HT is well suited under harsh conditions, high temp applications