

Conformal Coating Prevention, Temperature Dependence and Physical Analysis of Resistor Silver Sulfide Corrosion

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ABSTRACT

Thick film resistors are used in a variety of electronics applications. Silver in a conventional surface mount, thick film resistor is prone to corrosion, especially when sulfur-bearing gases are present in the environment. The growth of silver sulfide resulting from silver corrosion can cause an increase in resistance and eventually an electrical open in the resistor. Such sulfur-bearing gases are common atmospheric pollutants in certain industrial locations, agricultural regions, and growth market localities that rely heavily on coal-burning power plants. The best method to increase the robustness of resistors in these high sulfur environments is to employ Anti-Sulfur Resistors (ASRs) with a corrosion resistant construction. Occasionally, individual resistor part numbers have limited availability in ASR construction.

For the situations where ASR versions are not available, conformal coatings may be used to prevent, or at least delay, the growth of silver sulfide. Several sizes of standard thick film resistors with a variety of conformal coatings to mitigate silver sulfide corrosion were exposed to Flowers of Sulfur (FoS) testing at three test temperatures, 60°C, 80°C and 105°C, to determine an acceleration factor for the resulting silver corrosion. Two epoxy coatings were effective at protecting silver containing resistors from sulfur corrosion. Four other coatings were essentially equivalent to no coating, and one coating accelerated sulfur corrosion. This paper covers all the long-term test results as a follow-up to an earlier publication reporting interim results and preliminary conclusions [1].

Time-to-failure data in a few of the test cells from extended FoS testing at 60°C, when combined with the data generated earlier in the study at 80°C and 105°C, provided input to Arrhenius analysis enabling the calculation of the activation energy. The activation energy and other parameters can be used to predict the failure rate at temperatures of interest between 60°C and 105°C.

Physical analyses were completed to investigate possible differences in the failure mode at the various FoS test temperatures. In addition, conformal coating coverage and structural differences in the resistor body sizes were

evaluated to determine if those factors could have impacted the likelihood of corrosion and/or failure.

Key words: corrosion, flowers of sulfur, resistor reliability, conformal coating

INTRODUCTION and BACKGROUND

Information Technology (IT) hardware deployed around the world may be exposed to higher concentrations of corrosive sulfur contaminants such as sulfur dioxide (SO₂), hydrogen sulfide (H₂S), and carbonyl sulfide (COS) in some geographic areas. Natural sources include the ocean and volcanoes. Anthropogenic sources include coal fired power plants, refuse incineration, agricultural centers and manufacturing processes for petroleum products, rubber and synthetic fibers. When the ambient outside air is laden with contaminants, these same contaminants, even if attenuated with conditioning, will still be present in indoor air. Also, there are always paths for the outside air to enter conditioned buildings. Some IT equipment, such as for outdoor telecommunication or manufacturing floor applications, can be housed in unconditioned buildings.

Electronic assemblies and components, especially silver containing resistors, can fail when the IT equipment is installed in an environment conducive to sulfur corrosion. Sulfur bearing gases can attack any exposed silver on the electronic assembly and form silver sulfide. As the nonconductive silver sulfide forms, it can eventually lead to an electrical open [2]. As silver sulfide forms and the amount increases, mechanical stresses in the resistor termination layers also increase, which in worse case situations can cause cracks or breaks in the resistor termination layers. Additionally, resistors continue to decrease in size, and as some IT equipment environments are less controlled, i.e., located in areas with higher levels of gaseous sulfur, the chances of hardware failure from sulfur corrosion increase.

Suppliers have developed resistors that are corrosion resistant. Some anti-sulfur resistors (ASRs) employ an improved barrier coating to limit the migration of sulfur to the silver terminations. Other ASRs replace the silver electrode with a silver alloy, which improves the resistor

tolerance for sulfur. A third approach replaces silver with a different metal, such as gold. Removing the silver removes the possibility of silver sulfide corrosion but can significantly increase cost.

While ASRs may sometimes be a feasible option, there are situations when only standard resistors are available or cost effective. In these cases, applying a conformal coating to the completed printed circuit board (PCB) or card may be a more cost-effective option to mitigate silver sulfide corrosion.

Silver Corrosion Studies

The focus areas of this paper are the results of extended lower temperature testing, failure projection modeling based on multiple temperature data, and physical analysis of a previously published conformal coating study [1]. Highlights from the previous study [1] are also reviewed below.

Test Procedure - Flowers of Sulfur Testing

Several accelerated test approaches have been explored within the industry [3]. Current consensus is that the Flowers of Sulfur (FoS) test provides the most consistent and useful results and is the most practical to implement. The currently adopted FoS test for resistor corrosion robustness is described in EIA-977 [4], a modified test derived from ASTM B809-95 [5].

Test Condition B (105°C) of the FoS test procedure [4] was used in a past study [6] and for the best comparison between data sets was used again for this study. The FoS test used an airtight jar containing 50g of sulfur powder. Three different temperatures were used: 60°C, 80°C and 105°C. Test Condition A of the FoS test procedure [4] specifies 60°C. This 60°C test condition corresponds approximately to the temperature found inside computer server equipment, where printed circuit boards are found. However, because of the length of time required for failures to occur at 60°C, additional cells with higher temperatures were also used for accelerated testing. Previous conformal coating studies used 105°C and 80°C [3,7], and so were chosen again for this study. Ideally, accelerated testing at several temperatures can be used to determine an acceleration factor and predictive algorithm for the reliability performance at field conditions. The previous work showed an acceleration in failure from 80°C to 105°C that was similar among the suppliers. To improve confidence in developing an acceleration model, a third test temperature is added for this study.

CONFORMAL COATING CORROSION STUDY

As previously stated, in situations where ASRs are not appropriate due to cost, limited availability, or use of off the shelf solutions and products, applying a conformal coating after the surface mount soldering of the resistors to the printed circuit board is an option for corrosion mitigation, and may be more cost effective.

Past Work

The selection of an appropriate conformal coating to protect the resistors is essential in preventing corrosion. There are

many chemical families used for conformal coatings and many choices within a family. Work published by IBM researchers [8] concluded that epoxy-based encapsulants are a good choice to protect silver surfaces in a gaseous sulfur environment.

Subsequent studies confirm the findings of [8] that certain conformal coatings, such as epoxy, can prevent silver sulfide from forming [3], while the use of other conformal coatings, for example those containing silicone, can accelerate silver sulfide corrosion [6,9]. Selecting an effective conformal coating for use in the field requires verification through accelerated reliability testing.

The choice of a specific conformal coating is an important one. For this application, the coating needs to not only protect the components from the chance of corrosion, but also needs to be highly manufacturable; that is, the coating must be relatively easy to apply and cure within a standard IT electronics assembly manufacturing facility.

In 2016, a study [6] was conducted to review several sets of conformal coatings. Three main conclusions were drawn from these results: (1) polyurethanes provided some protection, but did not perform as well as the epoxy, (2) the nanocoating results were inconclusive and (3) no particular coating stood out as offering a high degree of corrosion protection with the added benefit of being highly manufacturable. Desirable elements of manufacturability include solventless, no mixing, and fast dry/cure at room temperature.

Previous Study Goals

The goal of the 2018 study [1] was to continue the review of coating materials, build on the learning from previous studies, and identify a conformal coating that would provide the best protection against sulfur corrosion, while also providing improved manufacturability.

Printed Circuit Board Test Coupon

A new test card with three distinct and identical test coupons was designed for the 2018 study. The test coupon is shown in Figure 1. A single coupon measures ~1-inch x ~3-inches and contains locations for resistor types 0201, 0402, 0603, 0805, 1206, and 2512, as listed in Table 1. The locations of the resistors on the coupon are noted by test location in Table 1 and Figure 1. Figure 2 shows a photograph of a single card with assembled resistors. Each coupon site contains four test locations per resistor size. Two coupons of each type were tested, so eight total test locations could fail for a given coating.

Conformal Coatings

A primary function of conformal coatings is to protect electronic components and assemblies from exposure to liquids, chemicals, and moisture. Additional benefits have been realized in protecting circuits and components from mechanical damage, dust, and contamination. It follows that with these added expectations for conformal coatings, that

formulations will vary. Also, a formulation that might be very good at liquid or chemical exposure protection might not be adequate in protecting against gaseous contaminants. In addition, there exists the possibility that a conformal coating that provides environmental protection could be detrimental to the thermal mechanical reliability of component solder joints [10]. Before applying a conformal coating in a field application, all aspects of the reliability of the completed assembly should be assessed.

Table 1. Resistor Sizes on Test Coupon

Resistor Type	Quantity of test locations	Resistor / Test Location by letter
0201	4	A, B, W, X
0402	4	C, D, U, V
0603	4	E, F, S, T
0805	4	G, H, Q, R
1206	4	I, J, O, P
2512	4	K, L, M, N

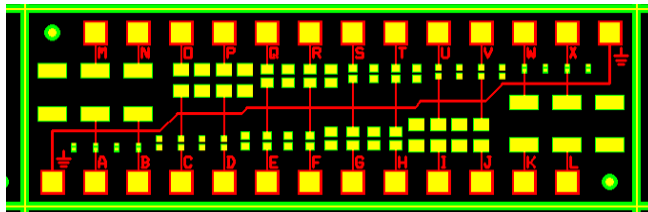


Figure 1. Test coupon with resistor test locations by letter

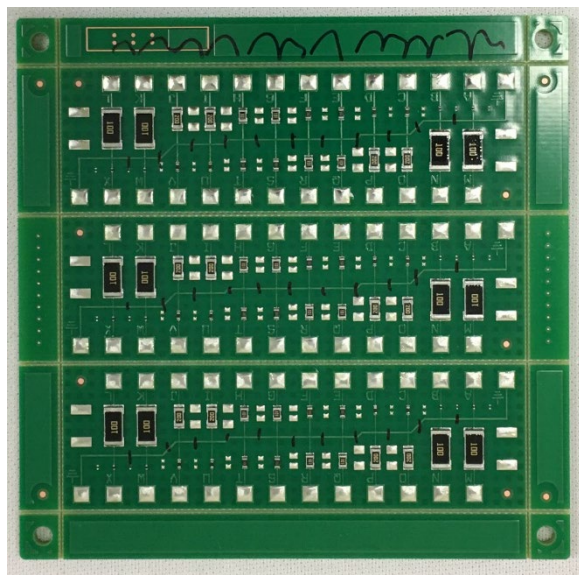


Figure 2. Test card photo with three fully assembled test coupons

Traditionally, conformal coatings have been formulated to be soft to facilitate removal for rework requirements. Consequently, many conformal coatings have glass transition temperatures (T_g) that are near or less than ambient temperature, for example, in the range of -45°C to 50°C . However, above T_g , free volume in polymers increases, as does chain segmental mobility [11]. Therefore, diffusion through the coating thickness is faster above the T_g compared

to below the T_g . EIA-977 [4], specifies two test temperatures, 60°C and 105°C , both of which are above the typical range for the T_g of conformal coatings. One objective in this study was to include a coating material that had a T_g above at least one of the test temperatures: 60°C , 80°C and 105°C .

Coating Materials

Six coatings were chosen for this study (Table 2) based on physical properties (such as T_g), novel chemistries and ease of processing [1]. Along with these six coatings, the top performer from the previous conformal coating study [6], EP2016, a two-part epoxy was used again, offering a link between the two studies. Additionally, a control card with no conformal coating was tested at the same time.

Table 2. Conformal Coatings under Test

Coating	Description	T_g $^{\circ}\text{C}$
EP2016	2 part epoxy + solvent thinning (from 2016 study)	19
RUB	Synthetic rubber + solvent thinning	-50
ACRY	Fluoroacrylate in hydrofluoroether solvent	53
EP1	1 part epoxy, UV cured, no solvent	25
EP2	1 part epoxy, UV cured, no solvent	86
RF	RF precursor plasma gasses in vacuum	-
POLY	Hydrophobic polymer in xylene	-45
Control	No coating	-

Coating Application Methods

The application of the coating to the card varied by the type of coating and is identified by coating type in Table 3. In some cases, the coatings were applied by the coating material manufacturer, while in other cases the coatings were applied by a local third party specializing in coating applications. One coating, ACRY, was applied at the laboratory by the test team, using the supplier recommended immersion dipping process.

Table 3. Conformal Coating Application Method

Coating	Application Method
EP2016	Spray by manufacturer
RUB	Spray by manufacturer
ACRY	Dip at Universal Instruments
EP1	Spray by 3 rd party
EP2	Spray by 3 rd party
RF	Vacuum deposition by manufacturer
POLY	Spray by 3 rd party

Test Process

Two coupons of each coating were placed in the oven at a given temperature to complete the FoS test procedure. The frequency of reading measurements and test duration varied by test temperature:

- 105°C : One or two readings per week for 140 days.
- 80°C : One or two readings per week for 211 days.

- 60°C: Approximately one reading every two weeks for 447 days.

RESULTS

Two coatings performed exceptionally well across all temperatures and all resistors: coating EP2016 (two-part epoxy repeated from the 2016 study) exhibited no resistor failures at any temperature, and EP2 (UV cured 1-part epoxy) exhibited only one resistor failure at 119 days for the 105°C test condition.

Several other coatings performed about equivalent to the uncoated control; only EP2016 and EP2 provided significant protection against corrosion for all resistor sizes. Interestingly, the coating POLY performed worse than the uncoated control coupons at 60°C, 80°C and 105°C.

The expectation was for smaller resistors to fail earlier than larger resistors based on shorter migration distances and feature sizes in the smaller resistor sizes, so the prediction was for the 0201 to fail first, followed by 0402, 0603, and so on. This prediction was found to not be valid for the 0201 vs. the other sizes, but was generally valid for all other sizes.

First Failures

Based on the results of the past studies and related field performance, the authors considered a reasonable goal for all coated resistors to achieve at least 30 days without any failures for the 105°C test condition, similar to EIA-977 [4]. Resistor failure criterion for this study was identified as an increase in resistance of one ohm or more. Because measurements were taken several days apart, when a failure occurred the timing was known only to be between the previous readout and failed readout.

Figure 3 presents the results for the 105°C test, showing the number of days when first failure was measured electrically for every coating material (listed along the ordinate axis) and every resistor size (color coded as identified in the bar graph legend). Resistor sizes that did not fail have no bars. In the uncoated control card, 0201 and 0402 resistors both showed first fails just before the goal of 30 days, failing at the 25-day readout. The RF coating had first failure at 28 days for 0402 and 36 days for 0201. All other resistor sizes far exceeded the 30 day failure free target. The EP2016 and EP2 coatings were the top performers, far exceeding 30 days with no electrical failure. EP2 had only one 0402 failure at the 119-day readout. The RUB coating showed early first failures at readouts < 30 days for 0402 and 0603, with the other resistor sizes surviving beyond the 30 day readout. EP1 had first failure on the 0402 at < 21 days, with all other resistors being stable beyond 30 days. The POLY coating performed more poorly than the uncoated cards with first failure occurring at < 21 days for 0201 and < 14 days for the other resistor sizes, similar to a silicone coating [6]. The ACRY coating offered good protection except on the 0402 resistor which showed electrical failure at the 21-day readout. All other resistor sizes exceeded 30 days without failure.

Figure 4 presents the results for the 80°C test over 211 days. The rate of thermally activated processes with activation energies near 1 eV will double for every 10°C increase in temperature. This rule-of-thumb was applied to the 30-day survival target used at 105°C to estimate a survival target of 180 days at 80°C that is displayed in Figure 4. The 0402-resistor size was most sensitive to the FoS test conditions, typically showing first fail between the 60 and 78 day readouts for the uncoated control and coatings RF, RUB, EP1 and ACRY. The 0402 resistors coated with POLY showed failure at the 29-day readout. EP2016 and EP2 had no failures on the 0402s, nor any of the resistor sizes even after 211 days. All resistor sizes for POLY had failures. The control, RF, RUB and ACRY experienced failure across multiple resistor sizes at less than 180 days. Figure 4 suggests that coatings RF, RUB, EP1 and ACRY are no better than the uncoated control, while POLY appears to be worse than uncoated. As in the 105°C test, EP2016 and EP2 were the top performers and POLY was the poorest performer.

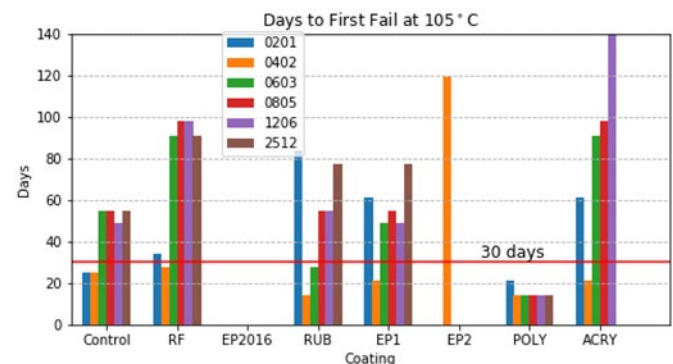


Figure 3. Days to first failure in FoS at 105°C. No bars indicate no failure.

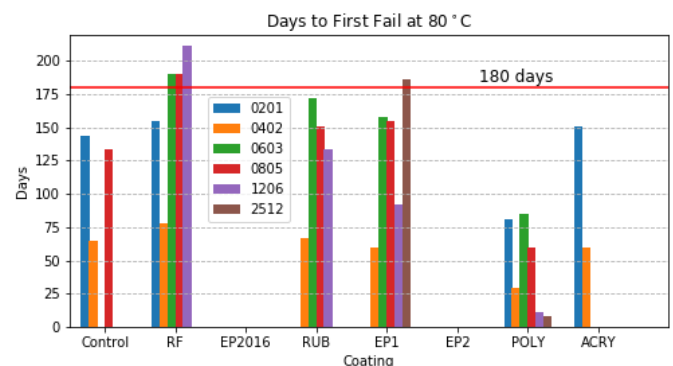


Figure 4. Days to first failure in FoS at 80°C. No bars indicate no failure.

Figure 5 shows the results for the 60°C test. As expected, fewer fails occurred during this long-term test over 447 days. The 0402-resistor size was most sensitive to failure, as previously observed during testing at 80°C and 105°C, where 0402 resistors failed fastest in the control, RF and POLY coatings. Again, the POLY coating had the poorest protection against corrosion.

Analysis of Resistor Failures

Figures 6 and 7 show grouped bar charts of the percent of resistors that failed at 30, 60, 90, 120, 140, 150 and 211 days. Each coating sample included a total of 48 resistors: four resistors per type, six types of resistors per coupon, with two coupons per coating type.

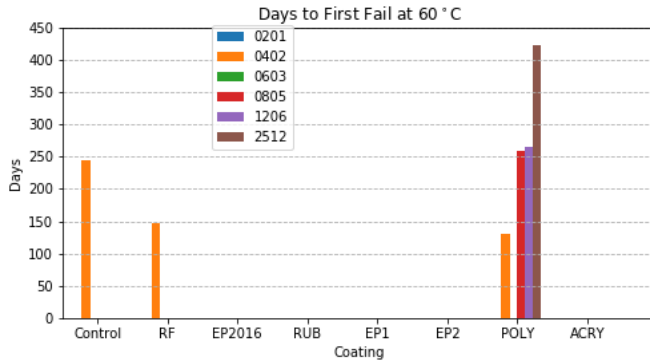


Figure 5. Days to first failure in FoS at 60°C. No bars indicate no failure.

After 140 days – 105°C

Figure 6 shows the total percent failure of all resistor sizes for every coating after 140 days at 105°C. Nearly all resistors have failed. However, not included in Figure 6 are EP2016 data which exhibited zero failures and EP2 data which exhibited one 0402 failure at the 119-day readout. EP2016 and EP2 are the clear best-in-class performers.

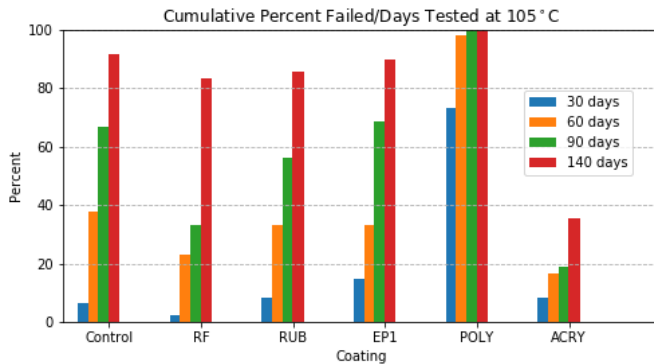


Figure 6. Percent of failures per number of days in FoS test at 105°C

Total Failures after 211 days – 80°C

Figure 7 shows the total percent failure of all resistor sizes for coatings after 211 days at 80°C. Only one coating, POLY, had failures at the 30-day readout. Cards coated with EP2016 and EP2 exhibited zero failures at 80°C through 211 days of test. The cumulative percent failure after 211 days (21-44%) is similar for the controls, RF, RUB, EP1 and ACRY indicating that there is essentially no corrosion protection provided by these coatings compared to no coating.

0402 Resistors

Figure 8 shows the number of fails by resistor type for 140 days of testing at 105°C. All the 0402 resistors failed for the coatings listed. EP2 had one 0402 resistor fail at 119 days of

test. Across all coating material test cells, the 0402 resistors performed poorer than all other sizes. Given shorter migration distances it would be expected for the smaller resistors to be more susceptible to corrosion failures, so it makes sense that the larger resistors performed better than the 0402 resistors. However, even 0201 resistors performed noticeably better than 0402. The 0201 resistors were a more recent manufacturing vintage. The differences and similarities in construction between the different resistor sizes are shown in the Physical Analysis section of this paper. Also, inquiries to the supplier regarding any differences in construction or manufacturing may provide additional clues to the relative performance.

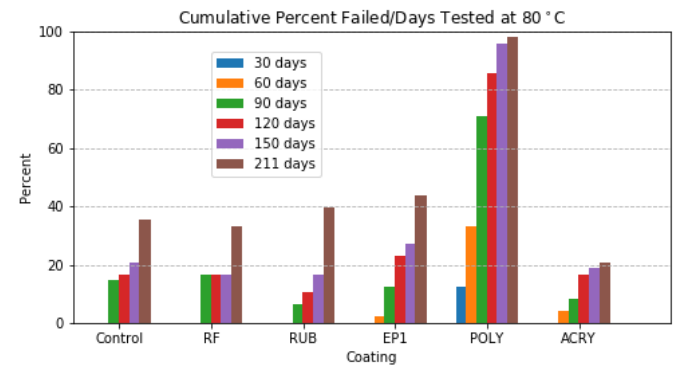


Figure 7. Percent of failures per numbers of days in FoS test at 80°C

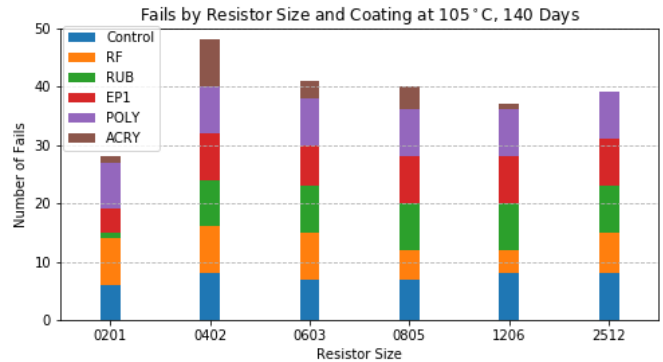


Figure 8. Total fails by resistor size and coating in FoS at 105°C after 140 days

The total number of fails broken down by resistor size is shown in Figure 9 for 211 days of testing at 80°C. Again, the 0402 is the most sensitive resistor in this study, with all the 0402 resistors failing during the 80°C test for the coatings listed. Its enhanced rate of failure is more pronounced at 80°C than previously observed at 105°C.

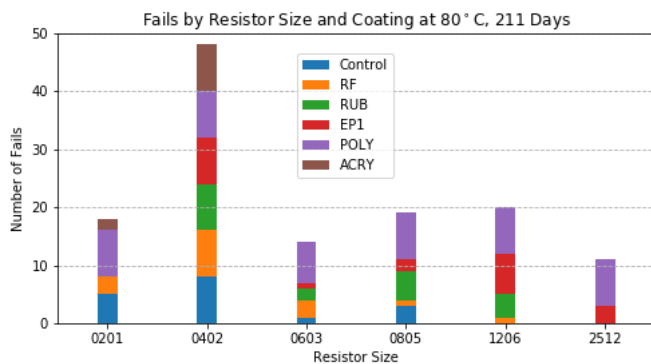


Figure 9. Total fails by resistor size and coating at 80°C after 211 days

Test Temperature Comparison: 105°C and 80°C

Figure 10 shows a lognormal analysis comparing the failure rate distributions of uncoated and coated resistors for all body sizes tested at 80°C and 105°C. The failure data for four coatings, RF, RUB, EP1 and ACRY, were pooled and survivors were right censored. The POLY coating was excluded since failure was accelerated compared to the no coating case. EP2016 had no failures and EP2 had only one, so these coatings were also excluded. At both 80°C and 105°C, there appears to be negligible difference between the failure distributions of the uncoated control and the four coatings that were pooled.

Electrical measurements were made over intervals of days and the exact time-to-failure is not known. Therefore, interval censoring was selected in doing this analysis with commercial reliability software. Maximum likelihood (ML) was used to estimate the two lognormal parameters: μ (location) and σ (scale.) The location parameter, μ , that appears in the table of statistics to the right of the plot in the column labeled “loc” is used as the exponent to the natural exponential, e^μ , to give the median days to failure. There is a small difference in median life between uncoated and the pooled coated resistors: 263 days versus 272 days, and 67 days versus 86 days for uncoated versus coated at 80°C and 105°C, respectively. Also evident in the plots, and as expected, median life is longer at 80°C compared to 105°C. The scale parameter, σ , is the standard deviation of the natural logarithm of the days-to-failure for all failed samples. A common scale parameter, σ , was used assuming that the failure mechanism was the same at both temperatures. Figure 10 shows that the days to failure data are in close proximity to the fitted failure rate distribution line.

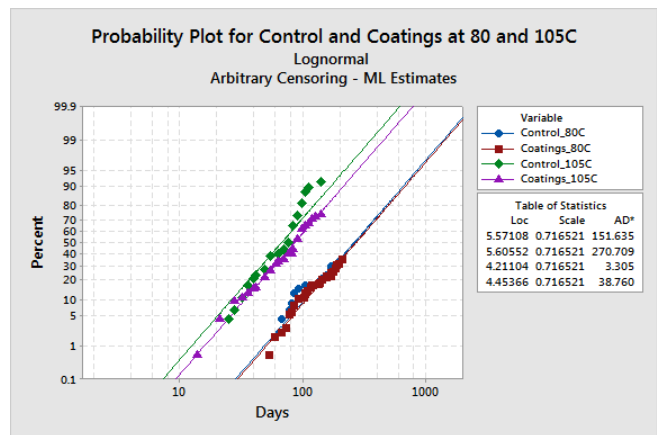


Figure 10. Comparison of FoS failure distributions by temperature, 105°C and 80°C, for all resistor sizes, uncoated controls and four coatings, pooled: RF, RUB, EP1, ACRY

The 0402 resistor was the most sensitive to corrosion failures and Figure 11 shows the lognormal analysis of 0402 failures in the uncoated controls at 60°C, 80°C and 105°C and the pooled coating samples at 80°C and 105°C. Only one failure occurred in the pooled coatings at 60°C, RF, between 130 and 147 days. The days to median life are similar for the controls and pooled coatings at both temperatures: 79 days versus 93 days, and 32 days versus 29 days at 80°C and 105°C, respectively. The coatings that were pooled for this analysis, RF, RUB, EP1 and ACRY, essentially offer no protection against silver sulfide corrosion in the FoS test.

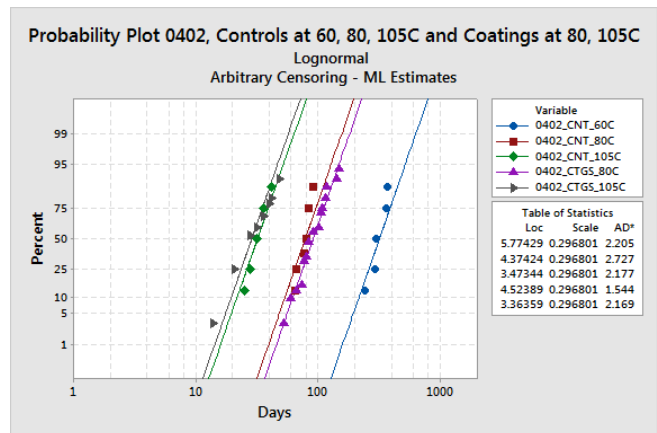


Figure 11. Lognormal plots for 0402 resistor failures, uncoated controls (CNT) versus pooled coated (CTGS)

Comparison to Past Study Results

In the previous study [6], the smallest resistor size was 0402, and all testing was performed at 105°C. In both the previous and current studies, EP2016 was the top performer. The uncoated control sample in the past study had first failures around 10 days for 0402, and 30 days for resistor sizes 0603, 0805 and 1206. The control in this study survived much longer: 0402 first fail was around 25 days, and the remaining resistor sizes had first fail at just less than 60 days. This difference is likely due to test variation, as gaseous corrosion tests are difficult to control and repeat.

Acceleration Factor Calculation

An objective of this study was to develop a time-to-failure model by testing at three temperatures. Figure 12 shows the lognormal analysis for the uncoated resistors at all three test temperatures. The location parameter, μ , is used to calculate the days to failure for the medians of the test populations at 60°C, 80°C and 105°C.

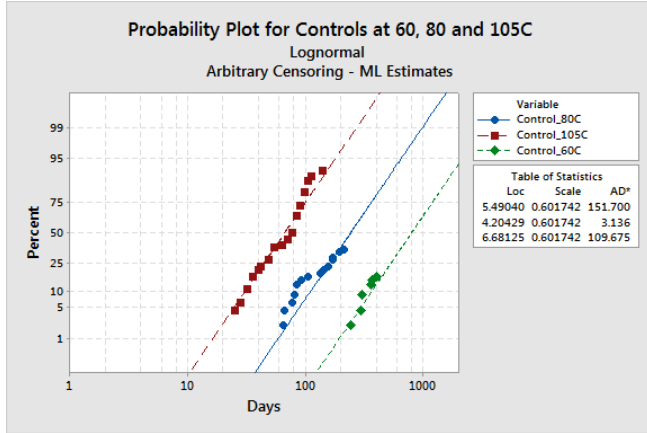


Figure 12. Lognormal analysis of the uncoated resistor fails and survivors at 60°C, 80°C and 105°C

Figure 13 shows an Arrhenius plot of natural log of inverse days-to-median failure, $\ln(1/e^t)$, versus the inverse of the absolute test temperature. The correlation coefficient, R^2 , is excellent, 0.99996, indicating that the wear-out failure mechanism is likely the same across all three test temperatures, supporting the assumption for the common scale parameter, σ .

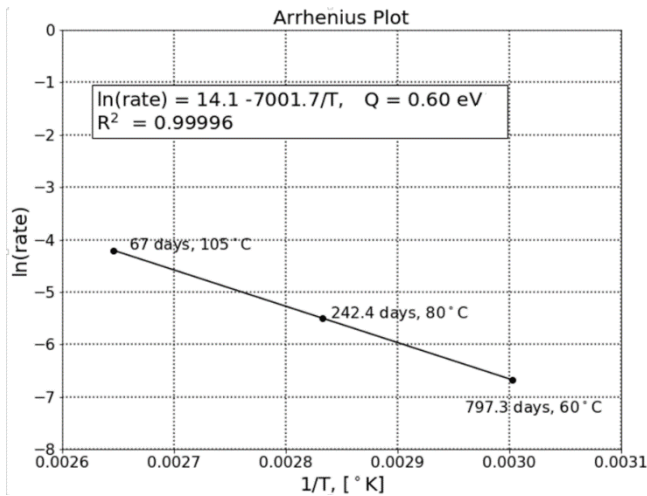


Figure 13. Arrhenius plot of $\ln(1/\text{days to median failure})$ versus $1/\text{absolute test temperature}$.

The Arrhenius equation is

$$\text{rate} = Ae^{\frac{-Q}{kT}} \quad (1)$$

where rate is expressed in inverse days, A is a constant, Q is the activation energy [eV], k is the Boltzmann constant, 8.6173×10^{-5} [eV/°K] and T is temperature, [°K]. Taking the natural logarithm of equation (1) yields (2):

$$\ln(\text{rate}) = \ln A - \frac{Q}{kT} \quad (2)$$

The regression fit to the plotted data in Figure 13 is

$$\ln(\text{rate}) = 14.1 - \frac{7001.7}{T} \quad (3)$$

The activation energy, Q, is 0.60 eV for silver sulfide corrosion.

Equation (4) can be used to estimate the percent surviving after so many days at a temperature of interest, $\mu_{\text{temperature}}$, between 60-100°C. Φ is the standard normal cumulative distribution function (cdf) and σ_{common} (0.602), is the scale parameter from the table of statistics in Figure 12.

$$R(\text{days}) = 1 - \Phi\left(\frac{\ln(\text{days}) - \mu_{\text{temperature}}}{\sigma_{\text{common}}}\right) \quad (4)$$

PHYSICAL ANALYSIS OF RESISTORS

Resistor Construction Analysis

Representative untested 1206, 0402, and 0201 resistors were cross-sectioned to evaluate the construction of the resistors. The basic construction of these standard ceramic resistors (Fig. 14) consists of:

- Ceramic body
- Pb-glass & RuO₂ resistive element
- Protective top coating
- Sintered silver termination
- Nickel plating over silver layer

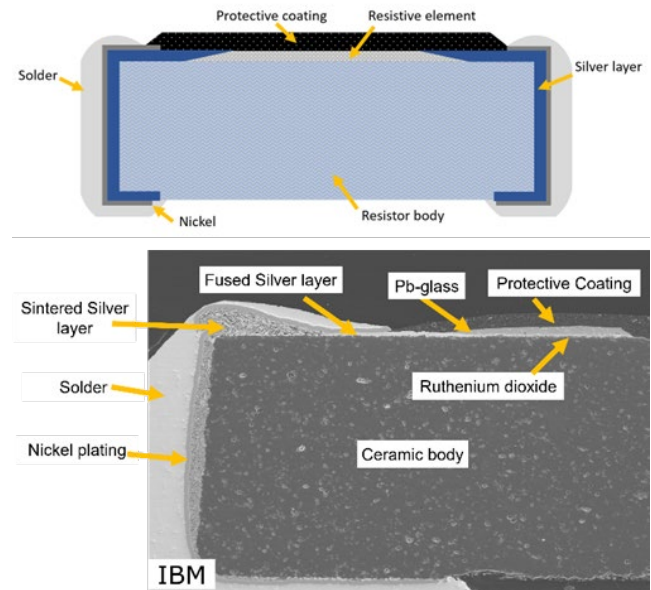


Figure 14. Basic ceramic resistor construction

Scanning Electron Microscopy and Energy-dispersive X-ray Spectroscopy (SEM/EDS) elemental mapping were completed to confirm the composition of the various elements of the resistor construction, as shown in Figure 15.

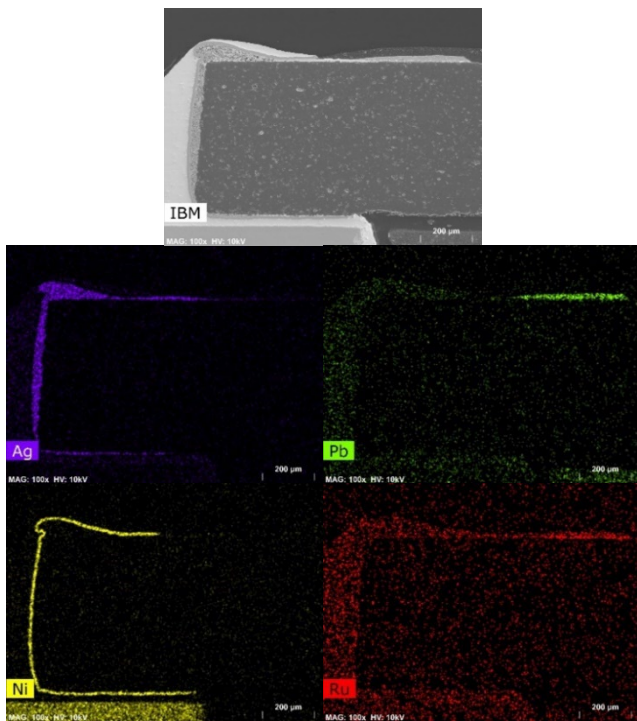


Figure 15. SEM / EDS mapping of a resistor

Differences in construction were observed among the different resistor sizes (Figures 16 and 17). Since the 0402 had the most fails of any resistor size, it was used as the basis of comparison to the other resistor sizes. The silver termination is comprised of two layers of silver. The first layer on the ceramic body is thin and appears solid or fused while the second layer is thicker and appears to be sintered silver. The sintered silver second layer of the 0402 resistor was coarser and had larger particles as compared to the 1206 resistor. A coarse silver layer may allow a faster diffusion rate of the sulfur and therefore, faster corrosion of the silver. The 1206 resistor had a more defined and thicker solid/fused silver first layer than the 0402 resistor. A thicker, solid silver layer will take longer to corrode than a thin layer.

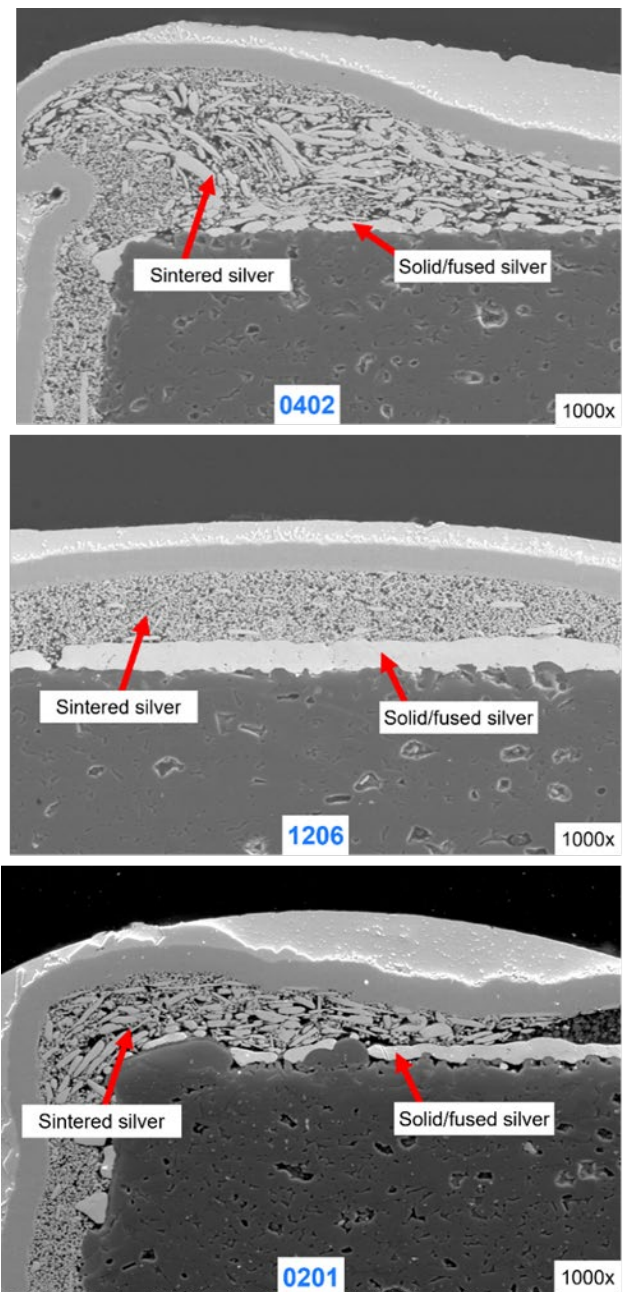


Figure 16. SEM images of 0402 (top) vs. 1206 (middle) and 0201 (bottom) sintered silver layer morphology

There were also differences observed in the silver morphology between the 0201 and 0402 resistor sizes. The 0201 resistor had a coarser sintered silver layer, like the 0402. However, the solid / fused silver first layer of the 0201 was thicker. The comparisons of the 1206 and 0201 resistor structure to that of the 0402 are shown in Figure 16.

Differences in the nickel barrier layer were also observed between the 0402 and 1206 resistor sizes. The nickel layer in the 1206 resistor is more protective, completely covering the sintered silver layer creating a longer diffusion path for the invading sulfur. The 0402 resistor has the sintered silver layer almost exposed at the termination. A comparison of the nickel layers in the 0402 and 1206 resistors is shown in Figure 17.

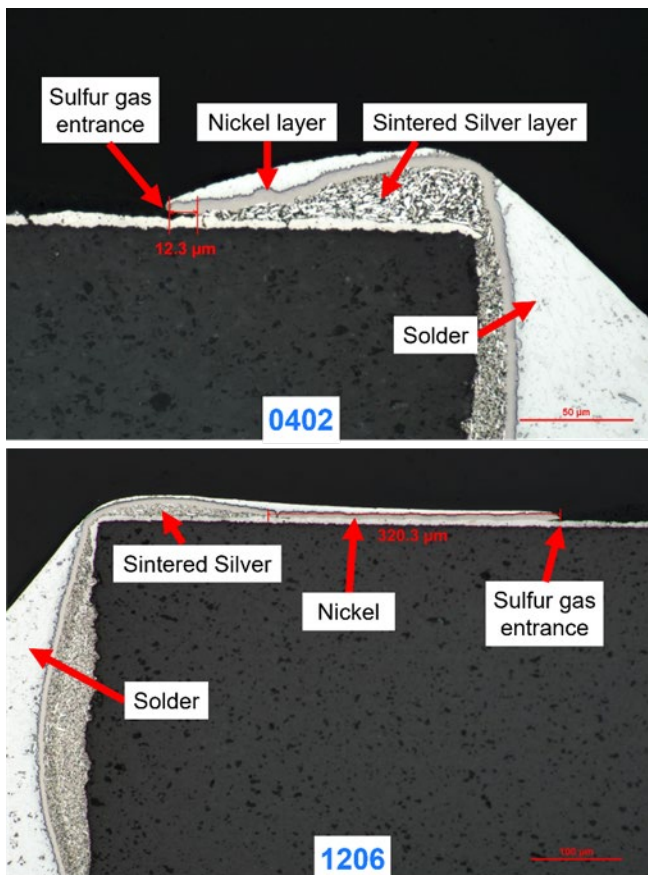


Figure 17. Brightfield images of 0402 (top) vs. 1206 (bottom) barrier layers

Conformal Coating Construction Analysis

The chemical differences in the conformal coatings were thought to be the most significant contributor to the variation in the amount of protection afforded by the coatings. The coating thickness and the coating morphology were also examined as possible contributors to good or poor protection performance. Representative untested 1206 and 0402 resistors with the seven different conformal coatings were cross-sectioned to evaluate the construction of the coatings.

Table 3 shows the process application method for all seven coatings. A glass slide was placed near the test coupons during the spray process to provide an estimate of the coating thickness. Similarly, a glass slide was dipped in the ACRY coating to provide an estimate. Coating thickness was determined from a micrometer measurement of the glass slide before and after coating application. Each material coating thickness on the glass slides is shown as the Process Monitor in Table 4. For comparison, the coating thickness over the PCB solder mask was measured in the cross-sections. The dip coating of ACRY had the largest discrepancy between the target thickness of 1 micron and process monitor thickness on the glass slide of 10 microns. The volume of ACRY available for this study was small. The carrier solvent in ACRY evaporates rapidly. The surface area of the laboratory process bath was large compared to the liquid depth, resulting in a high loss of solvent and therefore, a higher solids content

in the bath. Consequently, the thickness was 10x the target. For the other coatings, the target thickness is within the order of magnitude of the process monitor range of thickness. It is reasonable to think that the coating thickness on the PCB solder mask should be representative of the thickness on the glass slide, since both are flat surfaces. However, the agreement is typically poor, except for ACRY (dipped) and EP1 (sprayed).

Table 4. Conformal coating thickness measurements from the process monitor and cross-sectioning at the solder mask versus the target thickness.

Coating	Thickness (um)		
	Target	Process Monitor	Solder Mask
EP2016	75	89	25
RUB	40	38	24.4
ACRY	1	10	7.6
EP2	75	25-75	135.8
EP1	75	25-75	47
RF	0.05-0.1	<1	1.4
POLY	75	25-75	11.5

Table 5 shows the thickness measurements on the component termination and protective coating of the 0402 and 1206 resistors as measured in cross-sections. The more relevant coating thickness is on the silver termination, since the objective is to prevent sulfur attack in this region. Coatings that were sprayed had higher thickness (32-130%) on 1206 versus 0402 components. The 0402 was the most sensitive to corrosion failure. EP2016 had the thinnest coating thickness in the termination area (16.2 microns) for the spray coatings yet protected the sensitive 0402 from silver corrosion and electrical failure. EP2 (28.8 microns) performed nearly as well as EP2016, with only one 0402 electrical failure at 119 days of 105 °C. POLY had a coating thickness of 29 microns in the termination area and experienced 100% electrical failure on the 0402. The vacuum deposited RF coating had the lowest measured thickness values, 2 microns at the termination area, yet performed better than the POLY coating and similar to the RUB, EP1 and ACRY coatings. There is no direct correlation of coating thickness to days to failure. Figure 18 shows where the coating thickness was measured.

Table 5. Conformal coating thickness measurements from cross-sectioning: at the resistor terminations and over the protective coating on the resistor.

Coating	Thickness (um)			
	402		1206	
	Termination	Protective Coating	Termination	Protective Coating
EP2016	16.2	8.2	37.1	22.5
RUB	22	9.7	29.1	24.6
ACRY	24.7	18.9	8.2	4.3
EP2	28.8	2.7	43.3	34.1
EP1	27.1	8.4	49.8	48.3
RF	2.7	1.9	2	1.9
POLY	29	17.3	45.1	39.8

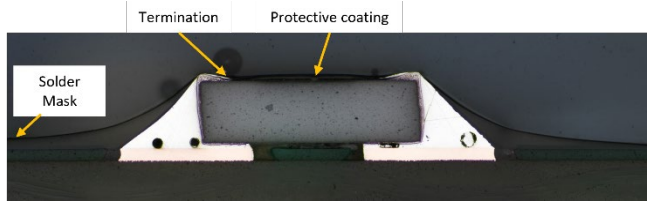


Figure 18. Location of coating thickness measurements

Six of the seven coatings appeared to be homogenous. The POLY coating appeared to have a heterogenous, particulate structure. These comparisons are shown in Figure 19.

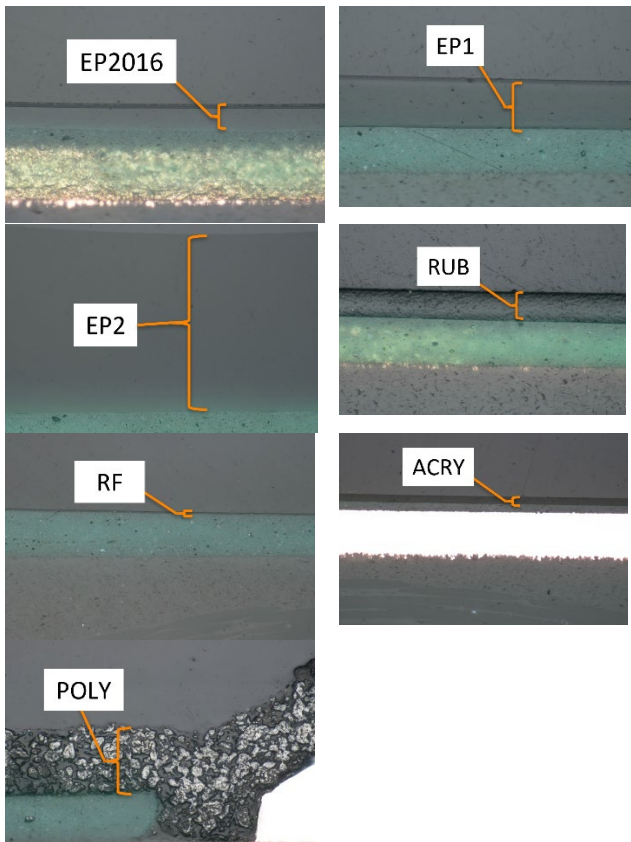


Figure 19. Conformal coating morphology (550x magnification)

Close examination of the POLY conformal coating reveals a coarse, particulate-like structure. This structure likely leads to higher gas diffusion rates between the particles resulting in a faster corrosion rate. These details are shown in Figure 20 on a sample only exposed to room temperature, 25°C.

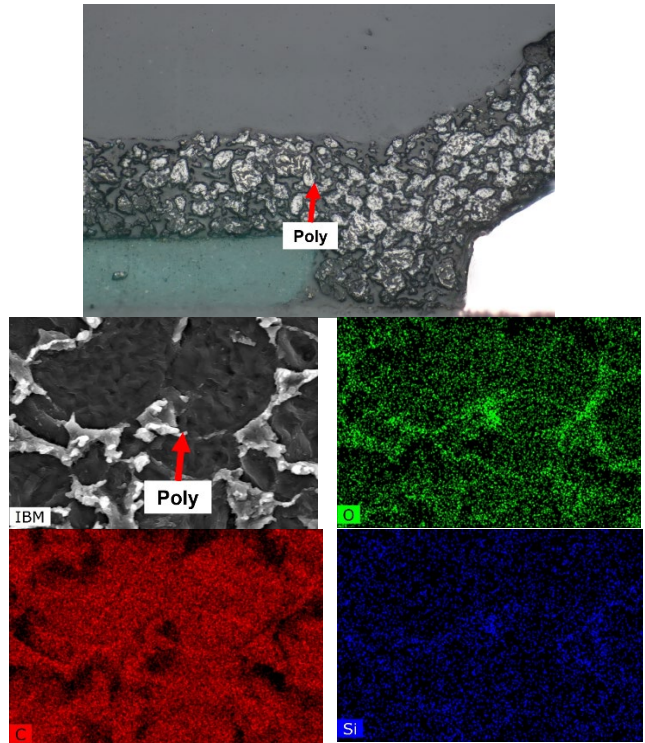


Figure 20. POLY conformal coating structure, sample only exposed to room temperature

This particulate-like structure of the POLY coating observed in the sample stored at room temperature does not appear to be stable when exposed to higher temperatures. The samples tested at 105°C and 80°C show that the coating has fused together. Refer to Figure 21 for a visual comparison of the coating when exposed to higher temperatures. The physical changes in the coating at elevated temperatures means that there may not be direct correlation between low temperature / room temperature performance and performance at elevated temperatures.

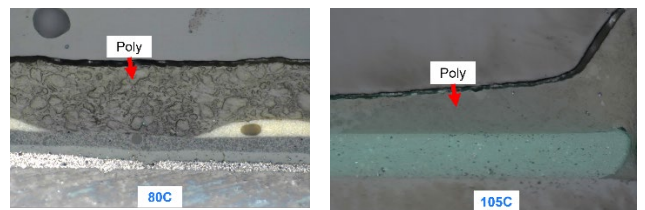


Figure 21. POLY coating after temperature exposure

Resistor Corrosion Failure Mechanisms

In the FoS testing, elemental sulfur (S₈) diffuses through the conformal coating and reacts with the silver layer, forming silver sulfide (Ag₂S). The silver sulfide is highly resistive and the reaction results in volume expansion of the conductive layers, which induces stress. These factors both

contribute to an increase in resistance and failure. Figure 22 shows the typical failure mechanism for resistor silver sulfide corrosion.

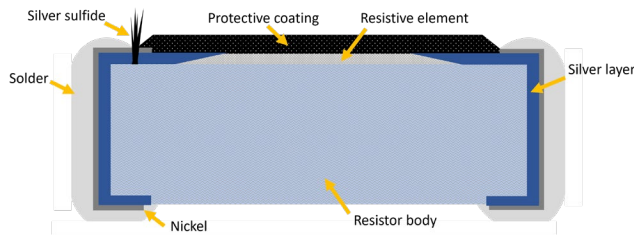


Figure 22. Typical resistor corrosion failure mechanism

Tested 0402 and 1206 resistors were cross-sectioned to evaluate the failure mechanism and the extent of the corrosion. The failure mechanism for the 0402 resistors showed that the silver-plating layer reacted to form silver sulfide, which disturbed the electrical connection to the resistive element. The failure mechanism was consistent across all studied resistors. A representative sample shown in Figure 23 had the following description and exposure:

- Resistor: C (0402)
- Coating: EP1
- Test Temperature: 105 C
- Days to failure: 28
- Total exposure: 140 days

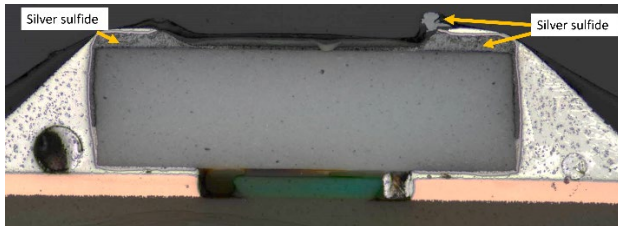


Figure 23. Typical 0402 corrosion failure mechanism

SEM/EDS analysis confirmed that the silver layer corroded and formed silver sulfide, as shown in Figure 24.

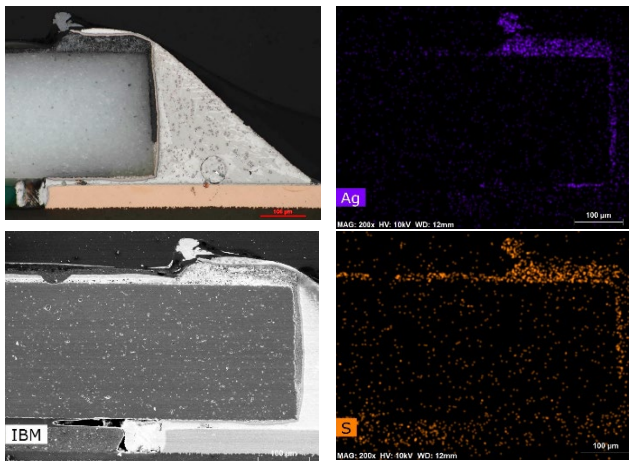


Figure 24. SEM/EDS analysis of a 0402 failure

Similarly, the 1206 failure mechanism also showed that the silver-plating layer reacted to form silver sulfide, which

disturbed the electrical connection to the resistive element. The particular 1206 resistor examined (Fig. 25) had the following description and exposure:

- Resistor: O (1206)
- Coating: EP1
- Test Temperature: 105 C
- Days to failure: 55
- Total Exposure: 140 days

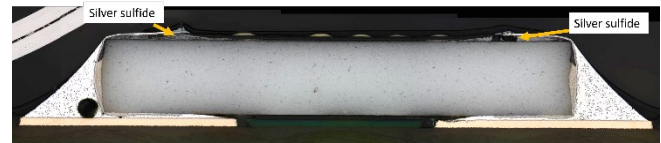


Figure 25. Typical 1206 corrosion failure mechanism

The SEM/EDS analysis of a typical 1206 failure also confirmed that the silver layer corroded and formed silver sulfide as shown in Figure 26.

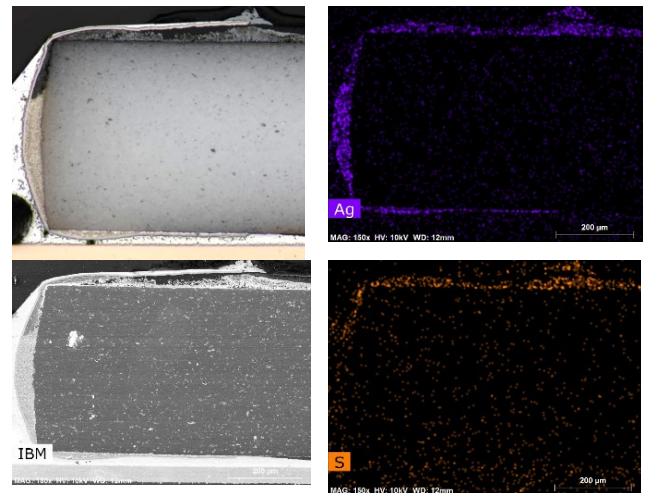


Figure 26. SEM/EDS analysis of a 1206 failure

Several non-failing resistors were examined and evidence of Ag_2S corrosion was observed. The corrosion in these cases was limited to small Ag_2S blooms and was not significant enough to disturb the electrical connection. SEM photos of example non-failing 0402 resistors tested at 80°C and 105°C are shown in Figures 27 and 28, respectively.

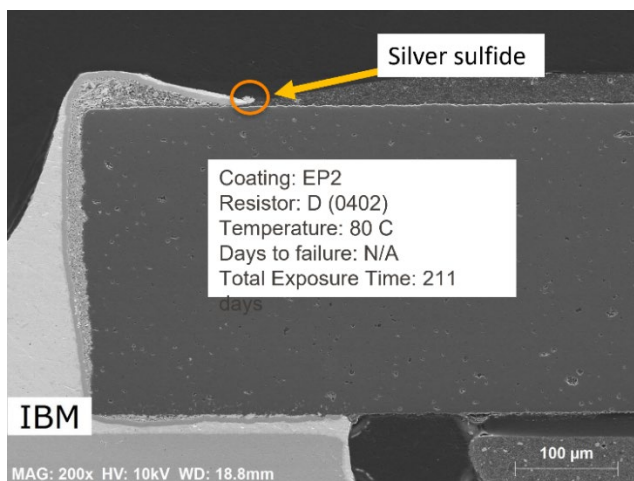


Figure 27. Example of silver sulfide corrosion on non-failing 0402 resistor tested at 80°C.

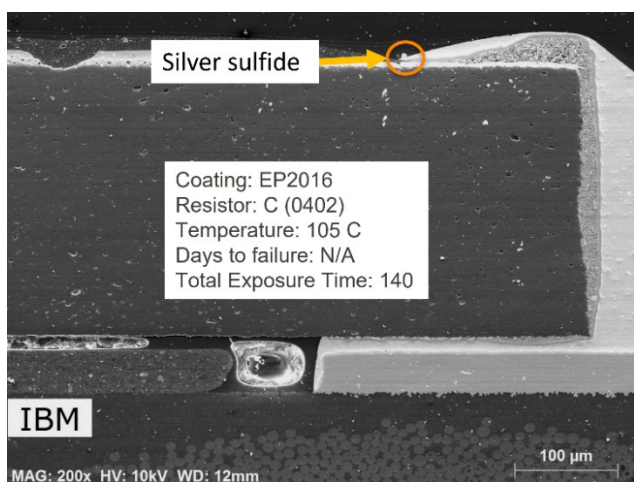


Figure 28. Example of silver sulfide corrosion on non-failing 0402 resistor tested at 105°C.

SUMMARY AND CONCLUSIONS

Of the coatings evaluated in this study, only the EP2016 and EP2 demonstrated any significant mitigation of silver sulfide corrosion in FoS testing at both 105°C and 80°C. There were no failures for EP2016 at 105°C after 140 days in test and only one failure at 105°C for EP2 after 140 days in test. EP2016 and EP2 also had no failures after 211 days in test at 80°C. Similarly, no failures were observed after 447 days in test at 60°C.

EP2016 has proven to consistently provide corrosion protection in FoS testing [3,6], and in field applications. The choice of EP2 epoxy with a higher T_g than EP1 appears to have been a good choice. The improved application and cure process manufacturability of EP2 as compared to EP2016 could make it the preferred coating material for future use. This finding is a significant outcome, resulting from many years of study.

The POLY coating made time-to-failure worse or sooner than no coating and the other coatings did not appear to extend the

life of the resistors beyond what was typical for an uncoated control card.

Coatings RF, RUB, EP1 and ACRY resulted in no significant protection against corrosion in the FoS test compared to no coating. Failures occurred in the no coating cells for all three temperatures, 105°C, 80°C and 60°C, and a lognormal analysis was used to determine the corresponding median life.

As expected, there were differences in characteristic life of the failure rate distributions among the three FoS test temperatures, with the resistors tested at 105°C failing consistently earlier than those tested at 80°C, which in turn failed earlier than those at 60°C. Median failure times from these data sets indicate that the silver sulfide corrosion driving failure mechanism is thermally activated.

An Arrhenius plot of the inverse of median life versus $1/(\text{absolute test temperature})$ yielded an activation energy of 0.60 eV and an equation that can be used to predict median life as a function of other temperatures. Knowing $\mu_{\text{temperature}}$ and σ_{common} , one can predict reliability for a temperature and operational days. Most of the conformal coatings tested are not protective against FoS corrosion, therefore, it is possible to apply the above analysis of uncoated resistors to make field predictions for these coatings: RF, RUB, EP1 and ACRY. This analysis contains a bias in that 100% of the 0402 resistors failed while the other resistor sizes had a much lower percent failure, for example, 40% or less in the 80°C test.

The physical analysis found that differences in resistor construction among sizes, such as the silver morphology and nickel plating layer between the 0402 and 1206 resistors could have contributed to failure rate differences. The failure mode observed in this study is consistent with other sulfur-induced corrosion resistor failures. Resistors that did not fail, like the epoxy coated resistors, did show some evidence of silver sulfide formation. The coating thickness did not appear to correlate to time to failure. The time to failure appears to be mainly dependent on coating chemistry.

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REFERENCES

- [1] P. Lembke, M. Cole, T. Tofil, J. Porter, J. Wertz, J. Wilcox, M. Gaynes, M. Meilunas, H. Rubin, "Testing and Mitigating Resistor Silver Sulfide Corrosion," in *SMTA International Proceedings*, 2018.
- [2] ASHRAE TC 9.9, "2011 Gaseous and Particulate Contamination Guidelines for Data Centers," 2011
- [3] M. Cole, "Harsh Environment Impact on Resistor Reliability," in *SMTA International Proceedings*, 2010.
- [4] EIA-977, *Test Method - Electronic Passive Components Exposure to Atmospheric Sulfur*, Electronic Industries Alliance, 2017.
- [5] A. B809-95, "Standard Test Method for Porosity in Metallic Coatings by Humid Sulfur Vapor (Flowers-of-Sulfur)," *J. ASTM Int.*, 2013.
- [6] M. Cole, J. Porter, J. Wertz, M. Coq, M. Meilunas and J. Wilcox, "Effectiveness of Conformal Coatings in Preventing Resistor Silver Sulfide Corrosion," in *SMTA International Proceedings*, 2016.
- [7] J. T. Wertz, J. T. Porter, J. Zhang, J. P. Kuczynski and D. J. Boday, "Metal Particulate-containing conformal coatings for improved IT hardware reliability in harsh environments," *Journal of Material Science*, vol. 52, no. 5, pp. 2879-2888, 2017.
- [8] B. Berry and J. Susko, "Solubility and Diffusion of Sulfur in Polymeric Matierials".*IBM J. Res. Develop*, pp. 176-189, 1977.
- [9] P. Singh, "Characterization of Conformal Coatings," in *SMTA International Proceedings*, 2015.
- [10] J. Wilcox, M. Meilunas and M. Anselm, "Harsh Environment Reliability of Micro-Leadframe (QFN) Componets and Conformal Coating Effects," in *SMTA International Proceedings*, 2015.
- [11] L. H. Sperling, *Introduction to Physical Polymer Science*, NY: Wiley Publications, 1992.
- [12] P. A. Ciullo and N. Hewitt, *The Rubber Formulary*, Norwich, NY: Noyes Publications, 1999.