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Evaluating the Effect of Conformal Coatings in Reducing the Rate of Conductive Anodic Filament Formation

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Abstract
Conductive anodic filament (CAF) formation is a failure mode associated with electronic circuits which operate at high voltage gradients and which are stored under high humidity conditions. Certain soldering fluxes and hot air solder leveling (HASL) fluids enhance this failure mechanism. Research was conducted to examine the effect of three different conformal coatings in reducing the incidence of CAF associated with a variety of water-soluble flux formulations. The fluxes chosen contained a water-soluble vehicle as 20 wt% in isopropanol. Some formulations contained 2wt% HCl, HBr, and/or monoethanolamine. The conformal coatings tested were acrylic (Humiseal 1B73), silicone (Humiseal 1C55) and parylene C. IPC B-24 test boards were coated with the flux, reflowed to create the thermal cycle, and then cleaned. Some boards were conformally coated and others were not. All test boards were exposed to SIR testing at 85°C, 85% RH and 100V bias for 28 days. This paper will report on the electrical results, as well as the number of CAF observed with and without conformal coating. It will also discuss visual observations of dendrites on boards with/without conformal coating.

Background
In the late 1970s a failure mode of printed wiring boards was observed involving the formation of a filament growing from the anode along the epoxy/glass interface of FR-4 substrate materials[1]. These growths referred to as conductive anodic filaments (CAF), represent a failure mode characterized by a catastrophic loss of insulation resistance between conductors held at a potential difference[2]. Failure occurs when the filament has grown to reach the cathode, resulting in a 'short'.

The current model of CAF process consists of two steps:[2]
1) The degradation of the epoxy/glass bond
2) An electrochemical reaction

The degradation of the epoxy/glass bond provides a path along which the products of the electrochemical reaction may be deposited. The epoxy/glass bond may be degraded due to poor glass treatment, the hydrolysis of the silane glass finish, or due to the mechanical release of stress.[2] The physical separation at the glass/epoxy interface is indicated by an 'articulation' or visual enhancement of the glass fibers around the anode[2].

Once there is a separation at the epoxy/glass interface, water is adsorbed at the glass surface. The adsorption isotherm of E-glass shows that significant adsorption can be expected at relative humidity above 80 percent.[1]

The adsorbed water becomes the electrolyte in an electrochemical cell. The electrodes are the copper conductors and the driving potential for the electrochemistry is the operating voltage of the circuit[1]. The following electrochemical reactions are possible.[3]

At the anode:

$$Cu \longrightarrow Cu^{n+} + ne^-$$

$$H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^-$$

At the cathode:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

$$Cu^{n+} + ne^- \longrightarrow Cu$$

In the presence of pure water which is neutral (pH = 7), the Pourbaix diagram for copper shows that there will be no corrosion of the copper anode due to the formation of a passivating layer of oxide or hydroxide on the surface of the copper. Over time however, the electrolysis of water creates a pH gradient between the anode and the cathode, since hydrogen ions are produced at the anode and hydroxide ions are produced at the cathode. As the pH at the anode reduces, the corrosion products of copper become soluble and migrate in solution until they reach a neutral region where they become insoluble and deposit on the interface[1]. Initial growth of the filament seems to be random but as time proceeds, the filament grows preferentially towards the cathode.[2] The filament will continue to grow as long as a pH gradient exists along the interface. Augis *et al*[4] reported that this filament contained copper with chlorine or sulfur both of which anions are contaminants associated with the board manufacturing process. Others[5, 6] have observed only chloride- or bromide-containing copper filaments.

In 1997 Jachim[7] implicated polyglycol-containing fluxes with the enhancement of CAF. Based on the earlier works of Zado[8,9] and Brous,[10,11] it is thought that polyglycols diffuse into the epoxy-glass board material during the soldering process when the board is above its glass transition temperature. Due to their hygroscopic nature these polyglycols promote absorption of moisture into the epoxy-glass board material. Lando *et al*[12] suggested that moisture caused hydrolysis at the epoxy/glass interface. A capillary of moisture at this interface could become available for the electrochemical reactions described above when a bias voltage is applied.

Conformal coatings are polymeric films used to protect assembled printed wiring boards (PWBs) and their components from the detrimental effects of humidity and moisture, corrosive chemicals, fungus and mildew, salt sprays, dust, and other contaminants. The conformal coating is applied over the PWB and its components in the last step of the assembling process. These coatings should also enhance the assembly's mechanical integrity, offer abrasion resistance, prevent thermal shock, protect against mechanical shock and vibration, and also augment the dielectric properties of the PWB. Conformal coatings are only required for circuit assemblies that will be exposed to certain hazardous environments and contaminants during their service life. As a consequence most PWBs do not require conformal coatings because their in-use environments are relatively benign. For an increasing number of applications however, conformal coatings play a critical role in the long-term reliable functioning of electronic systems.

Research was conducted to examine the effect of three different conformal coatings in reducing the incidence of CAF associated with a variety of water-soluble flux formulations. The fluxes chosen (Table 1) contained a water-soluble vehicle as 20 wt% in isopropanol. Some formulations contained 2wt% HCl, HBr, and/or monoethanolamine. The conformal coatings tested were acrylic (Humiseal 1B73), silicone (Humiseal 1C55) and Parylene C. IPC B-24 test boards were coated with the flux, reflowed to create the thermal cycle, and then cleaned. Some boards were conformally coated and others were not. All test boards were exposed to SIR testing at 85°C, 85% RH and 100V bias for 28 days. This paper will report on the electrical results, as well as the number of CAF observed with and without conformal coating. It will also discuss visual observations of dendrites on boards with/without conformal coating.

Experimental Procedure

Standard IPC-B-24 test coupons (Figure 1) were labeled and pre-cleaned using the Zero Ion System. Flux was applied to each comb pattern by pipette that deposited 400µl. The fluxes used are listed in the table below.

Table 1 – Flux Formulations Used in this Study

FLUX	COMPOSITION
PG1-2	20.0% Polyethylene glycol 80.0% IPA
PG3-3	20.0% Poly (ethylene/propylene) glycol, avg., MW 1800 5.5% HCl (37.4%) 74.5% IPA
PG6-6	20.0% Octyl phenol ethoxylate, 9-10 EO moles 9.40% HBr (48%) 3.44% MEA 67.16% IPA
PG7-3	20.0% Modified linear aliphatic polyether 5.5% HCl (37.4%) 74.5% IPA
PG7-5	20.0% Modified linear aliphatic polyether 5.5% HCl (37.4%) 3.44% MEA 71.06% IPA
PG7-6	20.0% Modified linear aliphatic polyether 9.40% HBr (48%) 3.44% MEA 67.16% IPA

After being processed with flux the boards were then placed in a JEM 310 batch convection reflow oven, individually, and heated using a predetermined temperature profile with a maximum board temperature of around 200°C. After reflow the boards were placed on racks and allowed to cool to room temperature. Upon cooling the boards were cleaned for five minutes at a temperature of 61°C in de-ionized water using a Branson 5210 cleaning system in ultrasonic mode.

After cleaning the boards were stored in contamination free Kapak bags until they were conformally coated. The acrylic and silicone coatings were spray coated onto the test coupons, while the parylene C coating was applied via a vapor deposition process. Conformal coatings were also applied to six control boards (2 boards per conformal coating) which were not processed with flux. The boards were then placed in a Thermotron environmental chamber and electrically connected to the test system. Over a period of hours the temperature and humidity were ramped up to the test conditions of 85°C / 85 % RH in order to prevent localized condensation of moisture on the surface of the test boards. The oven was allowed to stabilize at these conditions overnight, and then a computer program was executed to take the SIR measurements on all the boards at 24-hour intervals, over a 28-day period. The SIR testing was done using a bias voltage and a test voltage both of 100 V and the same polarity. At the end of 28 days, the temperature and humidity in the chamber were ramped down, the chamber opened, the boards removed and placed into contamination free bags for storage.

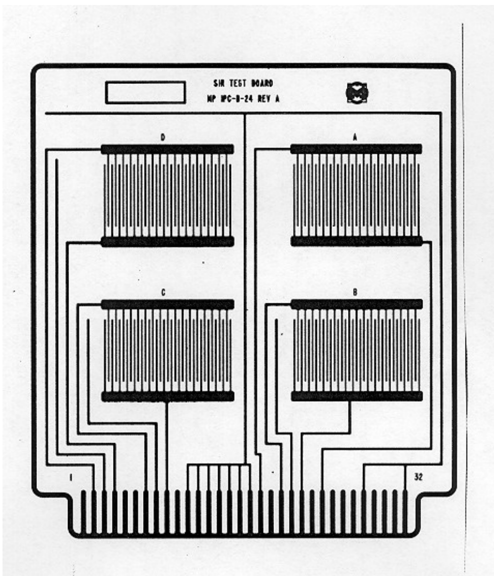

Figure 1 - IPC-B-24 Test Coupon

Analysis

SIR data were plotted for each comb pattern on each test coupon and a geometric mean value for each flux at each time period was determined.

An optical microscope (Olympus SZ-40) was used to examine the comb patterns on the boards. Both the transmitted and reflected illumination capabilities of the microscope were used in making these observations. Transmitted illumination (back-lighting) makes the detection of CAF and dendrites easier, while reflected illumination was used to observe any surface residues on the board. A camera connected to the microscope was used to capture the still images of the board surfaces showing the different residues present.

Results

SIR Data

SIR values for all of the conformally coated coupons exceeded 100 Mohms by the first day of testing, except for those coupons that had been treated with the PEG flux PG1-2. The SIR results for conformally coated PG1-2 coupons varied:

- Acrylic coated coupons gave final SIR readings above 100 Mohms
- Silicone coated coupons only reached values above 10 Mohms
- Parylene C coated coupons gave SIR readings below 1 Mohms

Due to variations in the SIR data for the coated PG1-2 coupons, the data for these coupons were not plotted.

The SIR data for all the other coated coupons are presented in Figures 2-4 based on the type of conformal coating used. In all three cases the graphs show that the control coupons which were not processed with flux, gave the highest SIR values. The graphs also show that of the coupons processed with flux, those processed with PG3-3 and PG7-5 gave the highest and lowest SIR values respectively.

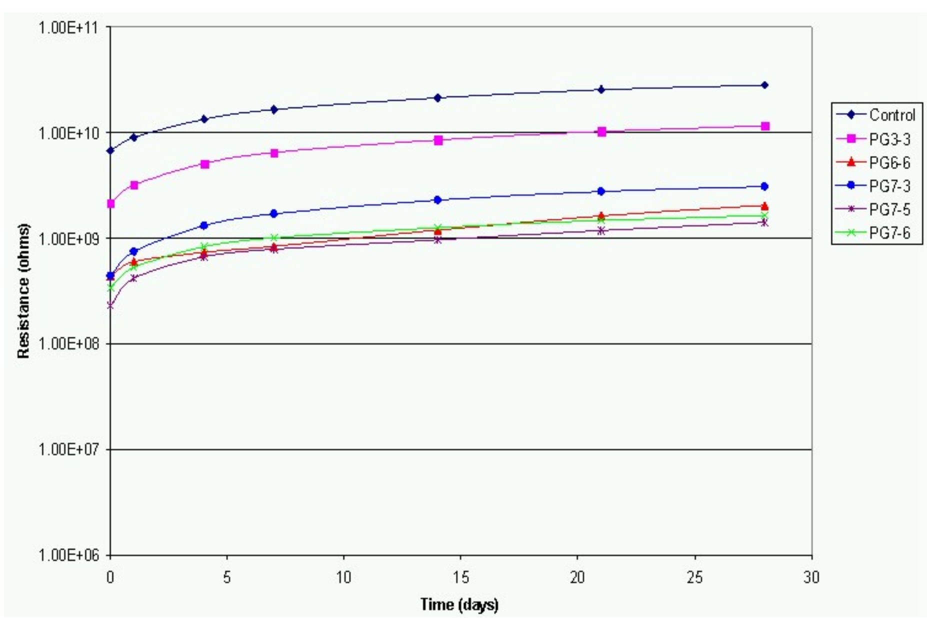

Figure 2 - SIR data for Coupons Coated with Acrylic

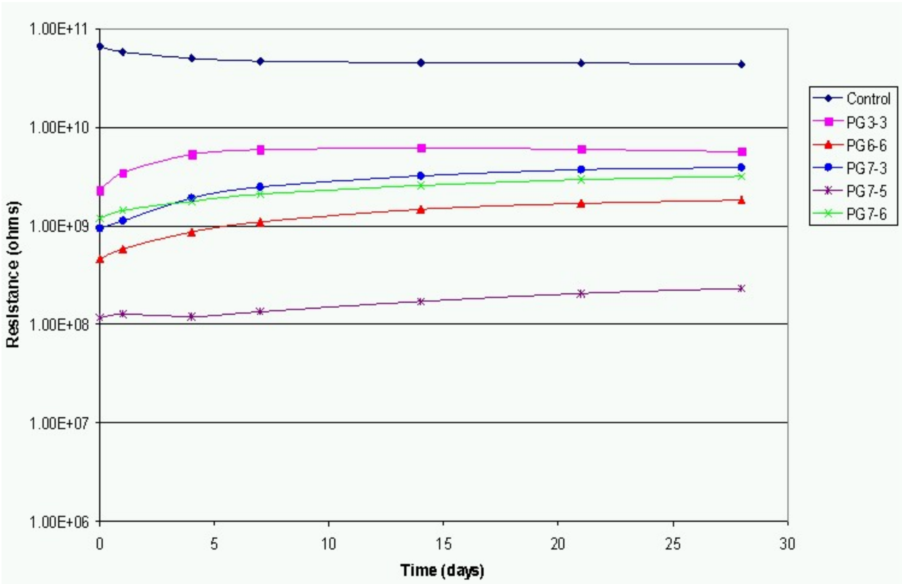

Figure 3 - SIR Data for Coupons Coated with Silicone

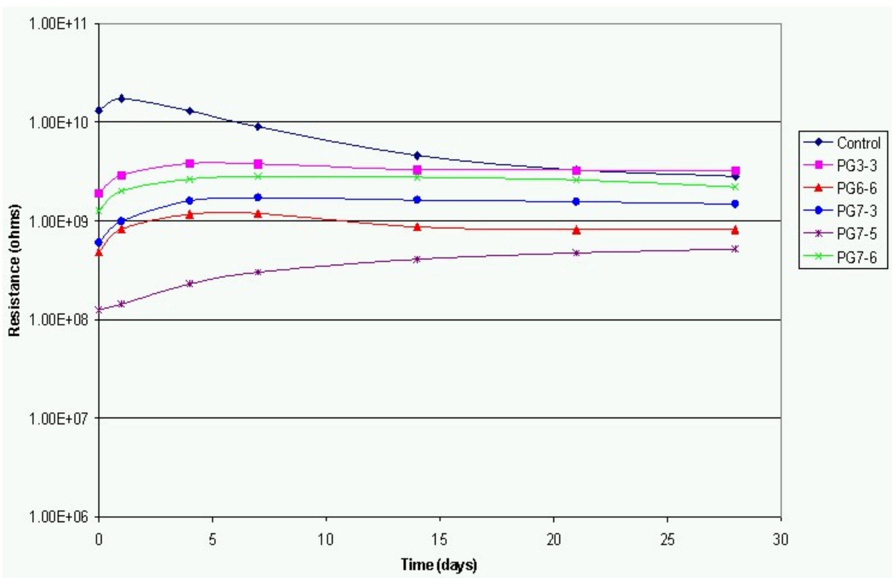

Figure 4 - SIR Data For Coupons Coated with Parylene C

Visual Observations

Dendrites were observed on the surface of the acrylic coated PG1-2 coupons and the silicone coated PG1-2 and PG7-5 coupons (Figure 5).

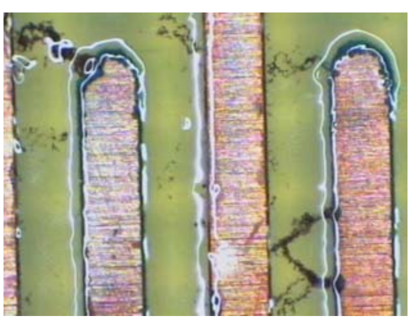

Figure 5 - Dendrites on the Surface of the Acrylic Coated PG1-2 Coupon

Surface residues were mainly observed on coupons treated with flux formulations containing monoethanolamine (MEA). Black and green surface residues were common to all the conformally coated coupons processed with PG7-5.

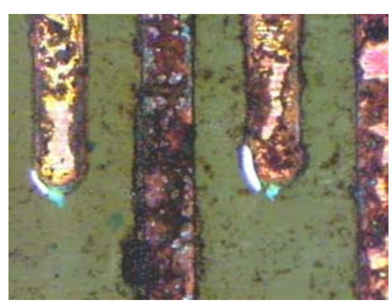

Figure 6 - Surface Residues on Silicone Coated Coupons Treated with PG7-5

During the visual examination, any defects in the conformal coating were also noted. Bubbles (Figure 7) were observed on all silicone coated fluxed coupons. Blister spots were also observed in the coatings of acrylic coated PG1-2 and PG7-6, as well as parylene C coated PG1-2 and PG7-3 (Figure 8).

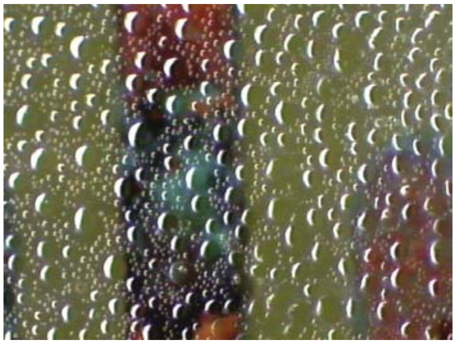

Figure 7 - Bubbles in Silicone Coating on Coupon Treated with PG7-5

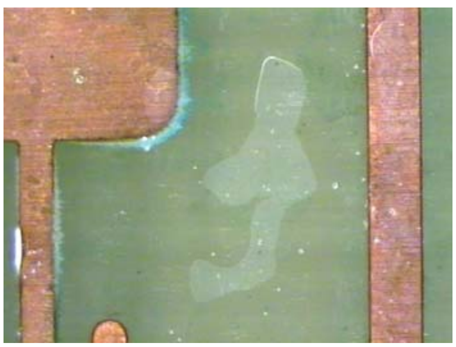

Figure 8 - Blister Spot at the Substrate/Coating Interface of an Acrylic Coated PG7-6 Coupon

A series of “white marks” in a crosshatch pattern (Figure 9) which seems to follow the edges of the glass fibers embedded in the epoxy were observed on acrylic and silicone coated coupons. These “marks” are thought to be the visual effect caused by de-bonding at the epoxy/glass fiber interface.

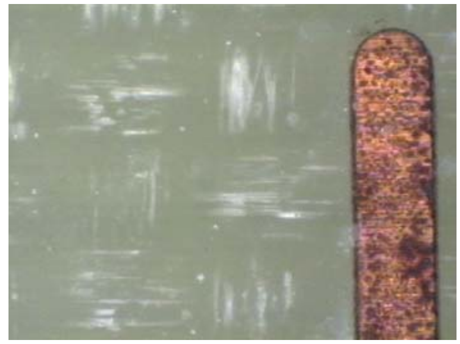

Figure 9 - Measling on Silicone Coated Coupons Treated with Flux PG1-2

Multiple cases of CAF were also observed on some of the coated coupons. The image below (Figure 10) shows a typical case of CAF as observed using reflected illumination. A complete listing of CAF results is presented in the Table 2.

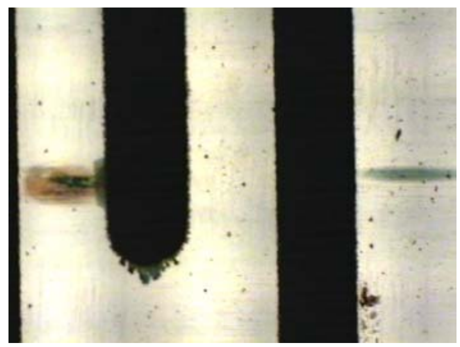

Figure 10 - Typical Case of CAF as Seen Using Transmitted Illumination.

Table 2 - CAF Results for Coated and Uncoated Coupons - The results for the Uncoated Coupons were Obtained During an Earlier Study - The CAF Results Listed are the Total Number of CAF Observed on all Coupons Processed with a Particular Flux

Flux	Uncoated	Acrylic Coating	Silicone Coating	Parylene C Coating
PG1-2 (PEG/IPA)	Yes (~ 90)	None Observed	None Observed	None Observed
PG3-3 (PEPG/HCl/IPA)	Yes (~ 21)	None Observed	Yes (~ 4)	None Observed
PG6-6 (OPE/HBr/MEA/IPA)	Yes (~ 62)	Yes (~ 40)	Yes (~ 16)	None Observed
PG7-3 (LAP/HCl/IPA)	Yes (~15)	None Observed	Yes (~ 20)	None Observed
PG7-5 (LAP/HCl/MEA/IPA)	Yes (~ 31)	Yes (~ 25)	Yes (~ 10)	None Observed
PG7-6 (LAP/HBr/MEA/IPA)	Yes (~ 27)	Yes (~ 14)	Yes (~ 9)	None Observed

The table shows that acrylic coatings were effective in preventing CAF formation on the PG1-2, PG3-3, and PG7-3 coupons but only reducing the rate of CAF formation on the PG6-6, PG7-5, and PG7-6 coupons. Silicone coatings on the other hand were only effective in preventing CAF formation on the PG1-2 coupon but reduced the rate of CAF formation on the PG3-3, PG6-6, PG7-5, and PG7-6 coupons. The rate of CAF formation increased on the silicone coated PG7-3 coupon. The Parylene C coating was the only coating that was effective in preventing CAF formation, regardless of the flux used to process the test coupon.

Discussion

Brous[10] had shown that polyglycols and their derivatives, which are absorbed by the substrate material during the soldering or reflow process, slowly diffuse out of the substrate when exposed to SIR testing conditions. He found that as a result of this diffusion, the SIR readings for coupons processed with these polyglycols increased with time. For the most part the SIR readings obtained during this study also increased with time suggesting that the polyglycols were diffusing out of the substrate materials when exposed to the SIR testing conditions (85 ^{o}C/85 % RH). The fact that the test coupons were coated with a conformal coating means that the polyglycol/polyglycol derivative would also have to diffuse up through the coating materials. The diffusion rates for polyglycols through Parylene C, due to its compact crystalline nature, is much lower than for polglycols through acrylic and silicone. A slower rate of diffusion of the polyglycols through the parylene C coatings would explain why most of the SIR readings for parylene C coated coupons (which were processed with a flux) were lower than the SIR readings obtained for acrylic and silicone coated coupons.

The dendrites observed on the surface of the acrylic coated PG1-2 coupons and the silicone coated PG1-2 and PG7-5 coupons imply that moisture was present on localized regions of the surface of these coupons. At least several monolayers of water on the surface of the substrate are required for dendrite growth to occur[13]. The water vapor must first diffuse through the conformal coatings and condense on the surface of the substrate in localized areas between the conductor lines, forming conductive pathways. Hygroscopic substances such as polyglycols or polyglycol derivatives, if present on the surface of these coupons will enhance moisture adsorption onto the surface[9,10].

Analysis of the CAF results for the coated and uncoated coupons presented in Table 2, show that the parylene C coatings were always effective in preventing CAF formation while the acrylic and silicone coatings were only effective in preventing CAF formation in particular instances. There are a couple of factors that could have contributed to these differences. First, both sides of the parylene C test coupons were coated, while only the functional side of the acrylic and silicone test coupons were coated. Since both sides of the coupons were protected by the parylene C then it is likely that the substrate absorbed less moisture. Second, it is likely that the elevated curing temperatures used to cure the silicone and acrylic coatings (105 and 170 ^{o}C), produced mechanical stresses at the epoxy/glass interface of the substrate due to CTE differences between the epoxy and the glass. Since the parylene C coated coupons remain at room temperature throughout the application of the coating, no such stresses were induced at the epoxy/glass interface of these coupons. The stresses induced at the epoxy/glass interface of the acrylic and silicone coated test coupons makes them more susceptible to CAF formation.

The fact that the conformal coatings were essentially effective in reducing the rate of CAF formation on the coated coupons was not surprising. Conformal coatings are designed to reduce the rate at which moisture is absorbed by the substrate material of coated test coupons. The coatings provided a barrier through which moisture must first diffuse before reaching the surface of the substrate. The added diffusion step reduces the rate of moisture absorption by the substrate material.

The “white marks” (Figure 9) observed in the substrate of the silicone and acrylic coated coupons (not the Parylene C coated coupons) seem to follow the edges of the glass fibers embedded in the epoxy. According to Lathi et al.[2], the first indication of a physical separation at the epoxy/glass interface is an “articulation” or visual enhancement of the glass reinforcement around the anode. It should be noted however, that the “white marks” observed on these test coupons were not necessarily restricted to areas around the anode lines but were concentrated in areas of the coupons that had been exposed to flux. From all appearances, there are no conductive anodic filaments growing along these epoxy/glass interfaces, there is only a separation at the interface. A possible explanation is that the aging that occurred during the 28-day SIR test at 85^{o}C caused a further curing of the coating, which placed stresses on the underlying epoxy/glass substrate. It may also involve a chemical interaction between the coating and the flux residues beneath. The lack of the “white marks” on Parylene C coated coupons implies that polymerization of the polymer was complete during the initial cure process .

Bubbles (Figure 7) were not observed in the silicone coatings on control coupons but only on the silicone coating on processed coupons. These bubbles are formed by the diffusion of the polyglycol/flux vehicle out of the substrate material and through the coating. Silicone is very permeable to organic molecules. Due to the thickness of the silicone coating, some of the polyglycol/vehicle did not have time to completely diffuse out of the substrate and through the coating during the 28 day test period. Thus, it was trapped as bubbles near the surface.

Summary

This work studies 3 conformal coatings (silicone, acrylic and Parylene C) and evaluates their effect in reducing conductive anodic filament (CAF). It reports electrical results and visual observations that include the number of CAF cases observed with and without conformal coating. Parylene C was the only conformal coating that proved to be effective in preventing CAF formation under the test conditions utilized. The silicone and acrylic coatings did not prevent the formation of CAF in all cases but did reduce CAF formation relative to uncoated coupons.

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