FINAL REPORT

Tin Whisker Inorganic Coating Evaluation (TWICE)

SERDP Project WP-2212

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14. ABSTRACT
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Final Report

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Cedar Rapids, IA

Abstract

This report describes the development, application and effectiveness of alkali silicate glass (ASG) coatings for inhibiting tin whisker initiation and growth. Tin whiskers are thin filaments that grow out of pure tin regions such as the surface finishes that are now commonly used in lead-free electronics assemblies. These whiskers can damage electronics by creating unintended short circuits between component leads, circuit board traces, etc. In past decades, a small amount of lead in the surface finish controlled tin whisker growth. However, this is not a viable option under current environmental legislative restrictions on the use of lead in commercial electronic components. The ASG formulations used in this study were deposited with equipment and conditions typical of those used to apply materials such as conformal coatings to electronic assemblies. These conformal coatings enhance the reliability of circuit boards used in harsh environments that are common to military applications by inhibiting contact between the ambient environment and the electronics. Processes for controlling ASG coating properties were developed and a number of coating combinations were applied to test components with pure tin surfaces. Coatings were applied both in a lab environment at Rockwell Collins and in a manufacturing environment at Plasma Ruggedized Solutions. Testing in elevated humidity/temperature environments and subsequent inspection of the test articles and representative production assemblies identified coating combinations that inhibited tin whisker growth as well as other material combinations that accelerated tin whisker growth. Additional testing at the University of Maryland characterized the effect of coatings on inhibiting Metal Vapor Arcing, which can be induced by tin whiskers. The most effective coatings for inhibiting tin whiskers were composites of ASG and alumina nanoparticles. These coatings did not eliminate tin whiskers, but they inhibited their growth such that whiskers did not appear capable of growing sufficiently long to damage electronic equipment.

Keywords

Tin Whiskers, Lead-free Electronics, Conformal Coatings, Harsh Environment Electronics, Metal Vapor Arc (MVA)

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List of Acronyms

85/85THC	85°C / 85% RH Temperature/Humidity Conditioning
AlO	Aluminum Oxide
ASG	Alkali Silicate Glass
DI	Deionized
D_k	Dielectric Constant
DoD	Department of Defense
DOE	Design of Experiments
JEDEC	Joint Electron Device Engineering Council
MVA	Metal Vapor Arc
PET	Polyethylene terphalate
PRS	Plasma Ruggedized Solutions
PWB	Printed Wiring Board
QFP	Quad Flat Pack
RF	Radio Frequency
RH	Relative Humidity
RMS	Root Mean Square
RoHS	Restriction on Hazardous Substances Directive
SEM	Scanning Electron Microscope
SERDP	Strategic Environmental Research and Development Program
SOIC	Small Outline Integrated Circuit
tan_d	Dielectric Loss Tangent
TiO	Titanium Oxide
TW	Tin Whisker
TWICE	Tin Whisker Inorganic Coating Evaluation
UofMd	University of Maryland
UVO	Ultraviolet Ozone
WEEE	Waste Electrical and Electronic Equipment
ZnO	Zinc Oxide

A. Extended Abstract / Executive Summary

Objectives: In response to legislation such as the Waste Electrical and Electronic Equipment (WEEE) and the Restriction on Hazardous Substances (RoHS) Directive, the commercial electronics industry has transitioned to lead-free solder technologies with material sets and processes optimized for consumer electronics. These regulations aim to reduce the amount of lead introduced into the environment, particularly at the two extremes of the product life cycle (manufacturing and disposal). The transition to lead-free assembly has led to the replacement of tin-lead solders with a variety of lead-free solders for component interconnections. In addition, component surface finishes, which were typically plated tin/lead are now primarily plated tin.

Life-critical and mission-critical electronics applications (i.e. aerospace, military, telecommunication, medical, etc.) often have exemptions that allow the use of tin/lead surface finishes. However, factors such as cost, component availability and global co-production programs dictate that lead-free components will inevitably find their way into Department of Defense (DoD) systems. Recognition of this has prompted many DoD electronics corporations and agencies to fund research in a number of lead-free electronics' reliability areas. One of these topics is tin whiskers, which are thin filaments of tin that can grow from a tin surface and potentially cause electrical shorting or other failure modes. While the tin whisker phenomenon was recognized decades ago, it was not an active area of research after it was determined that a small amount of lead (~2-4%) in a surface finish greatly diminished the likelihood of tin whisker formation. The recent transition to lead-free solders and surface finishes has eliminated this mitigation approach and has thus generated a need for other methods to inhibit the formation and growth of tin whiskers in high reliability electronics. Until universally accepted methods for mitigating tin whiskers are identified, military electronics designers will be increasingly forced to choose between using the non-state-of-the-art electronics that are available with leaded finishes and the potential reliability impact of the tin whisker phenomenon resulting from the use of the lead-free components designed for state-of-the-art commercial electronics.

Conformal coatings have been used for decades to enhance the reliability of circuit boards used in harsh environments that are common in military applications. These coatings inhibit contact between the ambient environment and the electronics to reduce the harmful effects of environmental exposure to condensing water, salt fog, etc. With the growing use of pure tin surface finishes, conformal coatings are also increasingly used as a method to reduce the risks of tin whisker-induced failures. These conformal coatings can affect circuit board cost and performance and no coating has been shown to completely eliminate whiskers. Therefore, ongoing research by industry and the DoD has attempted to better understand the tin whisker mitigation capabilities of existing conformal coatings and to develop alternate materials with improved performance.

Technical Approach: This report describes the development, application and effectiveness of using alkali silicate glass (ASG) coatings to inhibit tin whisker initiation and growth. The ASG formulations used in this study were deposited with equipment and conditions that are typical of those used to apply conventional conformal coatings, such as acrylic materials. ASG materials are inorganic materials and therefore are much less permeable to moisture and oxygen, both of which can promote tin whisker growth. The relatively high strength and stiffness of ASG coatings, compared to organic coatings allow them to better contain tin whiskers and alter their

growth characteristics. Finally, because ASG coatings can be applied in very thin layers and are inorganic, they have less impact on the electrical performance of circuits to which they are applied, particularly those operating at high frequency such as RF (Radio Frequency).

Results: The Tin Whiskers Inorganic Coating Evaluation (TWICE) program investigated formulations of materials that included composites with nanoparticles. Design of Experiments (DOE) was used to identify process parameter combinations for controlling ASG coating properties. A number of coatings with different material formulations, nanoparticle filler and thicknesses were applied to test substrates, test components specifically designed to exhibit tin whisker growth, and functional electronic components. The TWICE program included two phases. The first phase focused on material formulation and characterizing the effects of coatings on test samples. Phase 1 ASG coatings, as well as conventional coatings, were applied to samples both in a lab environment at Rockwell Collins and in a manufacturing environment at Plasma Ruggedized Solutions. These samples were subjected to an elevated humidity/temperature environment and subsequently inspected to characterize whisker growth over a range of exposure times. This testing revealed that some coating combinations inhibited tin whisker growth while other material combinations actually accelerated tin whisker growth. Locally high stresses within tin plating, due to residual stresses in the higher-stiffness ASG formulation, as well as unfilled cracks in the tin plating, led to above-average whisker growth. The most effective coatings for inhibiting tin whiskers were composites of more ductile ASG and smaller nanoparticles. Phase 1 also included testing at the University of Maryland to characterize the effect of coatings on inhibiting Metal Vapor Arcing (MVA), which can be induced by tin whiskers. That work showed that ASG coatings inhibited MVA in a similar manner as conventional coatings.

Phase 2 extended the work of Phase 1 to update material formulations, apply coatings to representative test board assemblies, evaluate the effect of coatings on tin whisker growth and conduct preliminary assessments of the system-level impact of using ASG coatings to mitigate tin whiskers. Coatings were again applied at both Rockwell Collins and Ruggedized Plasma Solutions. Inspection of coated assemblies revealed that coverage with ASG was better than with acrylic coating and two combinations of ASG coatings reduced the growth of tin whiskers relative to acrylic. Moreover, the ASG coatings disrupted tin whisker growth and reduced the risk of forming long tin whiskers that could lead to functional failures. Conventional acrylic coatings only slowed the growth of whiskers; it appeared that whiskers under this material will eventually penetrate through the coating and continue to pose a system risk.

Benefits: The ASG coatings will not provide a ‘silver bullet’ that eliminates tin whiskers. However, they can inhibit the formation of tin whiskers to as great, or greater, an extent as conventional conformal coatings such as acrylic. Since the ASG coatings not only inhibit the formation of whiskers but also significantly affect their growth, they can potentially provide a more significant risk mitigation approach as they minimize the occurrence of whiskers long enough to cause electronic failure. In addition, the dielectric properties of ASG may make them more suitable for certain electronics, such as RF systems. Further work is needed to characterize the long-term growth of whiskers on functional hardware and the robustness of materials in harsh environments such as salt fog and vibration.

B. Objectives

The objectives of the TWICE program were to demonstrate the use of ASG coating to mitigate tin whiskers and to establish manufacturing processes to implement the technology into DoD applications. Phase 1 of the program focused on establishing the viability of using ASG as a tin whisker mitigation method. Phase 2 leveraged the results from Phase 1 to improve upon the coatings developed and to transition the application processes to a manufacturing-representative environment.

The specific objectives of the Phase 1 activity included:

- Establish methods to apply controlled ASG coatings to better understand the mechanisms by which coatings can reduce tin whisker growth.
- Characterize the effects of parameters such as coating hardness, moisture permeability, dielectric strength, surface roughness, coating thickness, etc. on tin whisker formation to establish a better understanding of tin whisker growth mechanisms.
- Identify the impact of using nanoparticles, such as alumina and zinc oxide, to alter and optimize the characteristics of ASG coatings for tin whisker mitigation.
- In collaboration with the University of Maryland, conduct testing to understand the relationship between electrical and environmental parameters on tin whisker Metal Vapor Arc (MVA) and the role that ASG can play in mitigating that phenomenon.
- Determine the feasibility of transitioning ASG coating technologies to industrial manufacturing equipment and processes through collaboration with team member Plasma Ruggedized Solutions.

The objectives of Phase 2 included:

- Demonstrate that ASG coatings can be applied to a variety of component packaging styles at both Rockwell Collins and Plasma Ruggedized Solutions and evaluate the uniformity of coverage of these coatings relative to conventional coating materials.
- Characterize the effects of coatings on the formation and growth of tin whiskers on typical microelectronics components as well as test devices fabricated to promote the growth of tin whiskers.
- Assess the tin whisker mitigation behavior of ASG coatings with zirconium nanoparticles, which were shown in initial testing to provide more effective sealing against ambient conditions than the other ASG coating developed in Phase 1.
- Identify remaining tasks to transition the technology into production and quantify manufacturability characteristics such as inspectibility and hermeticity of coatings.

C. Background

In response to regulations such as the Waste Electrical and Electronic Equipment (WEEE) and the Restriction on Hazardous Substances (RoHS) Directive, the commercial electronics industry has transitioned to lead-free solder technology with material sets and processes optimized for consumer electronics. The goal of these regulations is to reduce the amount of lead introduced into the environment by the electronics industry. The evolution of component surface finishes from tin/lead plated surface finishes to tin plated surface finishes is one of the major material changes resulting from the global implementation of lead-free solder technology.

High Performance electronics applications (i.e. aerospace, military, telecommunication, medical, etc.) often have exemptions that allow the use of tin/lead surface finishes. However, factors such as cost, component availability and global co-production programs dictate that lead-free components will inevitably find their way into Department of Defense (DoD) systems. Recognition of this has prompted many DoD electronics corporations and agencies to fund research for a number of lead-free electronics' reliability topics. One of these topics is tin whiskers, which "can create short circuits, reduce solder joint integrity, and reduce reliability" [1]. While much of the recent efforts to mitigate tin whiskers began in the aerospace/military community, the recent discovery of tin whiskers in automotive electronics [2] clearly demonstrates the global impact of this issue. Tin whiskers are thin filaments of tin that can grow from a tin surface and potentially cause electrical shorting or other failure modes (Figure 1). While the tin whisker phenomenon was recognized decades ago, it was not an active area of research until recently. This is due to the fact that the presence of at least a small amount of lead (~2-4%) in a surface finish greatly diminishes the likelihood of tin whisker formation. The transition to lead-free solders has eliminated this mitigation approach and has generated a need for other methods to inhibit the formation and growth of tin whiskers in the High Reliability electronics used in DoD systems. Until universally accepted methods for mitigating tin whiskers have been identified, military electronics designers will be increasingly forced to choose between using the non-state-of-the-art electronics available with leaded finishes and the potential reliability impact of the tin whisker phenomenon resulting from the use of the lead-free components designed for state-of-the-art commercial electronics.

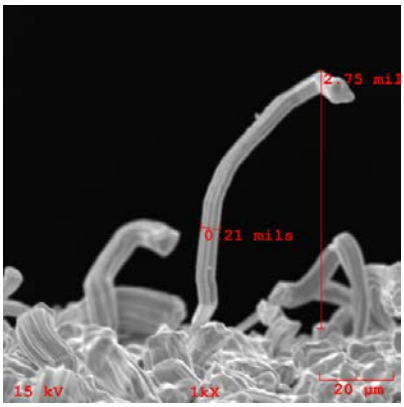

Figure 1 Tin Whiskers

Rockwell Collins led the Tin Whiskers Inorganic Coating Evaluation (TWICE) project under contract with the Strategic Environmental Research and Development Program (SERDP). Other team members on the project were Plasma Ruggedized Solutions (PRS) and the University of Maryland (UofMd). The objective of the TWICE program was to investigate the use of Alkali Silicate Glass (ASG) coatings to inhibit or prevent the growth of tin whiskers. The TWICE program was conducted in two phases, each with a duration of one year. Phase 1 focused on developing tin whisker mitigation strategies that utilize ASG coatings while Phase 2 emphasized implementing and evaluating these strategies on printed circuit assemblies that are representative of military electronics.

Prior to the start of TWICE, Rockwell Collins had developed formulations of ASG materials for enhancing the reliability and thermal management of electronics. The tin whisker mitigation approach of the TWICE program was to apply ASG-based coatings on surfaces to a) alter the stress conditions on an at-risk surface finish to reduce the formation of tin whiskers, b) contain any tin whiskers that do form so as to reduce their length and ability to contact nearby surfaces, and c) provide an electrically insulating layer that prevents tin whiskers on adjacent surfaces from making electrical contact. Rockwell Collins' roles in the TWICE program included managing the project, developing formulations of materials and preliminary processing methods, conducting tests to grow tin whiskers and evaluate the performance of various coatings, identifying next steps necessary to transition the technology to production and documenting/reporting the results. The role of Plasma Ruggedized Solutions was to coat test samples and boards with ASG materials as well as conventional conformal coat materials to establish and mature the manufacturability of ASG coatings relative to existing solutions. The role of the University of Maryland was to evaluate the performance of coatings, which include the ASG materials developed in the TWICE program, in mitigating one potential failure mechanism introduced by tin whiskers: Metal Vapor Arc (MVA). In MVA, a tin whisker initiates a high current electrical short across two adjacent surfaces that can, under worst-case conditions, sustain a plasma for a sufficient duration to cause widespread damage to an electronics system. See Appendix 1 for additional background information on the tin whisker phenomenon

Report Format

This report includes two primary sections that document activities for the two phases of the TWICE program. Each section includes a 'D.X' section that describes the Materials and Methods" used in Phase X (in which Phase X is Phase 1 or Phase 2) and a 'E.X' section that describes the Results for that phase. These are followed by section E.3 that provides a Discussion of the results from both phases.

D.1 Phase 1 Materials and Methods

Overview

Figure 2 shows a summary of the Phase 1 TWICE program activities with task area leads identified with color-coding. The initial work focused on developing suitable ASG coatings and identifying appropriate ranges for process parameters to ensure robust coatings. Initial Material Development work included a series of Design of Experiments (DOE) in which coating formulations were deposited on glass slides and flexible substrates. The coatings and process ranges developed in this activity were used in follow-on Material/Surface Effects studies to finalize the formulations that would be used on the test vehicles. These initial coatings were also provided to Plasma Ruggedized Solutions for use in preliminary Process Integration studies to ensure that the materials could be applied in a manufacturing environment. Rockwell Collins assembled the Phase 1 Test Vehicles that were then divided into two groups for coating under a range of formulations and processing conditions at Rockwell Collins and PRS. These test vehicles were subjected to elevated humidity/temperature testing, to promote the growth of tin whiskers, and thermal cycling to assess coating robustness. In parallel, the University of Maryland tested Metal Vapor Arc samples coated with ASG and conventional coatings to assess the impact of these coatings on inhibiting tin whisker-induced metal vapor arc events. The remainder of this section provides details on the material formulation and process development, the procedures used to assemble, and the methods used to evaluate the test vehicles.

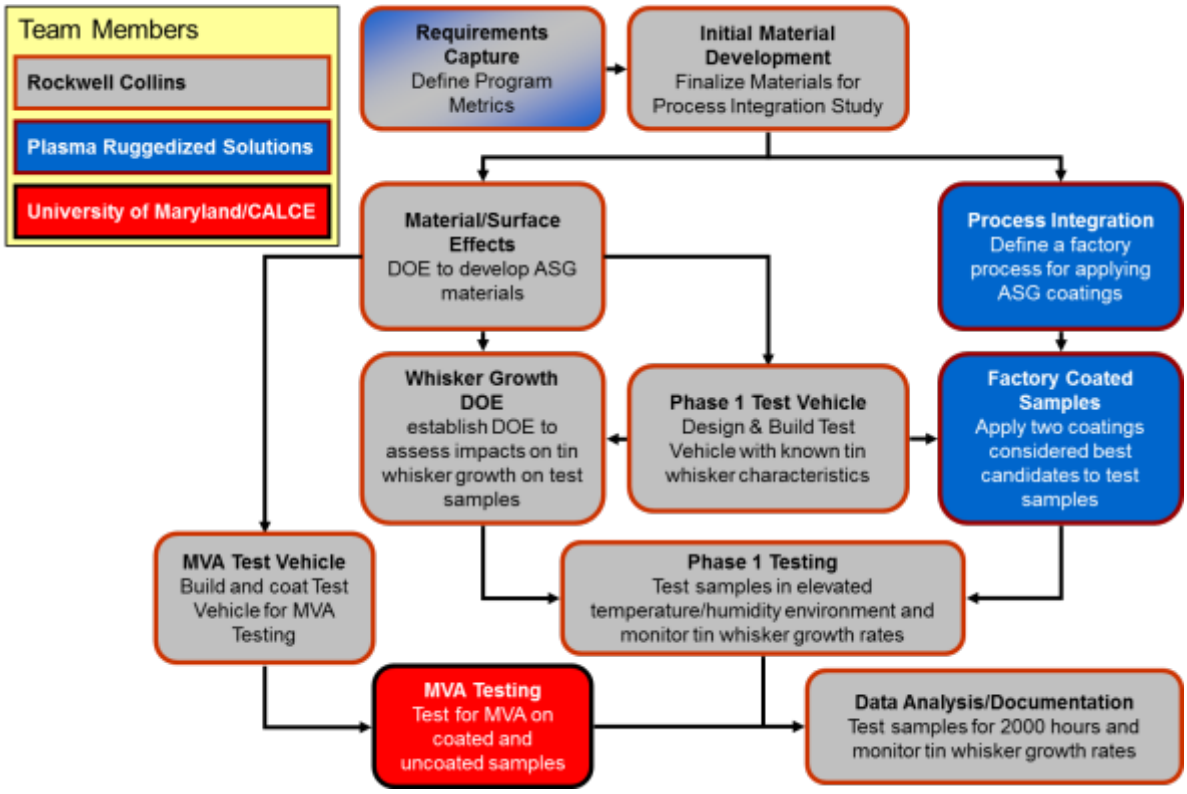

Figure 2 Phase 1 Project Flow

Initial Material Development & Material/Surface Effects Studies

The initial materials and process development for ASG materials primarily used glass microscope slides as the substrates for coatings. These slides were appropriate for this development work due to their low cost, the ease with which they can be handled, and their smoothness/flatness that simplified measurement of the coating thickness and roughness. A Design of Experiments to investigate deposition conditions and material formulations identified process control factors for systematically varying coatings to impact conditions at surfaces prone to tin whiskers.

Design of Experiments (DOE)

ASG Formulations

This study included two different formulations of ASG. Specific formulations of the ASG materials used in this study are proprietary to Rockwell Collins; therefore, they are not explicitly described in this document. Of the two materials, ASG4A has a lower r-value (the ratio of silica to alkali) and therefore has a lower elastic modulus, i.e., stiffness, and reduced durability that can potentially make it more susceptible to corrosion. **ASG5A** has a higher r-value, which makes it more durable but also potentially more brittle. To help differentiate between the two coating formulations in this document, ASG4A is generally shown in a normal font while **ASG5A** is shown underlined and with a bold font. See Appendix 2 for a description of ASG development activities at Rockwell Collins and Appendix 7 for a discussion on ASG formulations.

Deposition Methods

ASG materials were applied with the Asymtek Spectrum S-820 Spraying System, with an EFD 787 Micro Spray Valve, that is shown in Figure 3. This sprayer controls the location of the spray needle (in x, y, and z coordinates) by defining the needle height, the positions traveled by the needle while spraying, and the raster speed with which the sprayer travels. Material was deposited over a given surface by the sprayer passing over a region multiple times. These multiple passes were essential for producing a suitable coating with reasonable thickness (on the order of 1-10 microns). Work at Rockwell Collins has shown that applying unfilled materials in a single layer as thick as a micron leads to significant cracking in the coating as it cures.

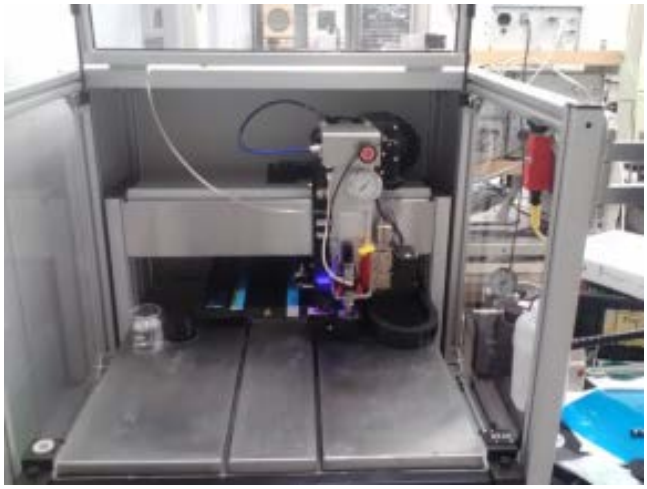

Figure 3 Asymtek Spectrum S-820 Spraying System

In a given application run, the spraying profile that was programmed into the S-820 established four primary process parameters: the area to be sprayed, the height of the spray tip above the surface, the number of spray passes over a given area, and the raster speed with which the sprayer moved. Since these parameters are controlled from a data file, their values can be changed during a given spraying run. Other process controls, such as the barrel pressure, the co-flow pressure, and the sprayed material, are manually set and therefore remained fixed during a spraying run. The barrel pressure is the pressure applied to the syringe that contains the coating material: the higher the pressure, the higher the flow rate of material. The co-flow pressure is the pressure of the air that 'co-flows' around the periphery of the needle while material is being sprayed: a high co-flow pressure increases the velocity of the co-flowing air. This increases the turbulence at the sprayed surface and reduces the static pressure at the nozzle tip, which increases the flow rate and the atomization/dispersion of the sprayed material. Parameters that define a given coating formulation include the specific recipe of the ASG material[1], the dilution (amount of deionized water mixed with the ASG materials), and what, if any, nanoparticle fillers are included in the liquid.

A final process control variable investigated in the initial DOE was the preparation of the glass slides prior to spraying. All glass slides were cleaned with soap and water and rinsed with deionized water. Following this, samples that received 'pre-treatment' were also subjected to a five-minute UV Ozone (UVO) process.

A primarily two-level (high and low treatments) DOE was conducted; as noted below, a third level for dilution was added to the test matrix during the study. All samples were sprayed with ASG4A with different levels of dilution. For the initial DOE studies, the formulations did not include any nanoparticles. Initial spraying tests were conducted to identify reasonable process ranges for each of the process parameter levels used (Table 1).

Table 1 Initial DOE Parameter Levels

Parameter	Units	Low	High
Number of spray passes	n/a	10	20
Height of spray tip above surface	inches	0.75	1.75
Barrel pressure (on sprayed fluid)	psi	0.15	0.5
Co-flow pressure (on co-flow stream)	psi	5	15
Raster speed of sprayer	inch/sec	5	10
Dilution: mass of water/mass of ASG	g/g	15	60[2]
Pre-treatment of surface	n/a	None	UV Ozone

[1] ASG formulations include one or more alkali silicate materials that include potassium, lithium or sodium

[2] Initially, the high value for dilution was set to 30:1, water:ASG. The first round of samples showed that dilution affected the results to a significant degree, so the test matrix was adjusted to include a higher dilution value of 60:1 to better assess this parameter.

The procedure for conducting a spraying test began by cleaning and, if designated for the test, pre-treating the glass slides. A portion of each slide was masked with tape that could be subsequently removed after spraying to allow for coating thickness measurement. Coating runs were generally conducted with eight slides positioned in the bed of the Asymtek S-820. Typically, four of the slides had no pre-treatment while the other four were pre-treated with UV Ozone. The four slides in a given set were then each coated with a different combination of tip height and number of passes. Following the deposition of the material onto the glass slides, they were removed from the spraying platform and cured at 125°C for 1 hour.

Evaluation Methods

Once the coatings had been deposited and cured, measurements were conducted to determine the thickness and roughness of the sprayed surface and tape-peel tests were used to qualitatively assess the adhesion of the coating.

Surface Measurements

The process of making surface measurements on the glass slides began by removing the tape that masked a portion of the slide and then measuring the coating with a Tencore Instruments Alpha-Step 200 Profilometer. The measurement profile would begin on the portion of bare glass that had been under the tape and continued across a distance of coated material; this allowed the material thickness to be measured. In addition, the profilometer characterized the coating roughness in terms of a root-mean-square (RMS) value as well as a maximum peak-to-valley. Three individual profilometer measurements were made on each sample of material. Figure 4 shows an example of a typical measurement.

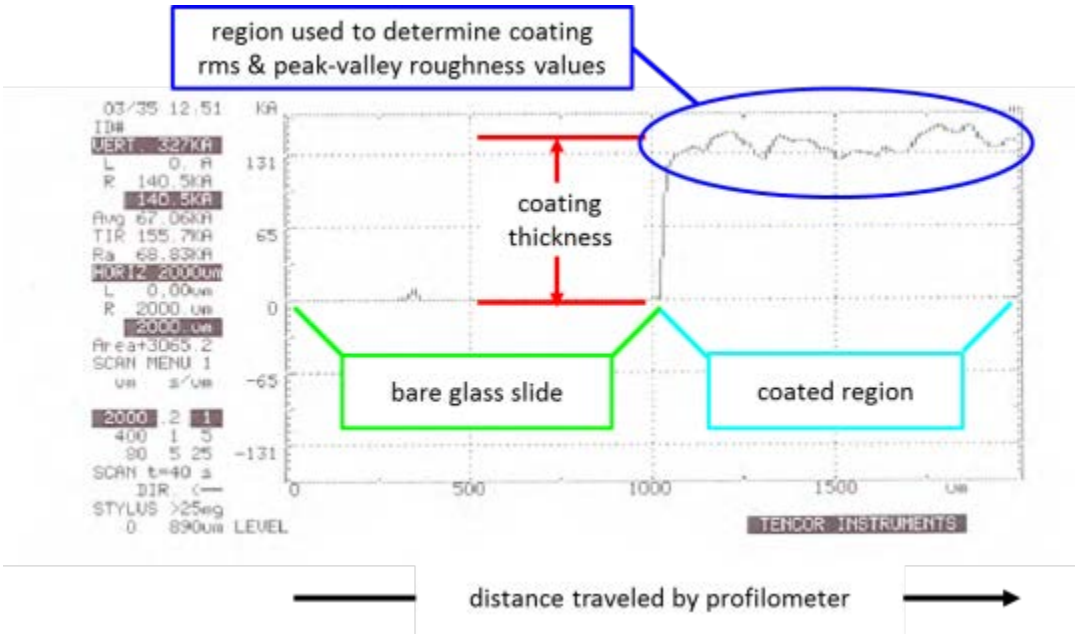

Figure 4 Typical Profilometer Measurement

Adhesion Tests

To assess the adhesion of the material to the glass substrates, conventional 'tape tests' were conducted on the sample. For this test, strips of Scotch and Kapton tape were applied to the coating, pressed down, and then removed by pulling on the end of the tape. This is a qualitative, pass/fail test that provides a relative assessment as to whether the coating is well adhered to the substrate. Generally, the adhesive on the Scotch tape is weaker than that of the Kapton, so if a coating passes the Kapton tape test it will likely pass the Scotch tape test.

Glass Slide DOE Results

Effect of Pre-treatment

Initial deposition runs all included sets of glass slides that were not treated with UV Ozone (UVO) prior to spraying. Visual inspection of these slides showed significant flaking and peeling due to poor coating adhesion. Because of the poor quality of the coatings on non-pretreated test samples, they were not characterized for thickness and roughness. All data shown in the following section for coatings on glass slides are for samples that received five minutes of UVO prior to spraying.

Effects of Process Parameters

Figure 5 shows an interaction chart for the coating thickness that resulted from the various combinations of process parameters used in this DOE. In general, Tip Height had relatively little influence on the thickness while dilution tended to have the most significant effect.

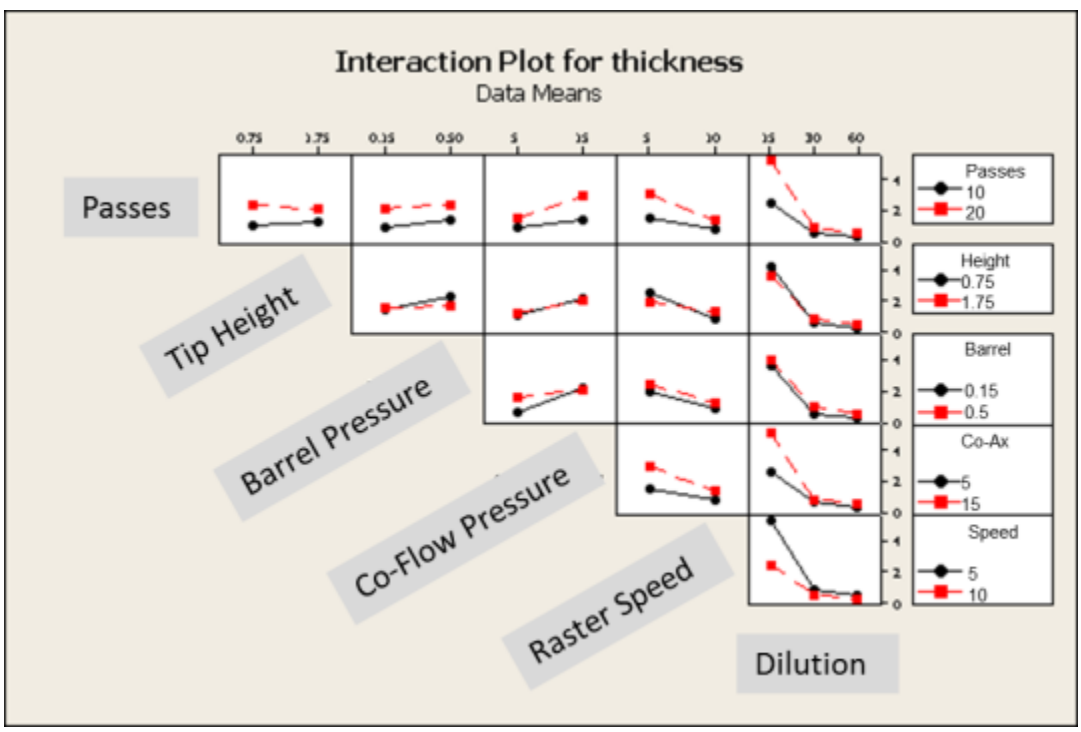

Figure 5 Interaction Plot for Coating DOE: Coating Thickness

The table below shows an Analysis of Variance (ANOVA) and Regression Model of the coating thickness data. This indicates that all of the parameters included in the ANOVA (with tip height not included) were significant in affecting coating thickness.

Analysis of Variance

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	179.299	179.299	35.860	235.034	0.0000000
passes	1	12.078	12.078	12.078	79.164	0.0000000
barrel	1	13.970	13.970	13.970	91.561	0.0000000
coax	1	13.722	13.722	13.722	89.938	0.0000000
rastor	1	13.850	13.850	13.850	90.780	0.0000000
dilution	1	125.678	125.678	125.678	823.726	0.0000000
Error	138	21.055	21.055	0.153		
Lack-of-Fit	42	17.391	17.391	0.414	10.848	0.0000000
Pure Error	96	3.664	3.664	0.038		
Total	143	200.354				

Regression Model

Term	Coef	SE Coef	T	P
Constant	4.40927	0.395285	11.1547	0.000
passes	0.83565	0.093921	8.8974	0.000
barrel	0.51740	0.054072	9.5688	0.000
coax	0.56197	0.059257	9.4836	0.000
rastor	-0.89486	0.093921	-9.5278	0.000
dilution	-1.65070	0.057515	-28.7006	0.000

S = 0.390606; R-Sq = 89.49%; R-Sq(adj) = 89.11%; PRESS = 22.8683; R-Sq(pred) = 88.59%

Best Fit: ln(thickness)= 4.40927 + 0.835651 ln(passes) + 0.5174 ln(barrel) + 0.561973 ln(coax) - 0.894862 ln(raster) - 1.6507 ln(dilution)

$$\text{i.e.,}\quad thickness = 82.2 * \frac{passes^{0.836} barrel^{0.517} coax^{0.562}}{raster^{0.895} dilution^{1.65}}$$

Limiting the coefficients to whole fractions produces a curve fit of:

$$coating\ \ thickness\ \ (in\ \ microns) \approx 0.59 + 200 * \frac{\#\ passes^{1.5} * coax\ \ pressure}{barrel\ \ pressure^{0.25} * raster\ \ speed^{1.5} * dilution^{3}}$$

An interaction plot for the roughness is shown in Figure 6. This shows that Tip Height, Barrel Pressure and Co-Flow Pressure generally had little impact on the roughness.

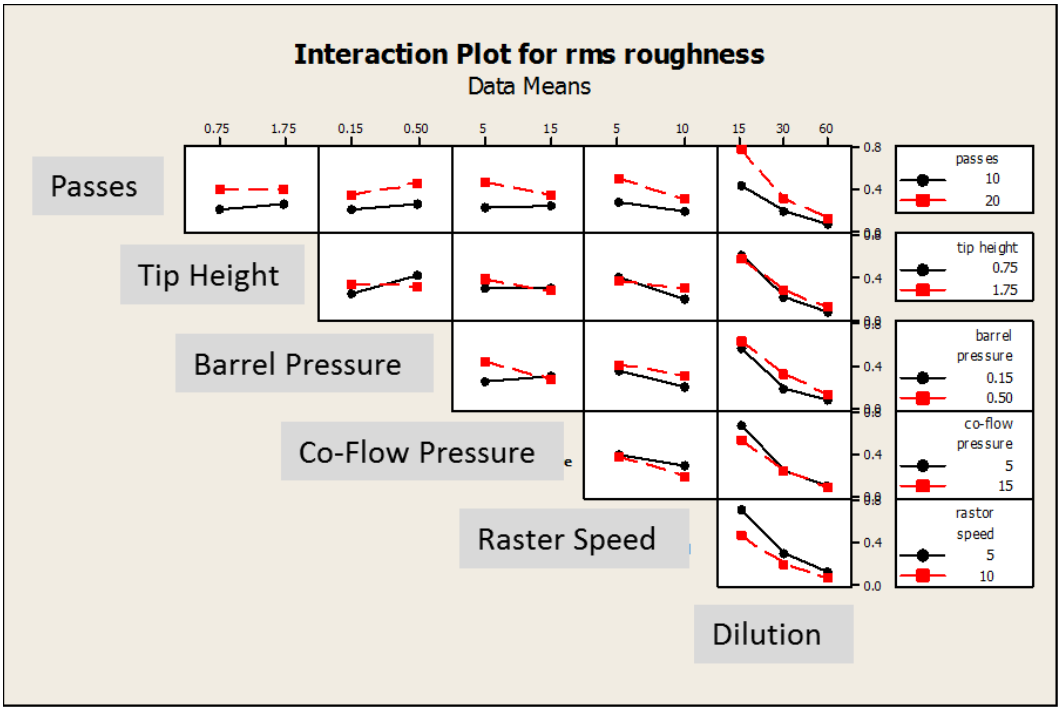

Figure 6 Interaction Plot for Coating DOE: Coating Roughness

A curve fit of the data to estimate the rms roughness of the coatings is shown below.

$$coating\ \ rms\ \ roughness\ \ (in\ \ microns) \approx 0.14 + 46.6 * \frac{\#\ passes}{raster\ \ speed * dilution^2}$$

Appendix 3 provides the complete set of thickness and roughness data collected in this DOE.

Flexible Substrates

In addition to the deposition process development work conducted on glass slides, coating was also sprayed onto samples of 2-mil thick polyethylene terphalate (PET) film. The goal of this spraying was to determine whether the adhesion of a given ASG coating was similar for the organic PET film as with the glass slides. The adhesion of the ASG to the PET was poorer than it had been on the glass slides, so alternative pre-treatment methods were investigated. This investigation showed that a light (3 minute) plasma etch using a PVA TePla M4L, RF Plasma system (13.56MHz) with 100SCCM Oxygen and 20SCCM CF4 at 100W provided excellent adhesion of the ASG materials to the PET as well as glass slides and tin-plated surfaces. Subsequent coating applications in nanocomposite developments and on test vehicles utilized this plasma etch recipe rather than UV Ozone.

In addition, coating the materials to the PET film also provided a qualitative indication of the residual stresses that formed within a given coating as it cured. The PET films were taped at their perimeters to a mounting plate during the spraying and curing processes. When this tape was removed, samples with coatings that had high internal stresses would curl – in some cases quite significantly. Coating samples that produced highly curled PET samples were considered to have excessive stresses and not to be suitable for tin whisker evaluation studies.

Nanocomposite Coatings

After establishing the baseline formulations and process ranges, the study investigated methods for incorporating nanoparticles into the coatings. Various dilution ratios for the ASG and mass loadings of nanoparticle to cured ASG were applied to slides with 10 and 20 passes. Table 2 shows examples of some of the results from the nanocomposite coating development work. These test samples were sprayed with **ASG5A** as the matrix material, a needle height of 0.75 inches, barrel pressure of 0.5 psi, co-flow pressure of 15 psi and a rastor speed of 5 inches/second.

Table 2 Typical Test Results for Nanocomposite Coating Development Work

Nanoparticle	Loading (1)	# of Passes	Dilution (2)	Thickness (microns)	Peak to Valley (micron)	Roughness RMS (microns)	Tape Test Results
Zinc Oxide	1:1	10	30:1	1.88	1.825	0.375	passed
Zinc Oxide	1:1	20	30:1	4.07	4.475	0.665	failed
Zinc Oxide	2:1	10	30:1	3.76	2.975	0.64	passed
Zinc Oxide	2:1	20	30:1	7.305	3.78	0.78	passed
Zinc Oxide	3:1	10	30:1	4.135	2.98	0.555	passed
Zinc Oxide	3:1	20	30:1	8.565	2.88	0.445	passed
Zinc Oxide	4:1	10	30:1	7.625	3.085	0.575	passed
Zinc Oxide	4:1	20	30:1	13.49	1.61	0.35	passed
Al Oxide	1:1	10	30:1	2.505	3.04	0.51	passed
Al Oxide	1:1	20	30:1	5.45	3.57	0.865	passed
Al Oxide	2:1	10	30:1	6.68	3.46	0.62	passed
Al Oxide	2:1	20	30:1	11.57	2.83	0.485	passed
Al Oxide	4:1	10	240:1	1.125	0.625	0.125	passed
Al Oxide	4:1	20	240:1	2.335	0.66	0.155	passed
Al Oxide	6:1	10	240:1	0.915	0.455	0.085	some particles removed
Al Oxide	6:1	20	240:1	1.925	1.185	0.245	some particles removed

Notes:
(1) Mass ratio of particle loading to cured ASG
(2) Mass ratio of water to ASG material

Figure 7 shows magnified images of some of the coating test samples generated during the development work on the nanocomposite materials. This shows that the larger zinc oxide (with particle sizes of 40 nm) tended to have less uniform deposition than the smaller aluminum oxide particles of 10 nm particle sizes. Also, the coatings with 20 passes tended to exhibit more cracking than the thinner coatings that only had 10 passes. See Appendix 8 for a discussion on factors that influence the use of nanoparticles in these ASG composites.

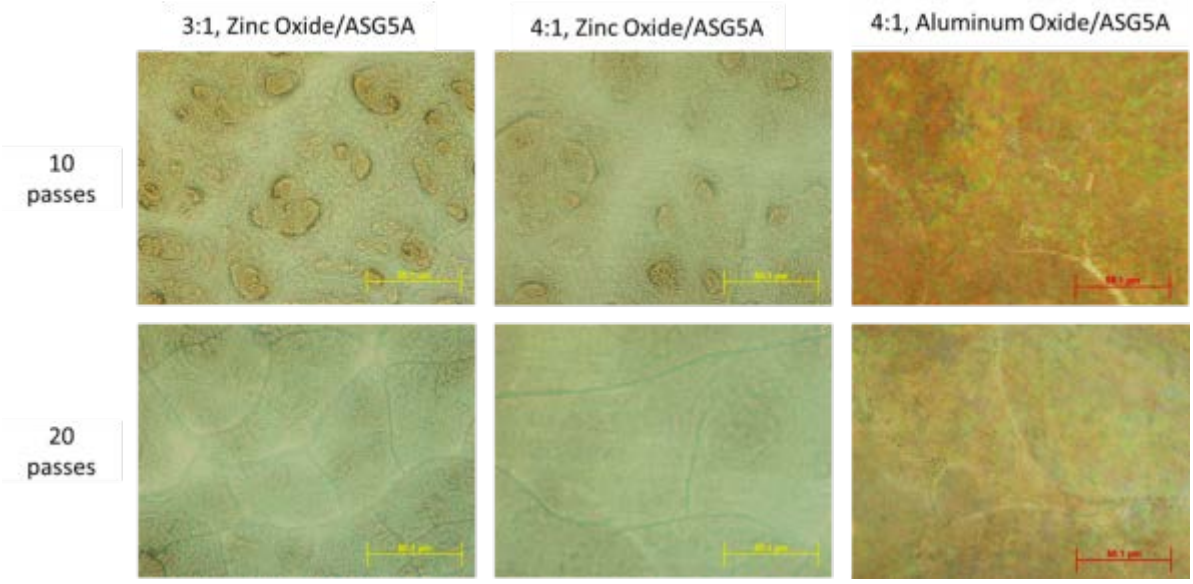

Figure 7 Typical Nanocomposite Coatings (at 100x Magnification)

Test Articles

Simulated SOIC Package, a.k.a. 'Tin Man'

In prior tin whisker research [3], Rockwell Collins established the use of the simulated small outline integrated circuit (SOIC) package (Figure 8) for tin whisker investigation. This test device is fabricated by etching multiple samples in a copper sheet that is subsequently plated with bright acid tin. Individual components are then cut from the copper sheet and the leads are bent to simulate the geometry of conventional SOIC components that are commonly used on a variety of electronic assemblies. This approach of using a simulated SOIC allows for full process control for investigating the effects of plating, lead forming and conditioning parameter variations. In addition, the low cost of these components relative to actual SOICs allows a larger number of test samples to be tested.

Because the SOIC test sample essentially consists of tin plated metal, it is informally referred to as 'Tin Man'. The small size of the 'Tin Man' device facilitates Scanning Electron Microscopy (SEM) examination, which is critical for accurately quantifying and documenting tin whisker growth. Rockwell Collins employs a bright acid tin plating bath, which serves as a consistent, reproducible tin whisker generator, as a control condition for tin whisker investigations. The organics that are co-deposited by the bright acid bath generate internal plating stress with plated tin grain size that correlates to tin whisker initiation predictions [4].

Simulated SOIC Component	
Material Requirements	Copper per ASTMB152
	Chemical Etch
	Finish: 0.010 inch Copper Electroplate and Bright Acid Tin Plate
	Bend After Plating

Figure 8 Simulated SOIC Tin Whisker Test Vehicle (a.k.a. 'Tin Man')

Phase 1 Test Vehicle

Assembly Build

Test vehicle assemblies included four of the simulated SOIC devices soldered to a 2”x2” FR-4 circuit board with a single layer of 1 oz. copper patterned with pads for the four devices. Devices were hand soldered to these circuit boards at the four corner leads with the remaining leads left unattached (Figure 9).

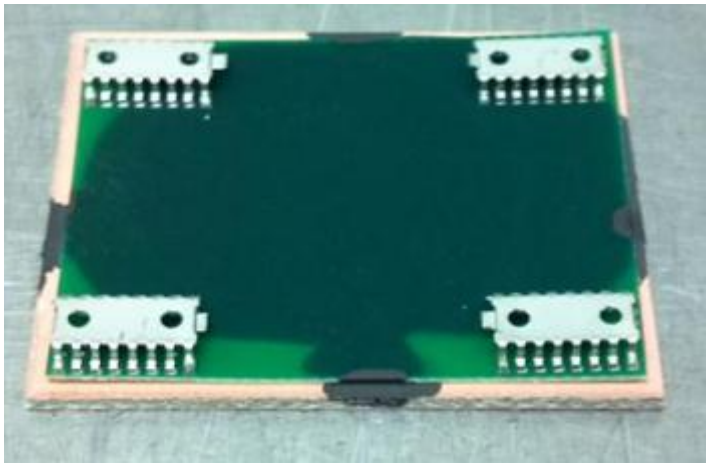

Figure 9 Tin Whisker Test Vehicle Containing Four Tin Man Devices

Coating

Coating Application

A total of 211 assemblies, each with four Tin Man devices, were produced for the Phase I effort. Of these, Ruggedized Plasma Solutions coated 70 assemblies with conventional and ASG materials while 141 remained at Rockwell Collins for coating. The objectives of coating test vehicles at both locations were to a) quantify the sensitivity of location and processes on the tin whisker mitigation effects of coatings and b) identify any issues that could inhibit transitioning ASG coatings for tin whisker control to a production conformal coating environment.
Test vehicle combinations are summarized in Table 3. This indicates the basic coating material, what nanoparticles were included (if appropriate), the types of samples that were produced, and the location(s) at which a given coating combination was applied.

Table 3 Test Vehicle Coating Combinations

Combination	Coating	Nanoparticle Mixture (1)	Samples (2)	Coater: (3)
1	None	n/a	A & B	N/A
2	ASG4A	none	A & B	RC & PRS
3	ASG5A	none	A & B	RC & PRS
4	Acrylic/ASG4A (4)	none	A & B	RC & PRS
5	Acrylic/ASG5A (5)	none	A & B	RC & PRS
6	Acrylic	n/a	A & B	RC & PRS
7	Parylene	n/a	A & B	RC & PRS
8	ASG4A	4:1/Alumina Oxide/10 nm / 0.5μm	A only	RC only
9	ASG4A	4:1/Alumina Oxide/10 nm / 2.0μm	A only	RC only
10	ASG5A	8:1/Alumina Oxide/10 nm / 0.5μm	A only	RC only
11	ASG5A	8:1/Alumina Oxide/10 nm / 2.0μm	A only	RC only
12	ASG5A	3:1/Zinc Oxide/40 nm / 0.5μm	A only	RC only
13	ASG5A	3:1/Zinc Oxide/40 nm / 2.0μm	A only	RC only
14	ASG4A	3:1/Alumina Oxide/40 nm / 2.0μm	A only	RC only
15	ASG5A	3:1/Alumina Oxide/40 nm / 2.0μm	A only	RC only
16	ASG4A	3:1/Zinc Oxide/40 nm / 0.5μm	A only	RC only

Notes:

(1) Nanoparticle mixture details indicate mass ratio of nanoparticles to cured ASG material / nanoparticle material / nanoparticle size / nominal coating thickness

(2) "A" samples removed once from 85/85THC for single evaluation, "B" samples returned to chamber for additional exposure.

(3) RC: samples coated at Rockwell Collins, PRS: samples coated at Plasma Ruggedized Solutions

(4) Unfilled ASG4A coating applied as a primer for subsequent acrylic coating

(5) Unfilled ASG5A coating applied as a primer for subsequent acrylic coating

Rockwell Collins coating processes for ASG materials utilized the same equipment and methods used in the 'glass slide DOE' that was previously described. Based on the results of the preliminary DOE, the ASG materials used on the test vehicles were deposited using application settings of: barrel pressure of 0.5 psi, coax pressure of 15 psi, rastor speed of 5 inches/second, and tip height of 0.75 inch. The ASG dilution level corresponds to the weight ratio of DI (deionized) water to dry ASG material in the formulation. Prior to the application of the coatings, test vehicles were pre-treated with the plasma etch recipe. Table 4 shows the specific application process used for each coating combination and the resulting coating thickness and roughness for each.

Table 4 Application Processes used for Test Vehicles Coated at Rockwell Collins

Combination	Coating Process Description	Thickness (μm)	Roughness (RMS) (μm)
1	Uncoated	n/a	n/a
2	ASG4A 30:1 dilution, 5 passes	Not Measured	Not Measured
3	ASG5A 30:1 dilution, 5 passes		
4	Combination #2 (ASG4A) applied, followed by application of Combination #6		
5	Combination #3 (ASG5A) applied, followed by application of Combination #6		
6	Humiseal 1B31 acrylic, manually sprayed in production process, nominal thickness of 1-3 mils (25-73 microns)		
7	Batch process Galxyl "C" formulation Parylene production process with nominal thickness of 0.5 mil (12.7 microns)		
8	ASG4A 240:1 dilution, 4 passes	0.735	0.055
9	ASG4A 240:1 dilution, 18 passes	1.870	0.105
10	ASG5A 240:1 dilution, 4 passes	0.720	0.140
11	ASG5A 240:1 dilution, 18 passes	1.635	0.170
12	ASG5A 60:1 dilution, 3 passes	1.105	0.235
13	ASG5A 60:1 dilution, 10 passes	2.525	0.515
14	ASG4A 60:1 dilution, 4 passes	2.035	0.395
15	ASG5A 60:1 dilution, 4 passes (note: nozzle was clogged when spraying was completed so it is likely that less than 4 passes were actually applied)	1.295	0.215
16	ASG4A 60:1 dilution, 3 passes	1.290	0.190

Testing

Elevated Humidity/Temperature

Rockwell Collins has utilized the JEDEC JESD201 specification [5] Class 2 criteria as a required segment of the product design protocol for tin whisker risk assessment. The JESD201 specification defines the conditioning, inspection and tin whisker dimensional acceptability requirements. This specification is not universally accepted across the High Performance electronics community; some consider the results of this testing to only be appropriate for characterizing a specific plating bath or component lot evaluation for tin whisker susceptibility. However, Rockwell Collins, along with many others in the industry, feels that the specification requirements provide an industry-consistent indicator of the capabilities and consistency of the processes used by the component fabricator. Specifically, Rockwell Collins has concluded that the JESD201 high temperature/high humidity condition exposure provides a reliable measure of tin whisker initiation and growth that is in good agreement with published data [6].

In many studies, tin whisker samples are removed from humidity testing for tin whisker growth measurements, placed back into the test environment, and data are reported in terms of

cumulative time in humidity. Some studies [7] have suggested that the process of removing samples from the chamber may 'reset' the whisker growth mechanisms and samples with 4000 consecutive hours of humidity exposure won't necessarily exhibit the same whisker growth as samples that have been periodically removed from the test chamber for measurement processes. This issue can be addressed relatively easily with uncoated samples by simply leaving some samples in the chamber for continuous exposure while other samples are periodically removed (a.k.a. 'interrupted exposure') for evaluation.

Conformal-coated samples, however, generally must have an angstroms-thick gold coating evaporated onto them for SEM inspection to prevent electrical charging. Although this gold coating is very thin and on the outer conformal coating surface, it is possible that its presence affects the tin whisker initiation and growth behavior. Studies at Rockwell Collins have shown that ASG coatings are sufficiently thin that they can be inspected in the SEM without metallization. Thus, because the potentially confounding factor of metallization application and removal are not necessary with ASG, these coatings provide a means to assess whether the 'reset' effects, which have been noted in other studies, will still occur. Therefore, to quantify the effect of this 'reset', this study included ASG coated samples that had continuous exposure to temperature/humidity conditioning as well samples that were periodically removed from the chamber for growth measurements and then replaced.

Rockwell Collins conducted JESD201 specification testing using an 85°C/85% Relative Humidity (RH) Temperature/Humidity Conditioning (85/85THC) with a minimum of eight complete sets of test vehicles for each combination studied. Of these eight 'Set A: Continuous Exposure' test vehicles, one test vehicle was removed from the chamber after every 500 hours of 85/85THC exposure and evaluated using scanning electron microscopy (SEM) inspection to measure tin whisker formation and growth. Once an 'A' test vehicle was removed and inspected, it was maintained in a dry nitrogen environment and not subjected to further 85/85THC. In addition to the 'A' samples, many of the combinations included one set of test vehicles, 'Set B: Interrupted exposure' that were removed after every 500 hours of 85/85THC, inspected, and then returned to the temperature/humidity chamber for continued tin whisker growth. Test samples were subjected to a total of 4000 hours of 85/85THC.

Temperature Cycling

One potential failure mechanism for any conformal coating relates to the stresses induced by coefficient of thermal expansion (CTE) mismatch between the coating and the substrate to which it is applied. To assess the impact of thermal stresses on the reliability of the coatings, thermal cycle conditioning was conducted in accordance with the IPC-9701 specification. In this test, samples were subjected to a -55°C to 125°C temperature range with a temperature ramp rate range of 5-10°C per minute and 15 minute dwells at each temperature extreme. As shown in Figure 10, these test constraints led to a cycle time of approximately 100 minutes. The test vehicles were removed after every 500 cycles for scanning electron microscopy (SEM) inspection to measure tin whisker growth rates. A total of 1500 thermal cycles were completed.

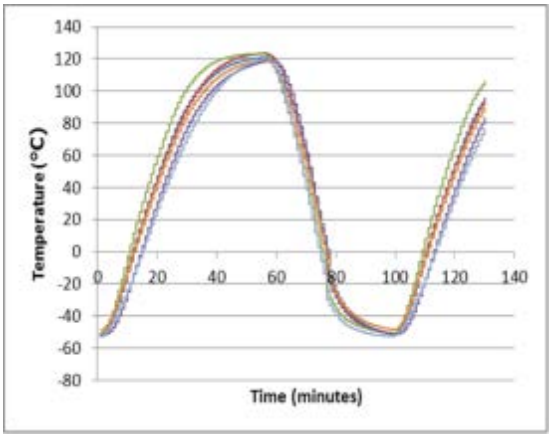

Figure 10 Thermal Cycle Temperature Profile (individual locations in chamber monitored)

Metal Vapor Arc Testing

Rockwell Collins collaborated with the University of Maryland to investigate the impact of conformal coatings, including ASG-based materials, on inhibiting tin-whisker-initiated Metal Vapor Arc (MVA). Tin whiskers can be the root cause of this electronic failure phenomenon, in which a tin whisker forms an electrical bridge between the two surfaces with a voltage potential. Under extreme conditions of high voltage potential and low atmospheric pressure, the tin whisker can vaporize and form an electrically conductive plasma, i.e. arc, that can sustain current flow for a sufficient duration to cause system-level damage to the electronics. The goal of this effort was to assess the effectiveness of various coatings on preventing MVA.

Testing used a standard MVA test vehicle and test protocol, which had been previously established by the University of Maryland. In this test procedure, tin whiskers harvested from known whisker-producing surfaces are carefully attached, using an electrically conductive adhesive, to two copper electrodes to form an electrical bridge (see Figure 11). The tin whisker is characterized in terms of its electrical resistance and then subjected to a pre-defined voltage to determine if a MVA can be initiated and sustained. A high-speed Phantom v210 camera using a 180 kHz frame rate recorded the MVA event. Different samples are tested with different voltage levels to identify the voltage required to initiate an arc (in which the tin whisker emits visible light and ultimately is destroyed) while the high-speed camera results measured the duration of the arcing event to determine if a plasma arc was sustained after the whisker had been consumed.

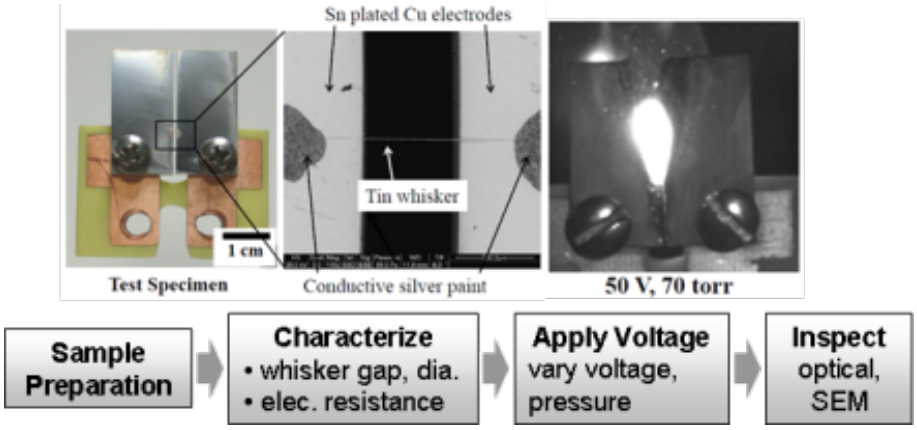

Figure 11 Metal Vapor Arc Testing

The preparation of the test vehicles for the MVA testing required coordination between the University of Maryland, which applied the tin whiskers and conducted the testing, and Rockwell Collins, which applied various coatings to the test vehicles. Two configurations were tested in this study: a) coated whisker: whiskers attached to the electrodes before the assembly was coated and b) coated surface: one electrode was coated and a whisker, which was attached to the other uncoated electrode, was physically placed against the coated surface. Both conventional acrylic conformal coating and ASG-based coatings were applied to test vehicles.

The process of shipping test vehicles between the two sites, combined with the delicate nature of the microscopic tin whiskers, led to a relatively low yield of samples that could be tested (18 in all). The testing found that coated whisker samples would arc[3] if a sufficient voltage difference (>5V) was applied across the whisker. However, the arc was contained within the coating and no sustained plasmas were observed. Two samples of the "coated surface" test vehicles did experience an arcing phenomenon; however, in both of these cases a measureable electrical resistance between the two electrodes had been identified prior to the voltage being applied. Thus, the coating did not provide a sufficient dielectric protective layer to prevent electrical conduction.
Overall, the MVA study showed that conformal coating does not prevent MVA unless it provides electrical insulation to prevent electrical connection between the tin whisker and one of the surfaces. If a tin whisker is encapsulated within a conformal coating, arcing can still occur; however, there is an extremely low probability that a sustained arc will be established. The type of conformal coating used does not appear to significantly impact the effect of conformal coating on tin whisker induced MVA. The Phase I Results section of this report provides a summary of the MVA study data; a full discussion of the work conducted by the University of Maryland is included in Appendix 4.

Scanning Electron Microscopy (SEM) Test Vehicle Assessment

An Amray FE 3300 SEM was used to document the test vehicle tin whisker densities and lengths. The tin whisker densities and lengths were determined from SEM images at five locations for each Tin Man specimen (four SOIC leads and one flat region) at 40X and 302X magnifications at a 21.1° angle. At each of these locations, the number of whiskers in each of three randomly selected areas was counted through visual inspection of the SEM image. The lengths of the longest three whiskers (with lengths of at least 40 microns) in a location were also recorded. Figure 12 illustrates the SEM Tin Man assessment locations and representative areas for local tin whisker assessment. While data were collected for the 'flat' region (location #5), the reduced stresses at this location led to far fewer tin whiskers being generated. Therefore, the majority of the data reported in this document refer to results at locations 1-4 on the lead bends.

[3] In this testing, a sample was considered to arc if visible light was observed at the tin whisker.

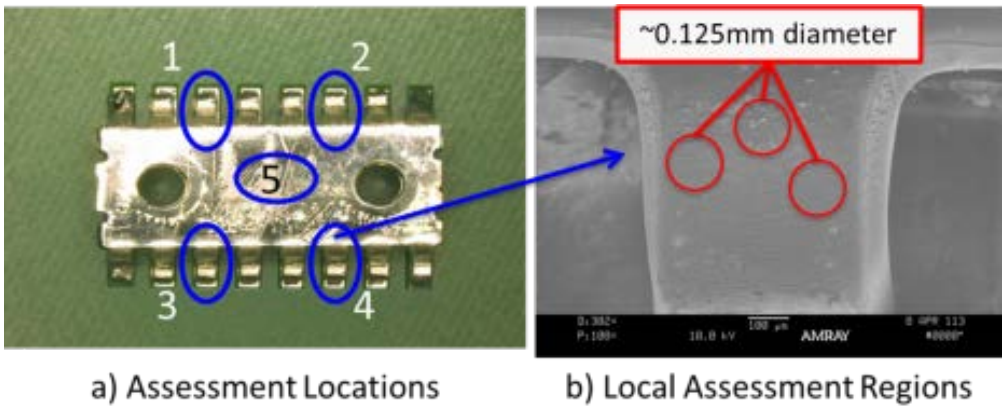

Figure 12 SEM Tin Man Assessment Locations

The primary focus of the whisker assessments was to determine the whisker density by counting the whiskers within each of the prescribed areas. The combination of the typical whisker diameter and the size of the inspection zone limited the number of whiskers that could be quantified within a given area. Once 20 whiskers were counted within an assessment region, it was considered to be 'saturated' such that a higher density could not reliably be determined.

Four tin man components were mounted to each test board, four leads were assessed on each component, and tin whisker density was determined in three separate regions on each lead. Thus, 48 (4 x 4 x 3) individual regions were evaluated for each test combination and each conditioning level (hours of 85/85THC).

Figure 13 shows examples of visual inspections for tin whiskers on leads and indications of the numbers and locations of whiskers. Figure 13 c) is an example of a 'saturated' sample in which the region within the ~0.125mm diameter circle contained at least 20 whiskers. Each assessment location included three of these circles, with specific locations randomly defined in the same general region relative to the bend in the lead.

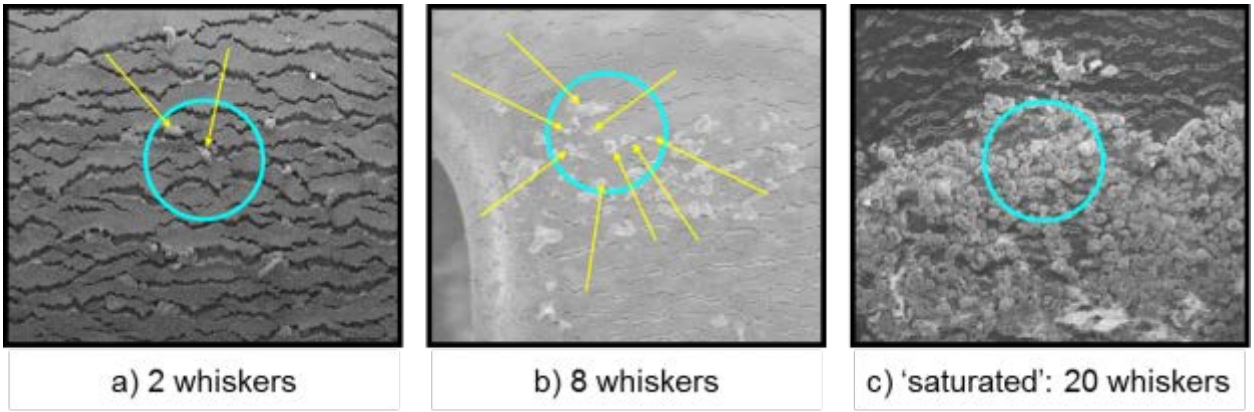

Figure 13 Example Tin Whisker Assessment Results

E.1 Phase 1 Results

Test Results

Coating Morphology Observations

Figure 14 illustrates one method by which coatings help to mitigate tin whiskers. Figure 14a) shows an uncoated lead at the upper bend of the component lead. A number of cracks in the tin surface finish are clearly apparent. These are a result of the standard process of plating the leadframe prior to its being singulated and having the individual leads formed by bending. In contrast, Figure 14b), which shows a similar lead that has been coated with a nanofilled ASG material, exhibits far fewer cracks and crevices than the uncoated lead.

Prior investigations, as well as the tin whisker assessments conducted in this program, have shown that tin whiskers invariably initiate at a stress concentrator such as a scratch, crack or crevice. ASG coatings fill these features with material, which has a relatively high modulus (once cured), that redistributes these local stresses to reduce the formation of tin whiskers. This is particularly true for materials filled with particles that are small enough to fill these defects in the tin surfaces to provide further reinforcement that reduces stress concentrations.

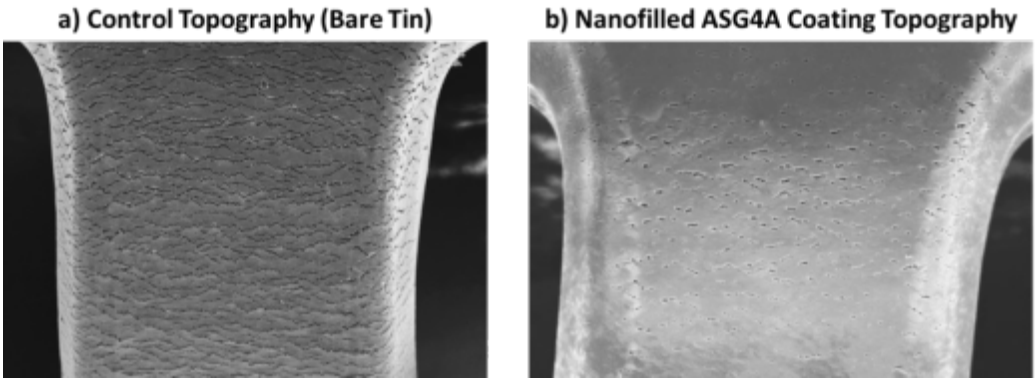

Figure 14 Effect of Coating on Surface Cracks at Lead Bends

In addition to reducing local stress concentrations, coatings are expected to provide a barrier layer between the surface finish and its surroundings to reduce chemical reactions,that can promote the growth of tin whiskers. This type of barrier coating needs to provide complete coverage and be sufficiently robust that it does not degrade after environmental exposures. Furthermore, since increased stress in the tin will promote the growth of tin whiskers, it is important that the coatings do not create localized stress concentrations such as those that could occur at cracks within the coating. Figure 15 shows the two coatings (ASG4A and **ASG5A**) at 302X magnification after 500 hours of exposure to 85/85 temperature/humidity conditioning. While both coatings exhibit at least some cracking, it is clear that the **ASG5A** has a much higher degree of cracking. The **ASG5A** material is harder and has a higher modulus than the ASG4A, which can make it more susceptible to cracking. This cracking can lead to higher tin whisker growth rates due to both the degraded local coverage at the surfaces and the stress concentrations occurring at the tin surface finish regions at these cracks.

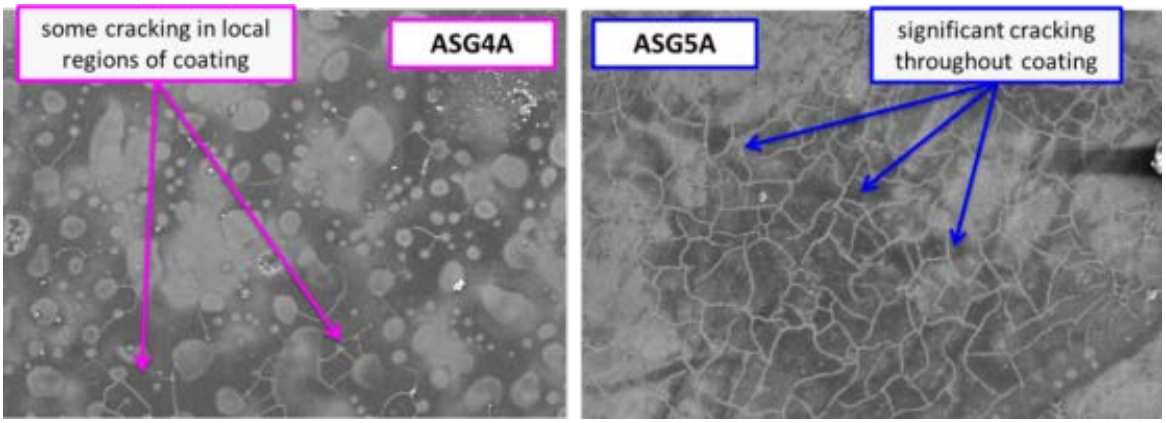

Figure 15 Cracks in Coating after 500 Hours of 85/85THC Conditioning

As discussed previously, an additional factor that could influence the long-term effects of ASG coatings on tin whisker mitigation is the potential degradation of the coating due to coefficient of thermal expansion (CTE) mismatch between the coating and the metal surface. Glass materials tend to have a very low CTE relative to metal leads; therefore, temperatures excursions would generate stresses within the coating that could lead to cracking. Thermal cycle was conducted to evaluate this potential effect. Figure 16 shows an example of an image at 302X magnification of an ASG4A coating after 1500 thermal cycles. While some cracks are visible in this image, the level of cracking was relatively low and no spalling of the ASG coating was observed in this sample as well as all the other samples evaluated after thermal cycle conditioning.

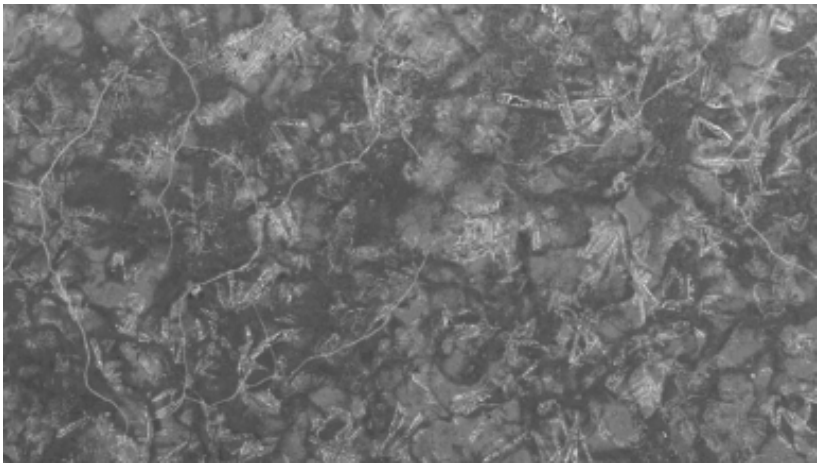

Figure 16 ASG4A Coating after 1500 Thermal Cycles

Tin Whisker Morphology Observations

The morphology of tin whiskers is a well-understood and well-characterized topic. Tin whiskers can initiate and grow as a number of crystallographic structures such as odd shaped eruptions that are curled or even scalloped. However, the traditional and more typical tin whisker structure is a straight, needle-like form with grooved striations. Figure 17 illustrates some of these crystallographic structures.

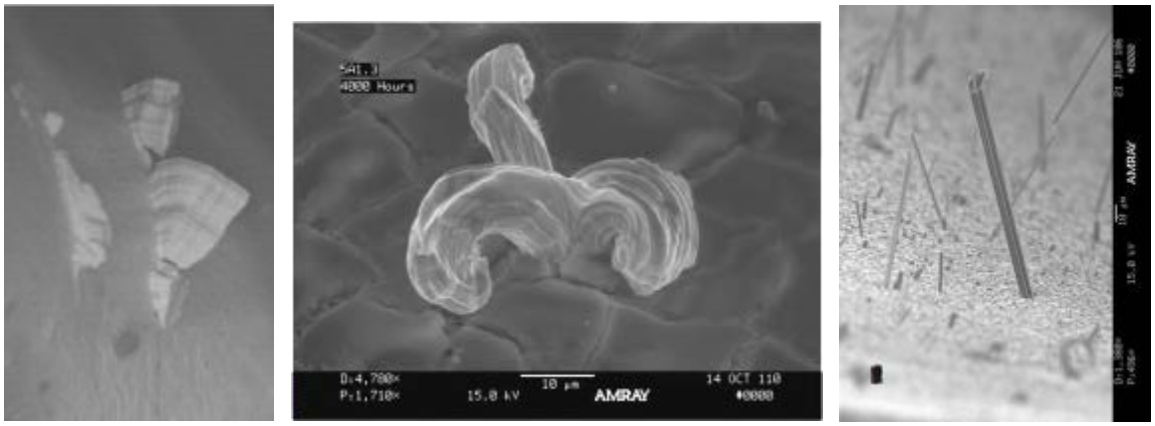

Figure 17 Tin Whisker Structures: Left – Scalloped [7], Middle – Curled, Right – Needle

Tin whisker morphologies observed in this study tended to be significantly affected by the coatings that were applied to the tin surface, as shown in Figure 18. Whiskers that grew on uncoated tin surfaces tended to be conventional needle crystalline structures emanating from cracks within the tin surface. Figure 18a shows that while the structures often had kinks, curls and bends, they tended to have reasonably straight regions with lengths of at least tens of microns. In comparison to these 'blades of grass' that grew on uncoated (control) tin surfaces, the samples coated with ASG materials tended to have whiskers that were more 'mushroom-like' with short stems that were often capped with ASG material, as shown in Figure 18b. The tin whiskers on samples coated with traditional conformal coating materials, such as acrylic, appeared to be similar to the whiskers growing on uncoated control surfaces. However, in these cases the soft acrylic coating temporarily contained the whiskers that only began to push through the coating after ~1000-1500 hours of elevated temperature/humidity conditioning (Figure 18c).

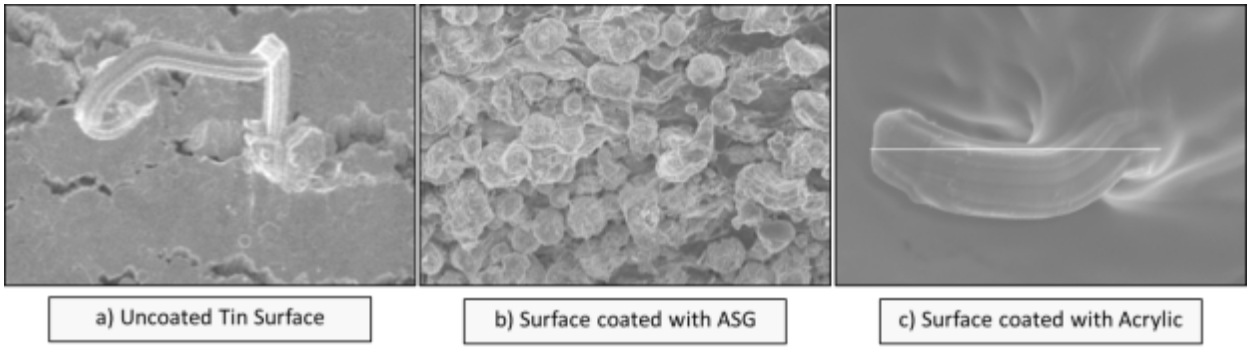

Figure 18 Examples of Whisker Morphologies in this Study

Tin Whisker Growth Measurements

Baseline Coatings (no nanoparticles)

Figure 19 shows results of tin whisker assessments for 'baseline' coatings without nanoparticles for 4000 hours of 85/85THC. These results include the two ASG coatings (ASG4A and **ASG5A**), the conventional conformal coatings (Acrylic and Parylene) and Control samples with no coating. These results are limited to assessments on leads, i.e. locations 1-4 on Figure 12 a), and only include 'A' samples that were continuously subjected to elevated

temperature/humidity prior to being removed from the chamber for analysis. Four sets of results are shown: average whisker density per unit area for all samples evaluated, the standard deviations of these data, the fraction of regions that were found to include at least one tin whisker, and the maximum number of tin whiskers observed (with a maximum of 20 whiskers per unit area).

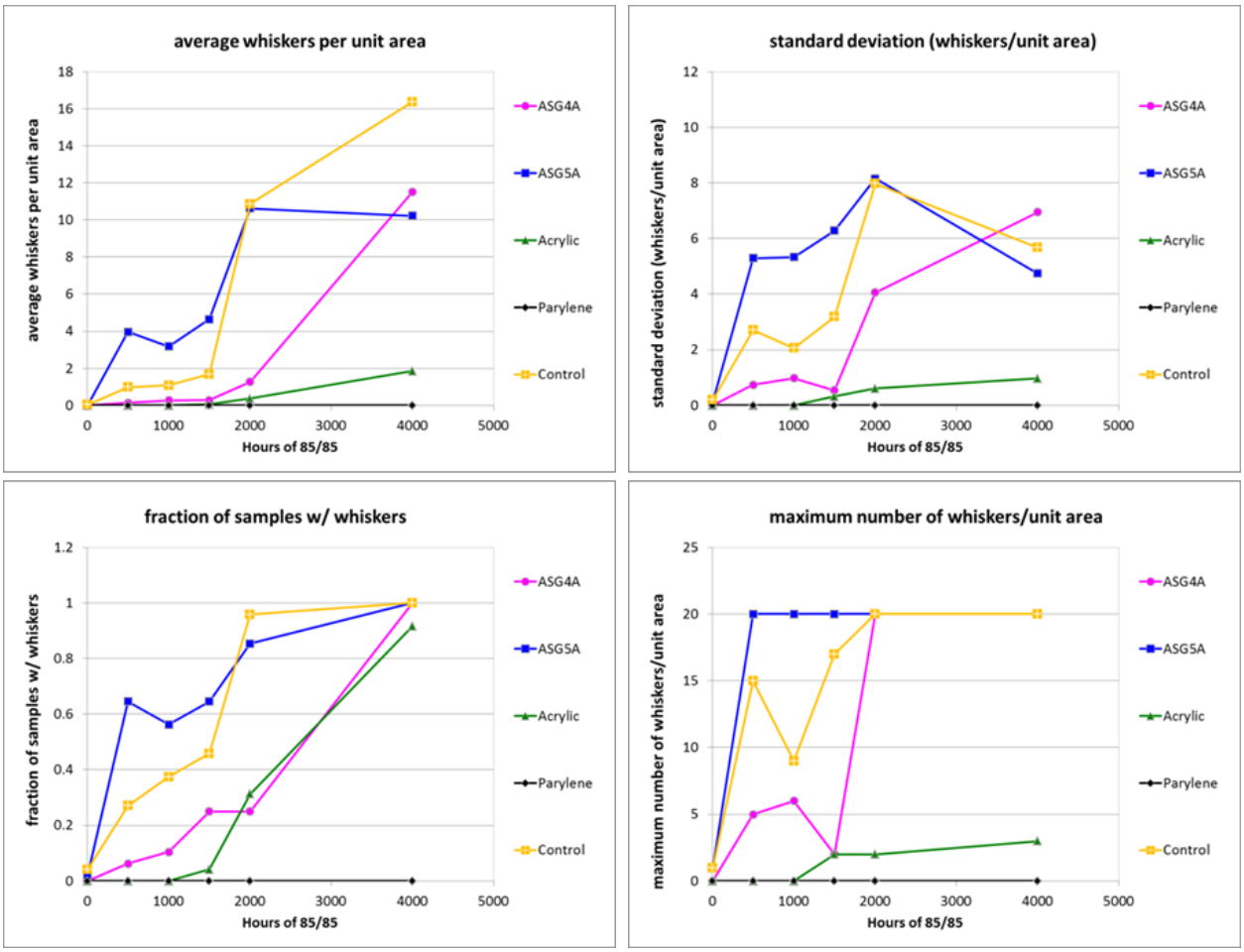

Figure 19 Tin Whisker Density Results for Baseline Coatings

Figure 19 shows that samples coated with ASG4A consistently had significantly fewer tin whiskers than the control samples, as did the conventional Acrylic and Parylene conformal coatings. Surprisingly, the **ASG5A** actually produced more tin whiskers than were observed on the Control samples, at least for the first 1500 hours of temperature/humidity conditioning. By 2000 hours, the number of whiskers on the Control Sample had reached the same level as those coated with **ASG5A**. The high stiffness of this coating and the high level of cracking within it likely led to locally increased stresses in the tin surfaces that accelerated the initial growth of tin whiskers.

The results shown in Figure 19 indicate that both ASG formulations led to higher levels of tin whiskers than the conventional Acrylic and Parylene coating. This result may be somewhat

misleading however. As shown in Figure 18c, close inspection of the conformally coated samples reveals the presence of many 'tents' that are due to tin whiskers that are pushing the coating up but have not yet penetrated it. The inspection criteria used in this study counted only those whiskers that had penetrated the coating with continued exposure to the elevated temperature/humidity conditioning, any currently existing tin whiskers will likely penetrate the coating and can be counted. This is somewhat indicated by the lower left hand graph in Figure 19, which shows that above 1500 cycles the acrylic coated samples were as likely to have at least one tin whisker as those coated with ASG4A.

Figure 20 compares these baseline measurements for average number of whiskers per unit area on the 'Tin Man' leads (regions 1-4 in Figure 12) compared to the flat region (5 in Figure 12). The numbers of tin whiskers are substantially lower on the 'flats' than on the 'leads', which is expected due to the lower residual stresses within the tin plating away from the bends.

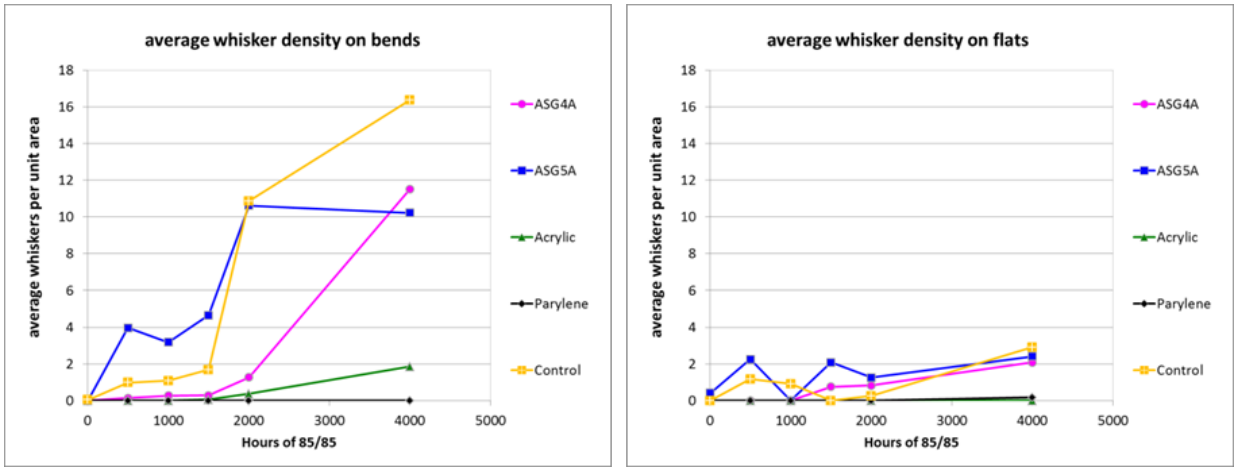

Figure 20 Effect of Location on Average Whiskers per Unit Area

Nanocomposites

To allow for the assessment of a larger number of nanocomposite materials, fewer replicates of each coating were included in the testing and their inspection cycle was increased from every 500 hours to 1000 hours of conditioning. Figure 21 presents average whisker density per unit area results for nanocomposite formulations developed with the two ASG materials (ASG4A and **ASG5A**) with comparisons to the relevant baseline materials and control samples. Figure 22 shows similar data but in terms of the fraction of samples that showed any whiskers. These data essentially indicate the ability of a coating to prevent whisker initiation rather than simply inhibit the growth and population of whiskers.

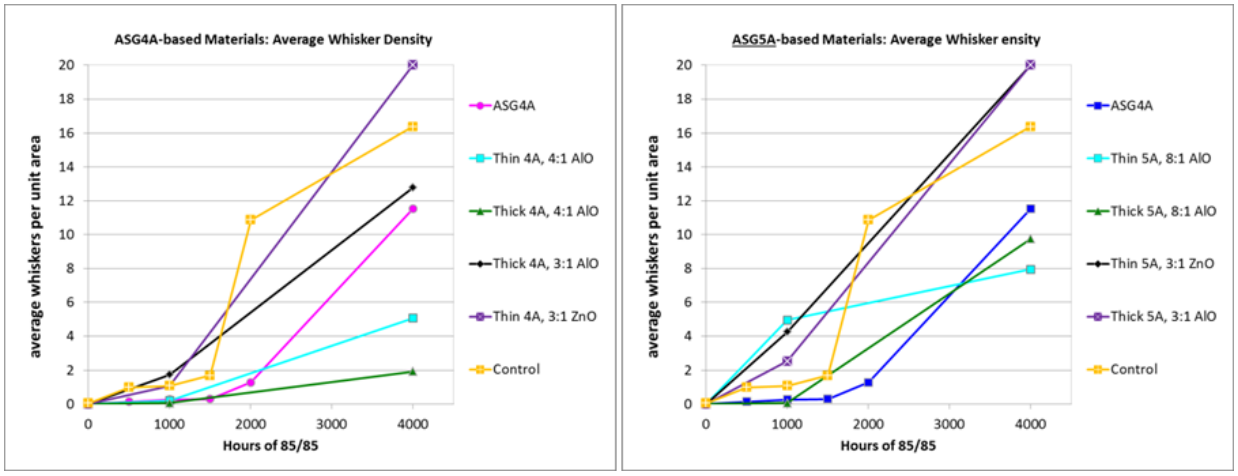

Figure 21 Average Whisker Density for Nanocomposites

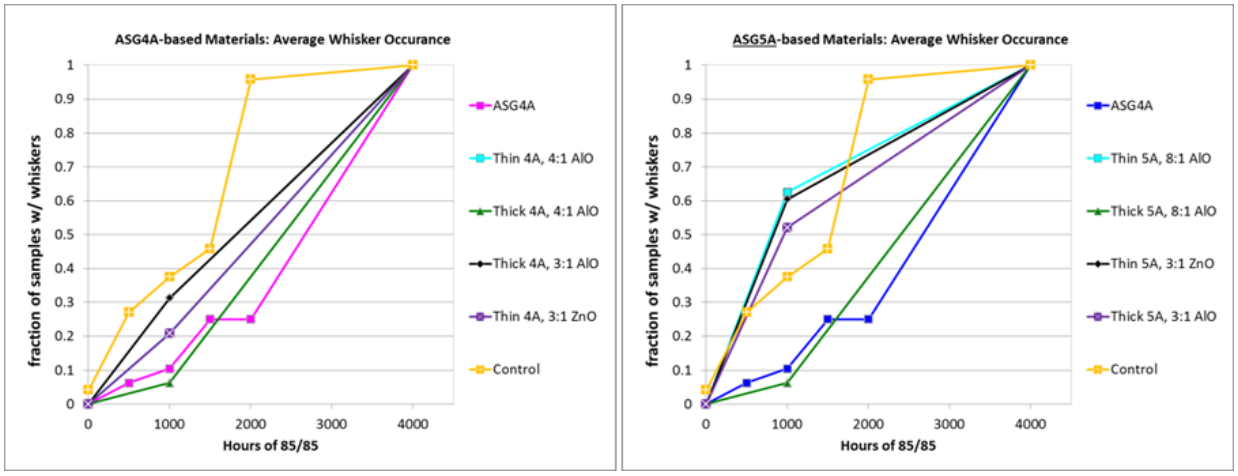

Figure 22 Nanocomposite Coatings Effect on Tin Whisker Inhibition

As discussed previously, the baseline ASG4A material reduced the average whisker density relative to the control samples; two nanocomposite formulations (Thin 4A, 4:1 AlO and Thick 4:1 AlO, i.e. Combinations 8 & 9 in Table 3) also appeared to be the most promising. With the exception of only one coating, the **ASG5A** materials actually increased the growth of tin whiskers relative to uncoated samples. The one **ASG5A** coating that inhibited whiskers was the Thick 5A, 8:1 AlO nanocomposite (Combination 11 in Table 3). In each case, the nanocomposite coatings that reduced the number of tin whiskers relative to control had the smallest nanoparticle size (10nm). The thin **ASG5A** 8:1 AlO (with these small nanoparticles) did not inhibit tin whiskers and, from a tin whisker prevention perspective, the thin coating of ASG4A with these smallest nanoparticles (Thin 4A 4:1 AlO in Figure 22) also had a higher fraction of samples with whiskers than the baseline ASG 4A material. (*Note: this is somewhat difficult to see on the Figure because the data for that coating is identical to that of the Thin 4A, 3:1 ZnO results*).

To summarize the Phase 1 results for the nanocomposite testing, it appears that only the smallest nanoparticle (10nm) filler materials help to inhibit or prevent tin whiskers. 'Thick' (which is a relative term since it corresponds to thicknesses on the order of 2 microns) coatings inhibit tin

whiskers to a greater degree than thin coatings. It appears that the best ASG coating configuration for preventing tin whiskers uses the ASG4A material, includes 10nm particles and is applied with the comparatively larger thickness of ~2microns.

Coating Process Facility Effects (Rockwell Collins and Plasma Ruggedized Solutions)

Coatings without nanoparticles (the two ASG formulations, acrylic coating, acrylic coating on ASG coatings used as a primer, and Parylene) were applied at both Rockwell Collins and Plasma Ruggedized Solutions. Figure 23 and Figure 24 shows test results for most of these materials (these figures do not show results for Parylene coatings because no whiskers were observed on any of those samples).

The two plots in Figure 23 show the average whisker density for coatings related to ASG4A and **ASG5A**. Each plot includes the baseline coating, results for acrylic coating (these results are repeated in the two plots), and the mixed coating approach in which acrylic was applied after the ASG coating was applied as a primer. Solid lines indicate coatings applied at Rockwell Collins while dashed lines correspond to those coatings applied at PRS. The same approach is used in Figure 24, which plots the fraction of test samples that exhibited any tin whiskers. Overall, the results agree with previous observations: ASG4A samples generally had fewer tin whiskers than those coated with **ASG5A**. Initially, samples with the ASG coatings had more tin whiskers than those with acrylic coating, but as earlier noted this is at least partially due to the assessment criteria that did not count tin whiskers until they puncture through the coating. At 2000 hours, the samples appeared to show the growth of whiskers in the acrylic coating to be increasing[4].

The samples coated by PRS consistently showed fewer whiskers than their counterparts that were coated at Rockwell Collins. At least part of this is likely because PRS cured their ASG materials at a higher temperature[5], which would have led to their being somewhat more robust. Appendix 5 is the report submitted by PRS to document their activities during Phase 1.

[4] Results for the PRS-coated samples for more than 2000 hours were not available due to a preparation error during SEM evaluations that irreversibly damaged them.

[5] Due to a miscommunication, PRS cured their ASG materials at 160°C while Rockwell Collins cured ASG materials at 125°C. Both cure steps were conducted for the same duration of one hour.

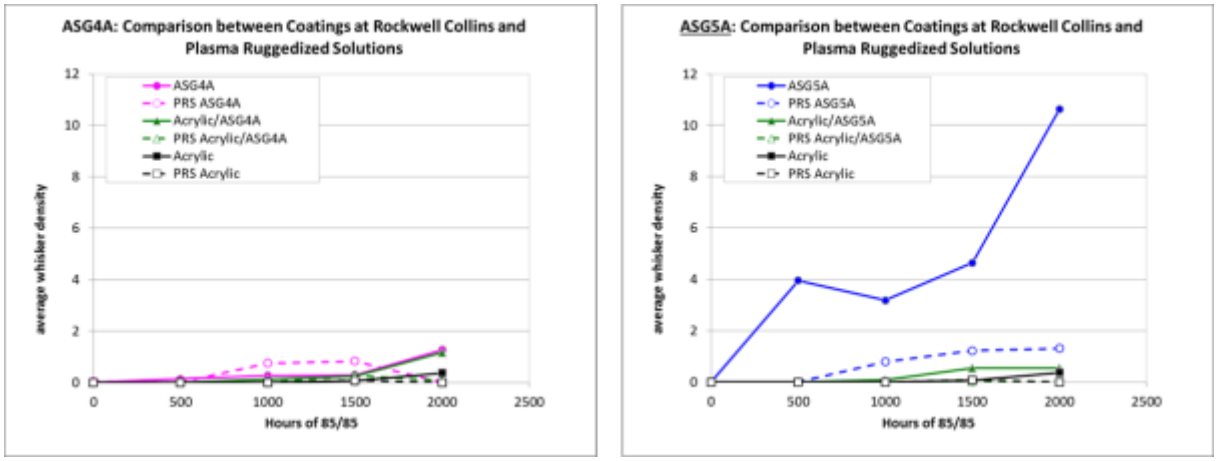

Figure 23 Whisker Density Results: Effect of Coating Location

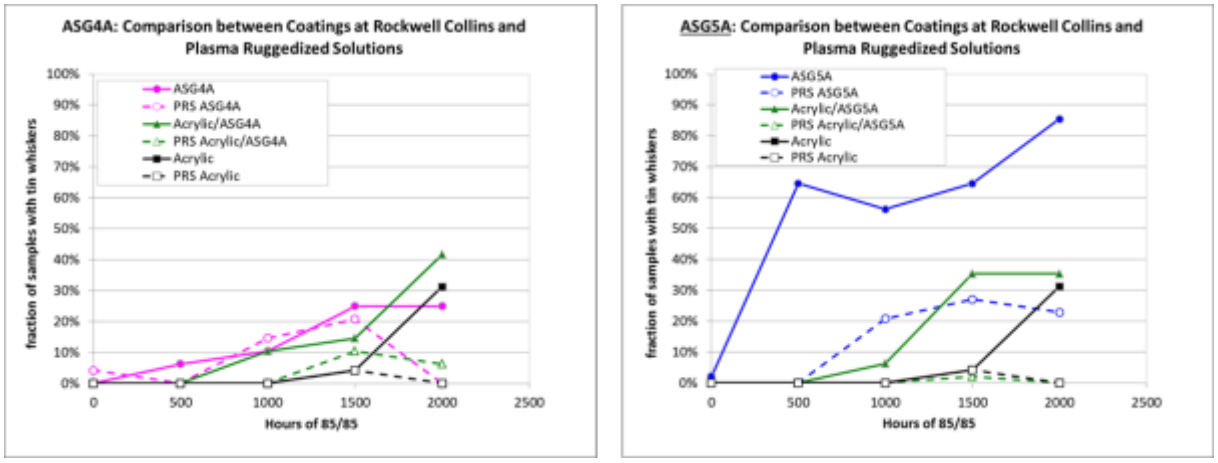

Figure 24 Occurrence of Whiskers: Effect of Coating Location

Continuous vs. Interrupted Conditioning Effects

As discussed previously, this investigation included a side study to address the impact of how tin whiskers are grown and evaluated. One approach is to include a number of individual samples that are exposed to elevated temperature/humidity with each sample removed at different levels of conditioning to assess the effects of these levels (these levels may be duration, relative humidity, temperature, etc.). Alternatively, the effects of time can be assessed with individual samples that are periodically removed from conditioning, evaluated and then returned to conditioning. Some researchers have observed that the process of removing samples from a chamber can disrupt the growth of tin whiskers and thereby provide results that differ from those obtained in continuous testing [8].

Figure 25 shows results for whisker density on control samples and on the ASG baseline (no nanoparticle samples). This compares the 'continuous' conditioning (solid lines) in which different samples are removed for each duration and the interrupted conditioning (dashed lines) in which samples are periodically removed for assessment. This figure shows that there is no

clear trend regarding how the different conditioning approaches impact whisker density. Samples with the ASG4A coating clearly had significantly more whiskers with the intermittent conditioning while the samples with **ASG5A** exhibited more whiskers for part of the intermittent conditioning but not at the final interim assessment at 4000 hours. In contrast, the control samples with intermittent conditioning tended to be similar to those with continuous conditioning, except for the samples evaluated at 2000 hours-hour mark in which the continuous conditioning samples had far higher whisker density.

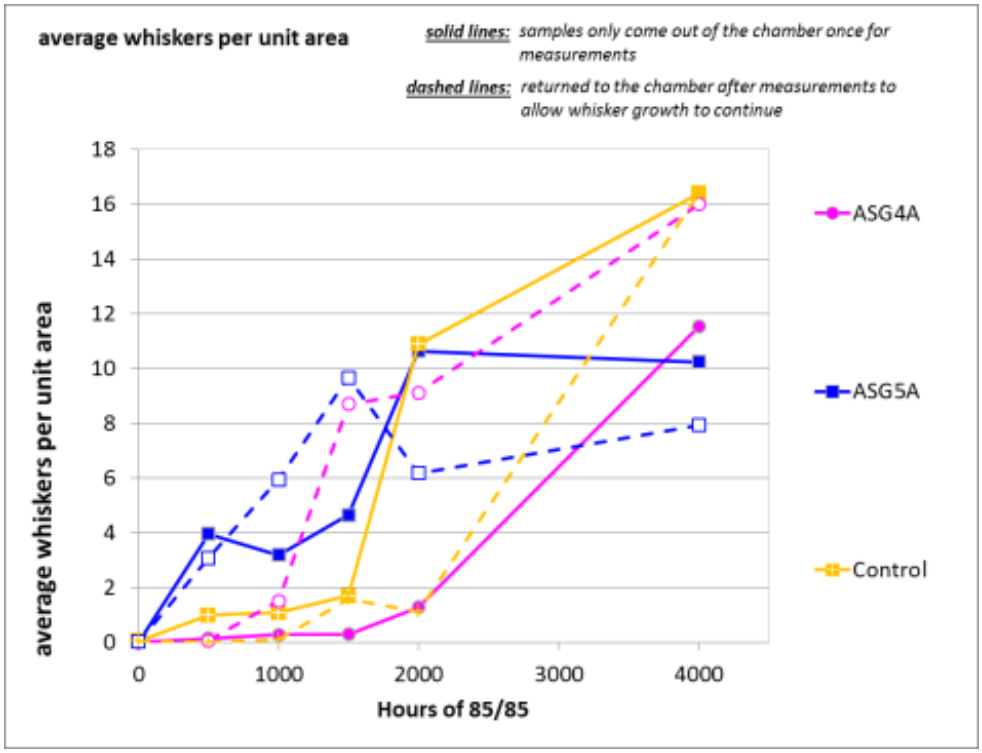

Figure 25 Effect of Testing on Whisker Density (Continuous vs. Interrupted)

Overall, the data suggest that tin whisker testing with evaluation interruptions may influence tin whisker invitation and growth, but not consistently. The optimum tin whisker testing methodology would be to minimize influencing test results through the use of multiple samples that are only removed once from environmental testing. Ideally, whisker evaluation would use non-invasive evaluation methodologies that do not require samples to be removed from environmental exposure or be subjected to processes, such as sputtering, that could alter whisker growth methods.

Figure 26 shows data for observations of long whiskers (greater than ~40 microns) on the test vehicles. This likewise presents data for the baseline ASG coatings and the control samples, with results for both the 'A' samples that were continuously exposed to temperature humidity and the 'B' samples that were removed from the chamber for assessment and then returned for continued 'interrupted' testing. While there is a general trend of the length increasing with time in the chamber, the paucity of data for long whiskers precludes drawing any significant conclusions.

Figure 26 Effect of Testing on Whisker Length (Continuous vs. Interrupted)

Metal Vapor Arc Measurements

Prior testing by the University of Maryland Center for Advanced Life Cycle Engineering (CALCE) has shown that Metal Vapor Arc events with tin whiskers tend to correlate with a 'cold current' metric, A_{cc} [9]. Equation 1 shows that this metric is defined in terms of the voltage applied to the test specimen divided by the total electrical resistance that includes the test circuit as well as the specimen.

$$A_{cc} = \frac{V_{applied}}{R_{specimen} + R_{circuit}} \qquad \{1\}$$

Testing at CALCE showed that whiskers subjected to cold current of A_{cc} > ~4 amps will arc. Whiskers are less likely to arc at lower levels of current that depend somewhat on the ambient pressure. This testing was conducted at a low pressure of 35 mtorr (<0.05 atm); under these conditions a minimum cold current of ~2 amps has typically been required to generate an arc.

The delicate nature of tin whiskers led to significant challenges in this testing, which included processing steps both at Rockwell Collins (Iowa) and the University of Maryland. Handling issues such as shock/vibration during shipment and creep mechanisms during transport and evaluation led to a number of samples failing prior to testing. Table 5 shows the results for 'coated whisker' samples, in which the ends of a tin whisker were connected to two electrodes and then subsequently sprayed with a coating. As shown in the table, many of the whiskers failed at some point in the assembly processes, which left an 'open' electrical resistance after receipt (these are shown in green font). With this open resistance, the Arc Metric A_{cc} was essentially zero. Of the eight coated samples that were tested, five did arc with the lowest arcing cold current level being 3.08 amps with a sample that was coated with acrylic (these samples that arced are shown in red font). One sample (A-16) that was coated with an alkali silicate glass did

not arc at a cold current of 4.59, which is high enough that on average it would generally lead to an arc event (samples that did not arc are shown in blue font). This is some evidence that the glass coating may inhibit MVA to a greater degree than the acrylic coating. However, it is dangerous to draw any firm conclusions from a single data point such as this. At a minimum, the results of the testing that the ASG coatings are no more likely to generate MVA than conventional conformal coating materials.

Table 5 Results for Coated Tin Whisker MVA Test Samples

Specimen #	Coating	Resistance Prior to Shipping (ohms)	Resistance upon receipt (ohms)	Arc Metric	Finding
A-1	acrylic	4.81	Open	N/A	Not Tested
A-2	acrylic	11.21	Open	N/A	Not Tested
A-3	acrylic	5.16	7.48	6.42	Arced
A-4	acrylic	26.21	Open	N/A	Not Tested
A-5	acrylic	10.42	9.57	5.02	Arced
A-6	none	7.65	Open	N/A	Not Tested
A-7	**ASG5A**	20.97	22.58	2.13	No visible Arc
A-8	**ASG5A**	11.63	Open	N/A	Not Tested
A-9	none	14.77	Open	N/A	Not Tested
A-10	ASG4A	4.21	5.4	8.89	Arced
A-11	ASG4A	32.47	Open	N/A	Not Tested
A-12	acrylic	11.13	Open	N/A	Not Tested
A-13	acrylic	33.14	16.18	2.97	No visible Arc
A-14	acrylic	10.83	Open	N/A	Not Tested
A-15	none	20.73	Open	N/A	Not Tested
A-16	ASG4A	11.32	10.56	4.55	No visible Arc
A-17	acrylic	9.61	Open	N/A	Not Tested
A-18	none	25.43	Open	N/A	Not Tested
A-19	ASG4A	5.25	4.59	10.46	Arced
A-20	acrylic	4.63	15.56	3.08	Arced

Note again that the 'arc' conditions reported in Table 5 simply indicate that light was observed when current was applied to the coated whisker; no sustained plasma events were observed in any of this testing.

Figure 27 shows an acrylic coated MVA test specimen (A-3) before and after voltage was applied. This indicates that though the tin whisker did arc, the acrylic coating primarily remained in place during the test. In comparison, Figure 28 shows the A-19 test specimen that was coated with ASG4A. One obvious difference between the two tin whiskers shown in these figures is that the ASG coating is much thinner than the acrylic coating. In addition, Figure 28 shows that after the arc event, the ASG4A-coated whisker had disappeared and there was visual evidence of surface damage to the electrodes. Therefore, it appears highly unlikely that the extremely thin ASG coatings would be able to contain an arc in a manner similar to the acrylic coating.

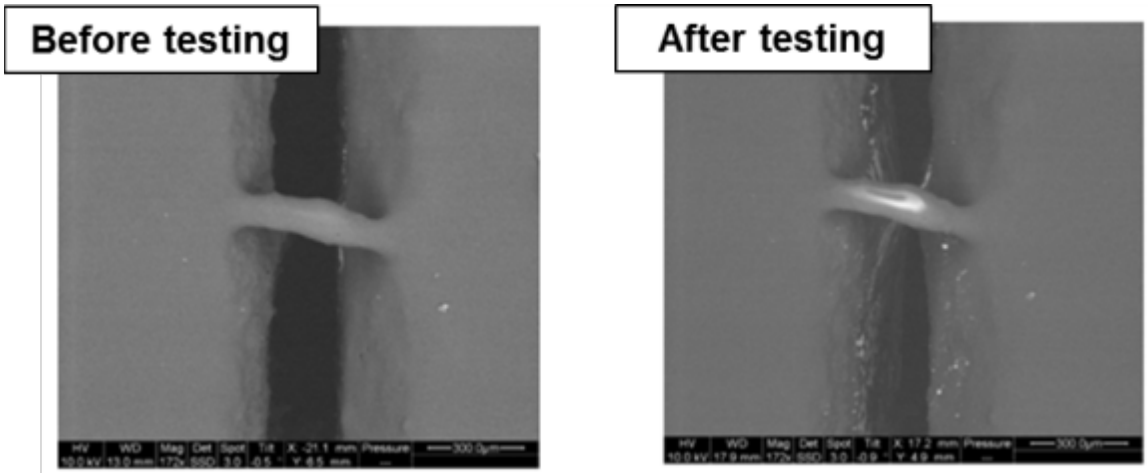

Figure 27 MVA Test Specimen with Acrylic Coating

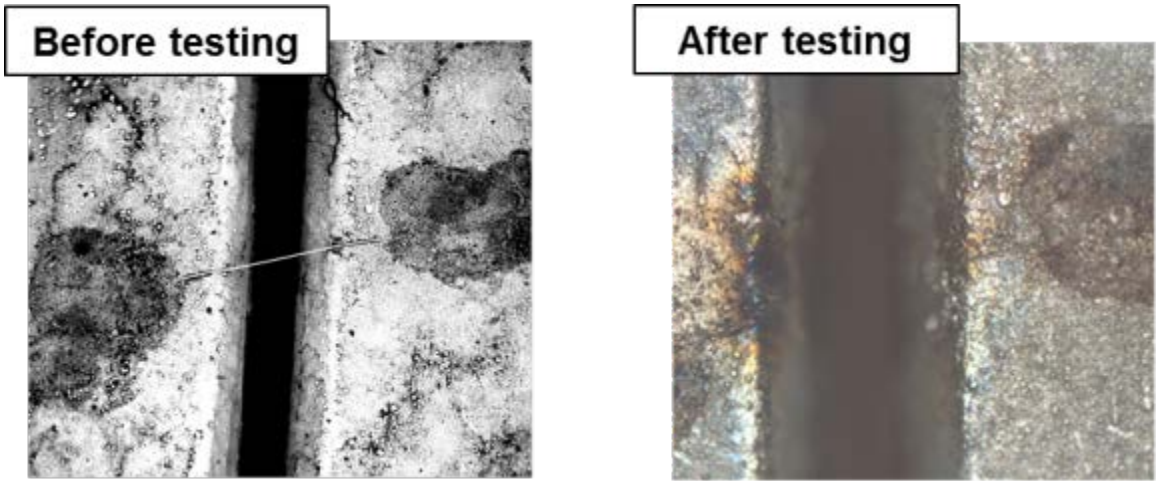

Figure 28 MVA Test Specimen with ASG4A Coating

Additional testing was conducted on 'coated surface' samples, in which one end of a tin whisker was connected to one electrode and the other end was physically held against a coated surface. On many of the samples, the coating provided sufficient electrical insulation that the whisker formed an open circuit. However, three of the samples (one each with acrylic, ASG4A and a water based acrylic/urethane blended conformal coating) did have a measureable electrical resistance that led to an Arc Metric in a range that would be expected to lead to arcing. As shown in Table 6, the three samples that did arc had Arc Metric values that were ~3.5 amps or higher. The arc characteristics of these samples are in agreement with the results of other tests results that have been conducted by CALCE. A summary of the Metal Vapor Arc testing results for all testing conducted, including this work with coated samples, is shown in Figure 29.

Table 6 Results for Coated Surface MVA Test Samples

Sample	Coating	Resistance	Arc Metric (A)	Arc Detected
1A-S1	acrylic	Open	NA	No
1A-S2	acrylic	6.11	6.95	Yes
2B-S1	Acrylic/urethane	Open	NA	No
2B-S2	acrylic/urethane	12.45	3.86	Yes
4A-S1	ASG4A	Open	NA	No
4A-S2	ASG4A	7.02	6.84	Yes
5A-S1	ASG5A	Open	NA	No
5A-S2	ASG5A	Open	NA	No

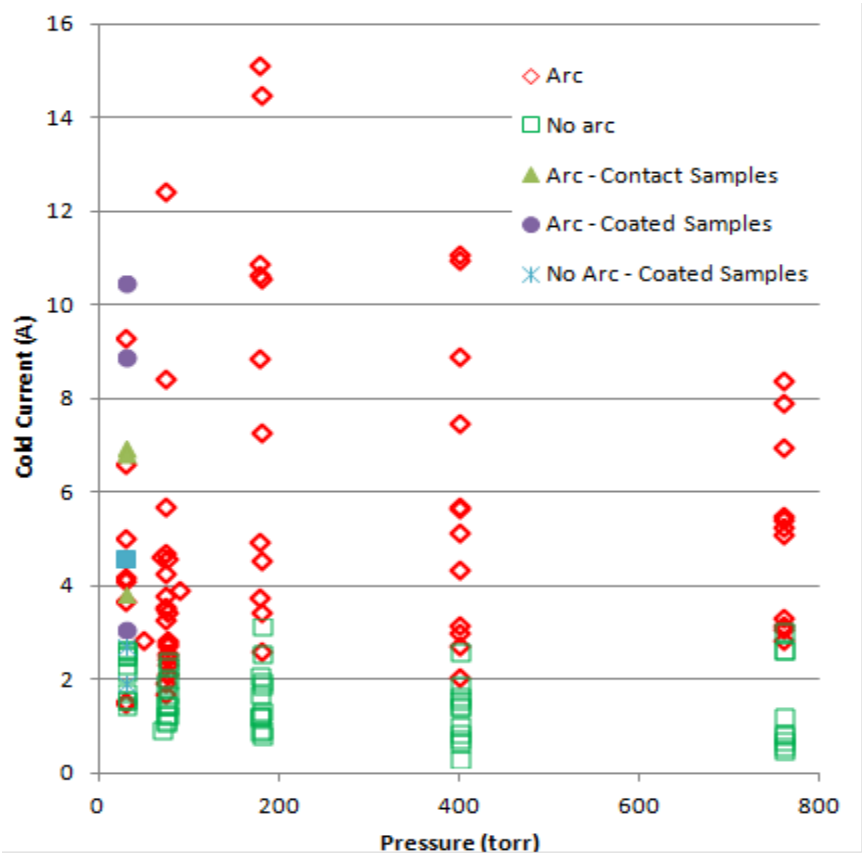

Figure 29 MVA Test Results from CALCE (including coated samples in current SERDP work)

D.2 Phase 2 Materials and Methods

Overview

Figure 30 shows a summary of the initial plan for Phase 2 TWICE program activities with task area leads identified with color-coding. Since the time required to complete 4000 hours of temperature humidity testing extended beyond the duration of Phase 1, Phase 2 included testing and analysis of Phase 1 samples to complete that activity. In addition, formulations and processes used in Phase 1 were updated to apply lessons-learned and new capabilities to the Phase 2 test samples. One particularly important development in Phase 2 was the introduction of using an ultrasonic spraying head when applying coatings; this greatly expanded formulation options such as nanoparticle type and loading density and also significantly reduced the required deposition times.

Unlike the rather small custom test devices used for tin whisker evaluation in Phase 1, Phase 2 evaluated coatings when used on more representative circuit card assemblies that included conventional parts as well as the same custom test device. This allowed coatings to be evaluated for their coverage effectiveness and for the identification of any critical manufacturing issues. Test boards were again coated at both Rockwell Collins and Ruggedized Plasma to verify that the materials could be applied in an independent manufacturing environment. Coated devices were subjected to the same elevated temperature/humidity testing conditions and duration used in Phase 1, but with fewer samples and longer intervals between inspection under the SEM.

In addition to the activities identified in Figure 30, the TWICE project investigated a number of other factors related to improving the robustness, manufacturability and design impact of ASG coatings. These activities included quantifying the impact of ASG coatings on RF circuitry, measuring the permeability of the coatings to water vapor, assessing new formulations with alternate nanoparticles that were made possible through the use of the ultrasonic spraying head, and including ASG coatings in an ongoing study on tin whisker mitigation that is being conducted by the National Physics Laboratory.

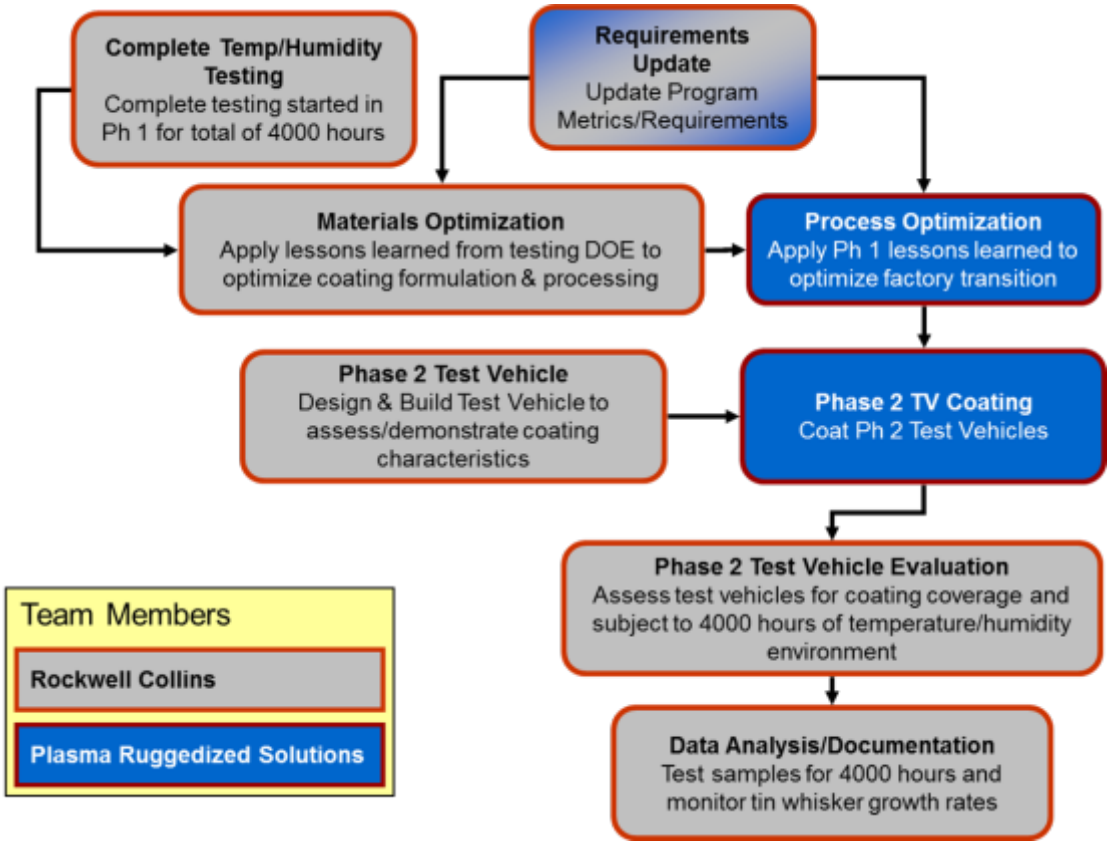

Figure 30 Phase 2 Project Flow

Phase 2 Material Development

The Phase 2 materials development investigation introduced two new parameters to the formulation recipes and deposition. Since the Phase 1 work had shown that ASG4A materials tended to inhibit whisker growth better than the **ASG5A**, this second phase primarily focused on the ASG4A material. Initial work in this phase included spraying coatings onto copper samples that were then placed into an elevated temperature to promote copper oxidation. Visual inspection was used to determine the extent to which coatings reduced oxidation to identify those that best inhibited the ingress of oxygen and presumably moisture. Figure 31 shows an image of eight test coupons with nanoparticles of Zirconium (ZnO), Titanium Oxide, Rutile phase (TiO(R)), Titanium Oxide, Anatase phase, (TiO(A)), or Alumina (AlO) coated in 4 or 15 passes. These images were typical of all tests that included elevated temperatures ranging from 125-175°C and durations of 2-12 hours. Samples with 15 passes generally showed less oxidation than those with 4 passes. Formulations with Zirconia nanoparticles exhibited the least oxidation. The samples coated with TiO(R) particles also exhibited less oxidation, but the adhesion of these materials, as measured with a tape test, was relatively poor. Based on these oxidation tests, formulations with zirconia nanoparticles, as well as some of the alumina nanoparticle formulations that had performed well in Phase 1, were used in the Phase 2 evaluations.

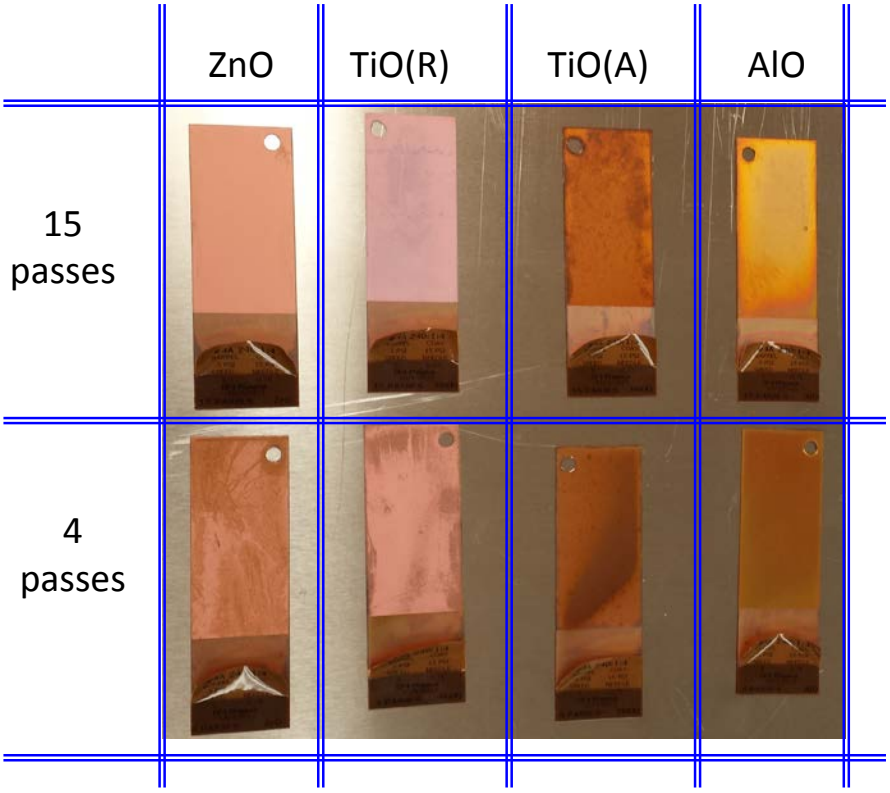

Figure 31 Coated Copper Test Coupons after 7 hours at 175°C

An additional variable included in the Phase 2 coating development was the method used to deposit materials in the Asymtek Spraying System. Preliminary investigations showed that the deposition rate could be substantially increased through the use of a custom built ultrasonic spraying head. This spraying head was included as a test variable in defining the test combinations included in the Phase 2 testing. Since only one ultrasonic spray head was procured for this study, the test samples coated by PRS only included those samples that used the 787MS spraying head. The seven different coating combinations selected for Phase 2 evaluation are listed in Table 7.

Table 7 Phase 2 Coating Combinations

ID	ASG #	Thickness	Spray Valve	Nanoparticle
1	4A	2 microns	787MS	10 nm Alumina
2	4A	2 microns	787MS	40 nm Zirconia
3	4A	4 microns	Ultrasonic	10 nm Alumina
4	4A	4 microns	Ultrasonic	40 nm Zirconia
5	4A	2 microns	Ultrasonic	40 nm Zirconia
6*	4A	2 microns	787MS	10 nm Alumina
7	5A	4 microns	Ultrasonic	40 nm Zirconia
Coating 6 was a primer to which acrylic coating was applied*				

Phase 2 Test Approach

The standard SMTA Saber Evaluation Board was procured from Practical Components, Inc. as the test vehicle for Phase 2 of the TWICE program. This assembly provided a means to

demonstrate the ability to coat a range of Surface Mount Technology (SMT) component styles. The evaluation boards were assembled with standard components, with one exception: a Tin Man component was reflow soldered to the board in place of one of the two Small Outline Integrated Circuit (SOIC) components as shown in Figure 32. After automated assembly, coating, and initial visual inspection of the test vehicles, a portion of the board was cut out of the Saber board so that the Tin Man, SOIC and Quad Flat Pack (QFP) components could be inspected in the SEM.

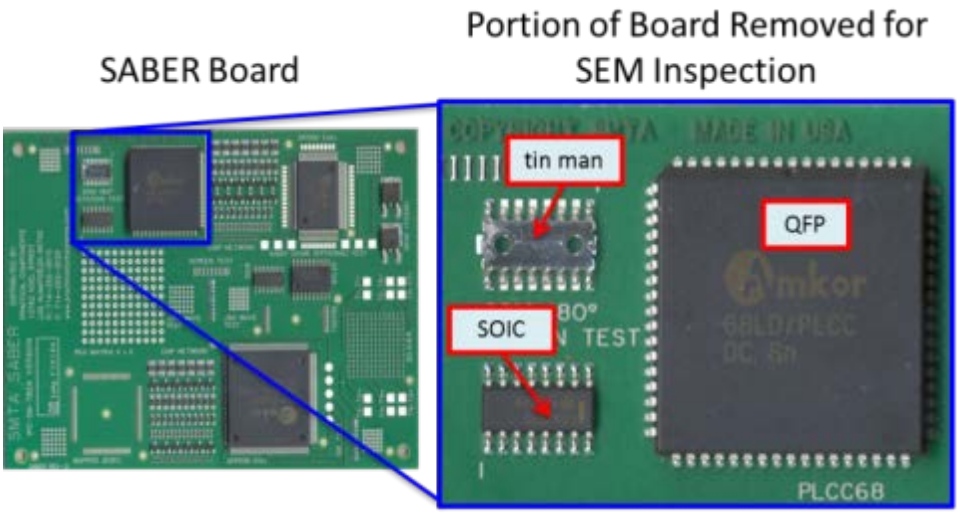

Figure 32 Phase 2 Test Board and Components Evaluated for Tin Whiskers

One of the limitations of many conformal coatings typically used by the electronic industry is that coverage may be thin or non-existant on sharp corners or edges of component leads. Additionally, the back sides of component leads can exhibit poor coverage if the conformal coating application process does not utilize multiple application angles. Osterman [20] conducted an investigation using 6 different conformal coating materials applied to a 184 I/O Quad Flat Pack (QFP) components that were monitored for tin whisker growth. The investigation results revealed that the edges of the component leads were most prone to tin whisker initiation/growth due to the minimal coating coverage (see Figure 33).

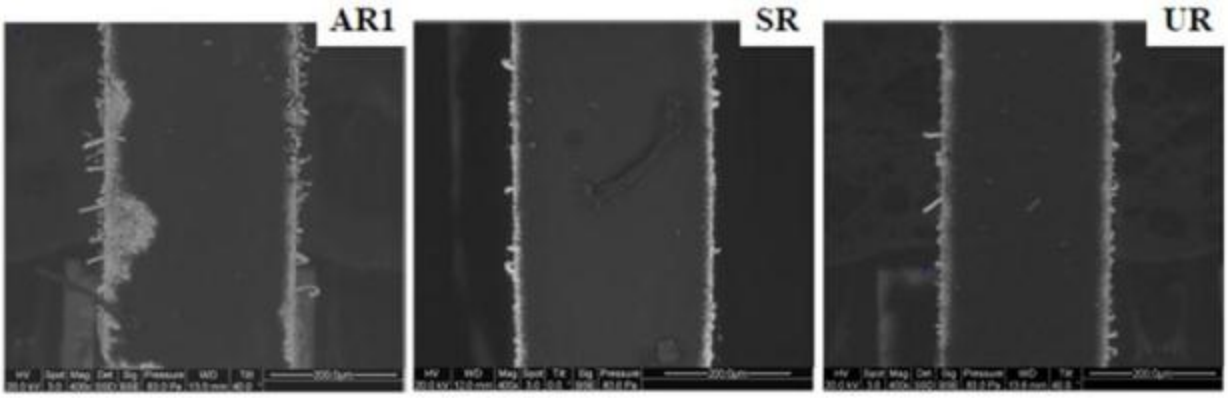

Figure 33 QFP Components with Tin Whisker Growth on Lead Edges [20]

The extremely thin TWICE ASG coatings have an advantage over conventional conformal coating formulations because their thickness allows for more uniform coverage over sharp edges where the radius of curvature is very small. The ultrasonic spraying head with multiple pass/application angles also enables more uniform and consistent coverage of component lead backsides and edges. Optical and SEM inspection of the TWICE coating components on several Phase 2 test vehicles verified complete and uniform coverage of the ASG coatings on the SOIC and QFP leads. In contrast, the conventional acrylic coating exhibited incomplete coverage on the toes (Figure 34) and the backside of the leads.

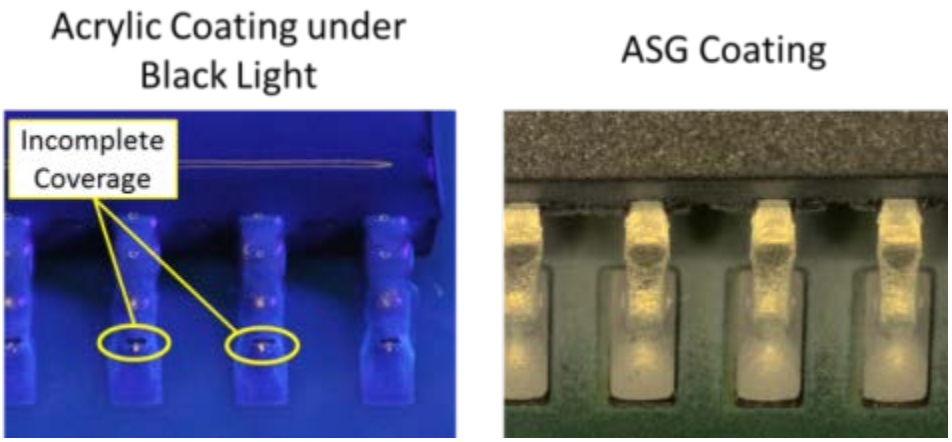

Figure 34 Coating Coverage on SOIC Components

A set of the Phase 2 test vehicles were processed with the ultrasonic spray valve, multiple passes, and with a target coating thickness of 2 microns. Metallographic cross-sectional analysis revealed the typical coating all component surfaces including edges and lead backsides to range from 1.09 – 2.21 microns (see Figure 35).

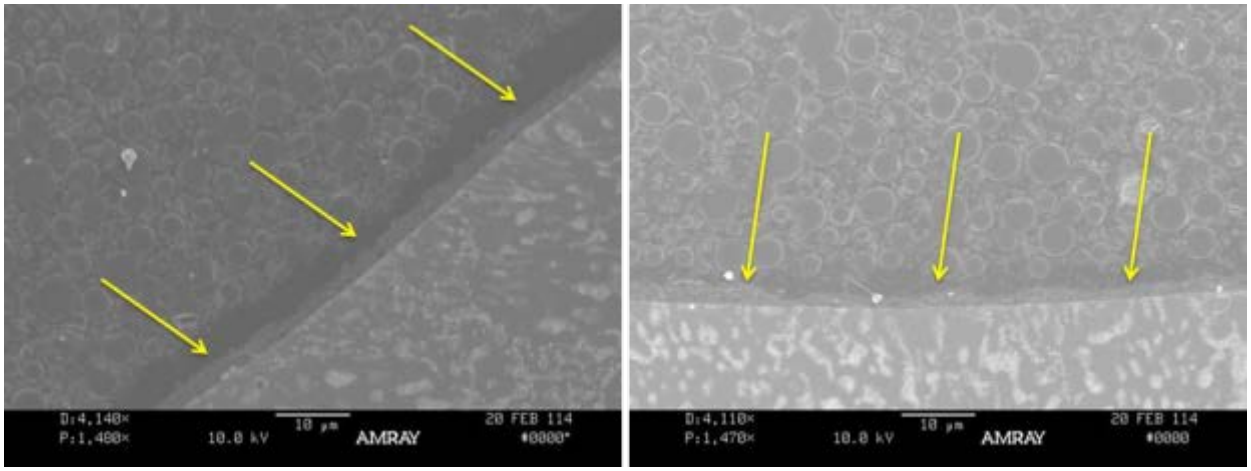

Figure 35 Metallographic Cross-sectional Views of TWICE Coating on Solder Joints

E.2 Phase 2 Test Results

Temperature/Humidity Whisker Growth

The portions of the Saber Evaluation Board with the SOIC, QFP and Tin Man components were placed in the same Temperature/Humidity chamber used in Phase 1 and subjected to 85°C/85% RH conditions. Up to two samples for a given coating combination were removed after 1000, 2000, 3000 or 4000 hours of exposure. Combinations not expected to exhibit significant whisker growth, such as those coated with Parylene, were to be removed only at 2000 and 4000 hours (however, a processing error led to some samples being removed at 3000 hours rather than 4000). Once removed from testing, samples were not placed back into the test chamber. The Tin Man samples were inspected for tin whisker density with the same methodology used in Phase 1 at the general locations shown in Figure 12. Leads on the SOIC and QFP were randomly selected for inspection to determine if any tin whiskers were observed.

Figure 36 shows the average whisker density for each test combination included in Phase 2. These data are also shown in Table 8; combinations that were not included in a given inspection interval are shown as NA in the table and are missing symbols in the figure. In general, the whisker density did increase with 85/85THC conditioning time, however this was not always the case. As in Phase 1, the results show a wide variety of tin whisker mitigation potential with many of the ASG formulations actually producing many more whiskers than the Control surfaces while some formulations had far fewer whiskers. No coating in Phase 2, including Parylene, was found to completely prevent the formation of tin whiskers.

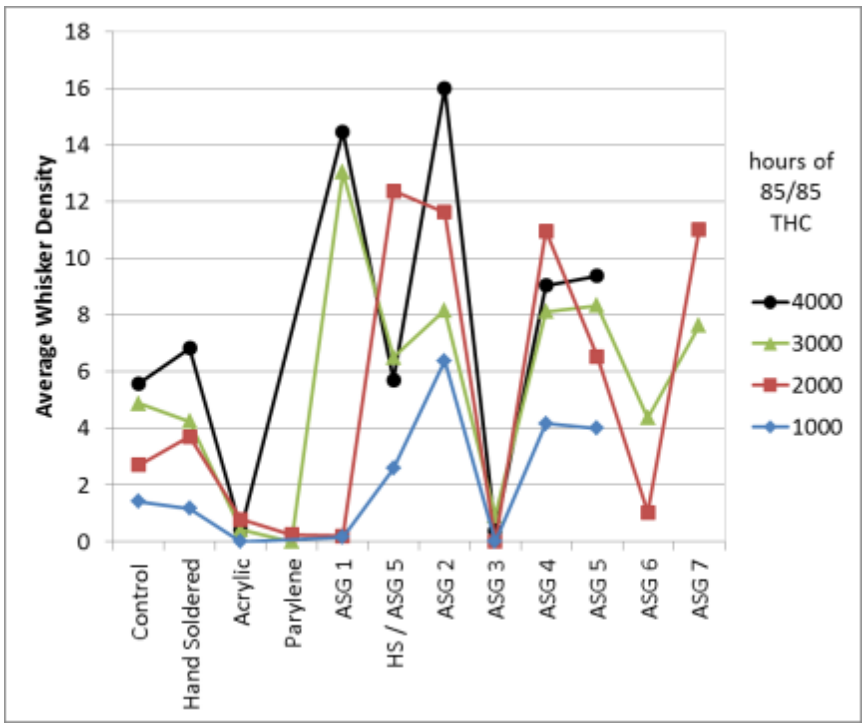

Figure 36 Average Whisker Density: All Combinations

Table 8 Average Whisker Density on Tin Man Parts

Coating	Hours in 85/85THC			
	1000	2000	3000	4000
Control	1.4	2.7	4.9	5.6
Hand Soldered	1.8	3.7	4.3	6.8
Acrylic	0.0	0.79	0.35	0.51
Parylene	NA	0.25	0.25	0.0
ASG 1	1.1	0.31	7.9	8.5
Hand Soldered/ ASG 5	2.6	12	6.5	5.7
ASG 2	6.9	14.	9.3	12.
ASG 3	0.0	0.0	0.92	0.38
ASG 4	4.2	11	8.1	9.0
ASG 5	4.0	6.5	8.3	9.4
ASG 6*(ASG 1/acrylic)	NA	0.63	2.7	NA
ASG 7	NA	11	7.6	NA

Figure 37 compares all of the coatings that led to fewer tin whiskers than the control samples. Samples for ASG 6, which was actually a composite approach in which a layer of ASG 1 was used as a primer coating for a subsequent acrylic coating, were only inspected at 2000 and 3000 hours of 85/85THC. Interestingly, none of the other samples that were shown to reduce whisker density exhibited monotonic growth over time. The highest whisker densities for Acrylic and Parylene occurred after 2000 hours while the highest average whisker density for ASG3 was seen after 3000 hours. These results are somewhat indicative of the 'uncooperative' nature of tin whisker formation, which is a relatively constant growth rate plus random noise. Inhibiting the constant growth, such as with coatings will increase the relative impact of the random portion of whisker initiation and lead to less monotonic increases in whisker density.

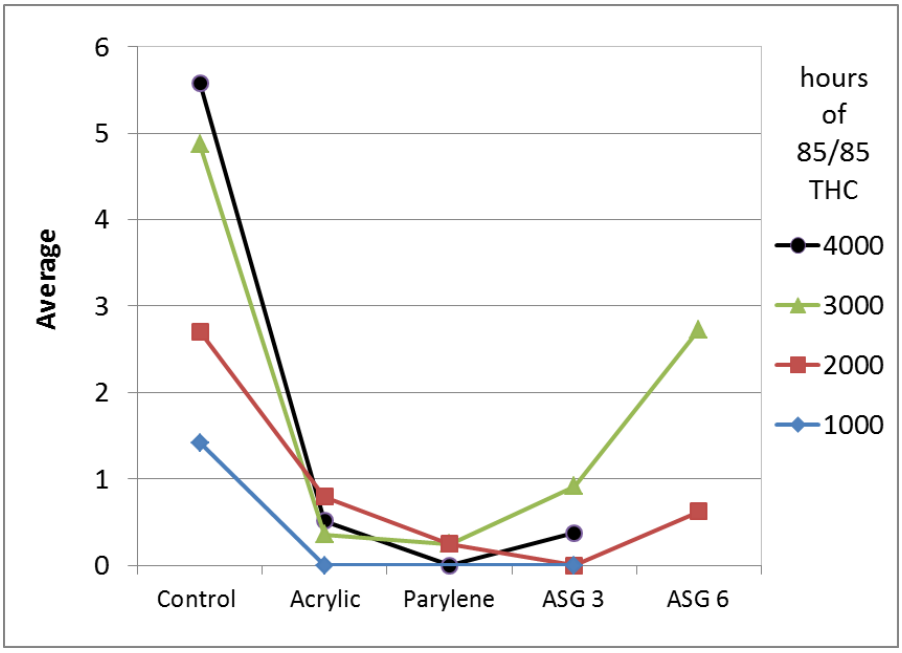

Figure 37 Tin Whisker Density: Mitigation Coatings

It should also be noted that the smaller tin whisker densities with Acrylic and Parylene conformal coatings are, to some degree, “false positive” since they only include tin whisker that had either breached the conformal coating or were clearly forming a “tent” under the coating. Other perturbations to the coating, which were likely due to whiskers, were not counted in the SEM inspection. While the test results clearly show that both traditional conformal coatings inhibited tin whisker growth, the extent of that inhibition is confounded by this whisker measurement approach. Figure 38 illustrates a tin whisker erupting through the traditional acrylic conformal coating.

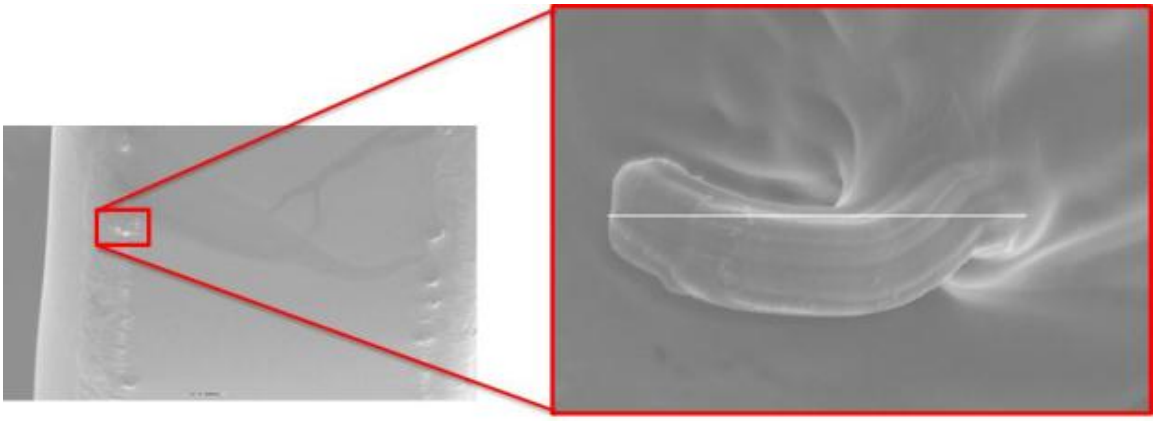

Figure 38 Acrylic Coating with Tin Whisker Eruption

To determine whether tin whiskers that had not breached the coating surface were in fact present, the Acrylic coating was passively stripped with a solvent from a number of test vehicles after the completion of THB testing. SEM inspection of these test vehicles verified the existence numerous tin whiskers that were not included in the whisker density measurements but would have eventually breached the Acrylic coating surface. Figure 39 shows two examples of the tin whiskers that were revealed to exist under the Acrylic coating. Due to the chemical stability of Parylene coating, its removal process requires mechanical abrasion that would have also removed any tin whiskers present. Therefore, no attempt was made to remove Parylene from test vehicles to likewise verify the presence of underlying tin whiskers.

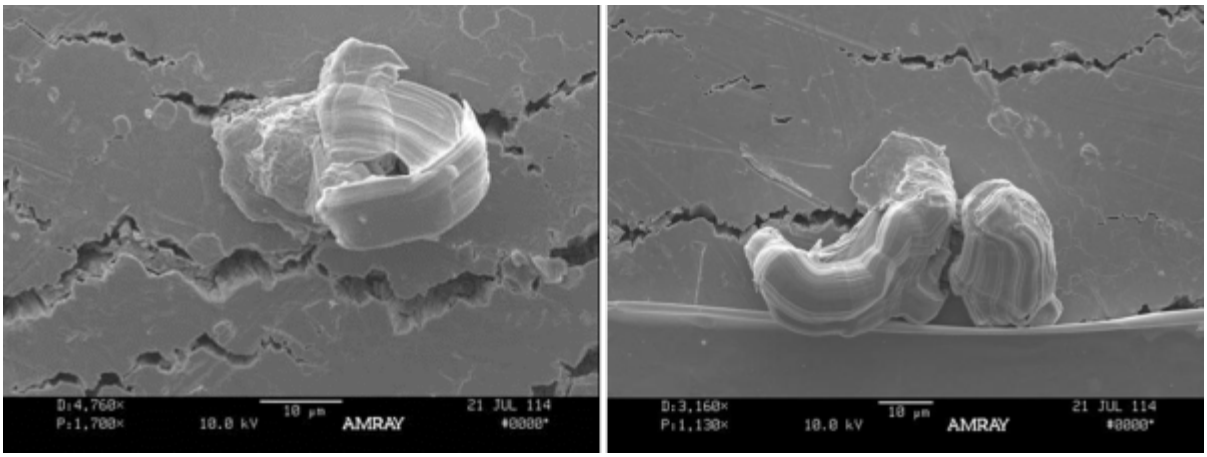

Figure 39 Tin whiskers Present under Acrylic Coating

Figure 40 compares the average whisker densities for the ASG composites with the two different filler materials. Preliminary materials development had suggested that the zirconium-based nanocomposites would perform better than the alumina nanocomposites, since the coatings had prevented oxidation on copper surfaces to which they were sprayed. However, the tin whisker density measurements clearly showed that the composites with alumina nanoparticles had fewer whiskers than the control samples while the samples with zirconia composites had more whiskers.

In retrospect, this result could have been partially foreseen since the size of the zirconia nanoparticles was larger (40 microns) than the alumina nanoparticles (10 microns). Phase 1 testing had demonstrated this and it was hypothesized that the smaller particles more effectively filled cracks in the tin plating from which whiskers tend to initiate.

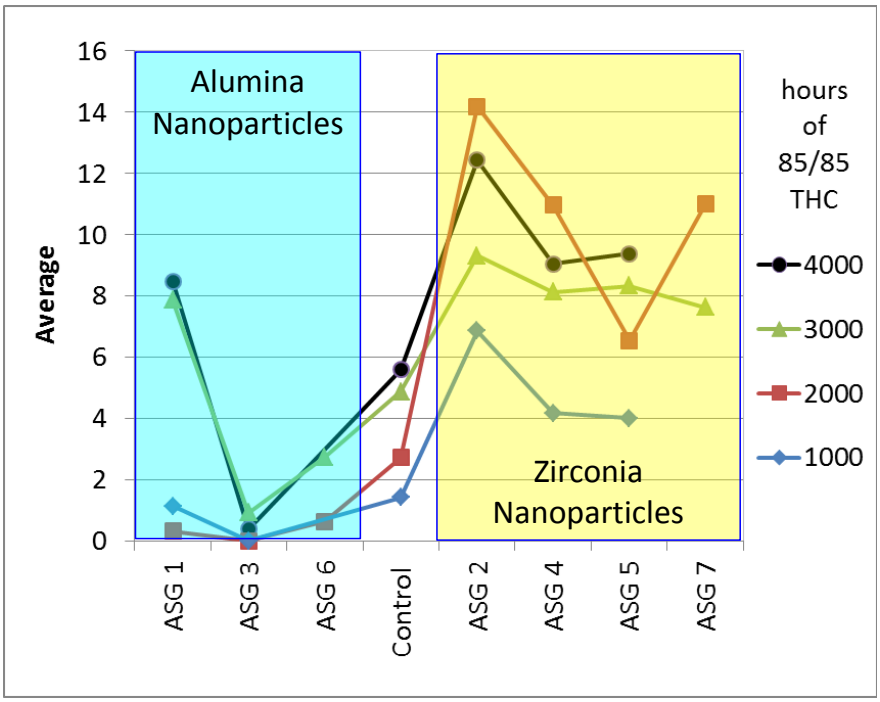

Figure 40 Tin Whisker Density: Comparison of ASG/Nanoparticle Composites

Figure 41 compares the tin whisker density on control and coated samples assembled in the reflow system and by hand soldering. It has been hypothesized that exposure to the tin/lead solder alloy reflow oven temperatures could relieve tin plating stress and thereby reduce the tin whisker initiation and growth driving forces. The Hand Soldered test samples were not exposed to the reflow oven temperatures and therefore should have had higher tin whisker density results. The test results illustrated in Figure 41 do not show any consistent trends that would indicate that reflow soldering reduces whiskering. This result is consistent with the work of Cisco and Jabil [23], which demonstrated that tin/lead solder alloy reflow temperatures had minimal impact on tin whisker initiation and growth.

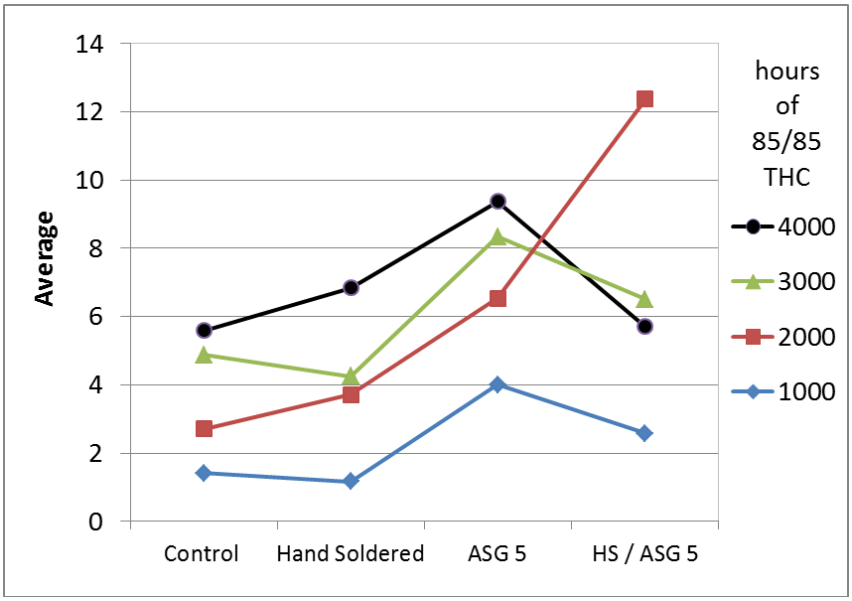

Figure 41 Effect of Hand Soldering Tin Man

Figure 42 compares the whisker density for the two locations at which coatings were applied. In general, the samples coated at Plasma Ruggedized Solutions showed somewhat fewer whiskers than those coated at Rockwell Collins. Overall, the results again demonstrate that the coating process could be successfully implemented at multiple manufacturing sites. Appendix 9 documents the activities of PRS during Phase 2.

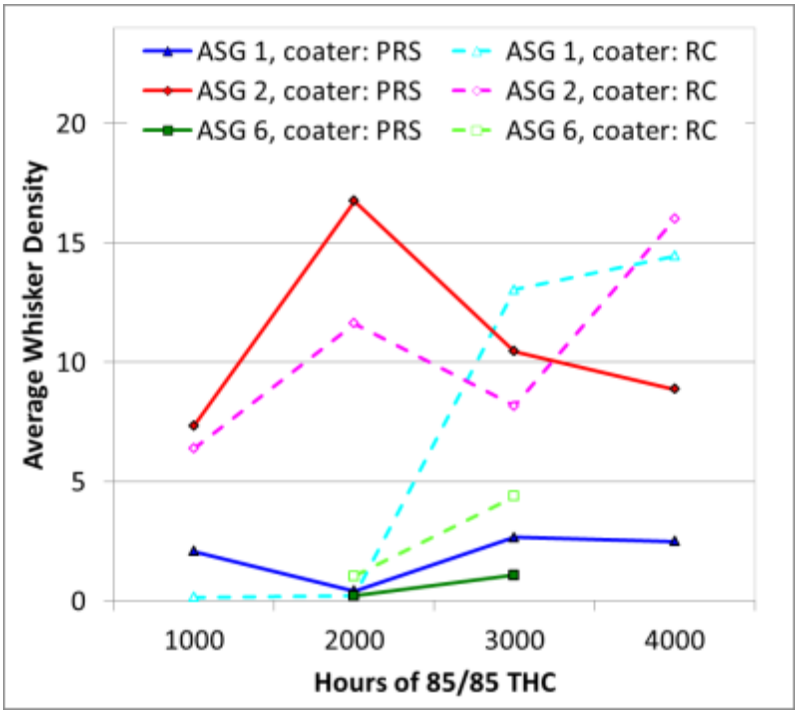

Figure 42 Effect of Coating Location

In addition to the Tin Man samples, the two production SMT components (the QFP and the SOIC) were inspected for the presence of tin whiskers. No tin whiskers were observed on any of

these parts until the inspections conducted after 3000 hours of 85/85THC. Table 9 shows the results of inspections on these parts at the 3000 and 4000 hours of exposure. A minimum of two samples were inspected for each combination and the table shows whether any whiskers were observed. In all cases, no more than a handful (less than 3) whiskers were observed on a given component.

Coating Conditions	QFP			SOIC	
Hours in 85/85=>	**3000**	**4000**		**3000**	**4000**
Control (none)	No	No		No	No
Hand Soldered	**Yes**	**Yes**		No	Yes
Acrylic	No	**Yes**		No	No
Parylene Coating	No	No		No	**Yes**
ASG 1	No	**Yes**		**Yes**	**Yes**
ASG 2	No	No		No	No
ASG 3	No	No		**Yes**	No
ASG 4	No	No		**Yes**	**Yes**
ASG 5	No	NA		No	NA
Hand Soldered / ASG 5	**Yes**	**Yes**		**Yes**	No
ASG 6*(ASG 1/acrylic)	**Yes**	NA		**Yes**	NA
ASG 7	**Yes**	NA		No	NA

Table 9 Occurrence of Tin Whiskers on SMT Components

Additional Work

In addition to the direct investigation of the effectiveness of ASG coatings on mitigating tin whiskers pure tin surfaces of electronics components, this project included a number of studies targeted at better characterizing the coatings. These included permeability measurements of coated plastic membranes, inclusion of the ASG coatings in an independent investigation that is being conducted by the National Physics Laboratory and characterization of the effects that ASG coatings have on RF circuits.

Coating Permeability Evaluations

To better quantify the degree to which ASG materials can protect tin whisker prone surfaces from moisture and oxidation, additional testing was conducted to measure the permeability of a number of candidate coatings. For this testing, coatings were applied to Polyethylene terephthalate (PET) film and then subjected to standard permeability testing by Mocon, Inc. This testing required that processing methods be modified to ensure coatings would have sufficient strength and adhesion on the PET film. This work also included additional assessments of alternate nanoparticles and treatments to extend the earlier materials development work conducted in the project.

Coatings evaluated for permeability testing were applied to both copper substrates and PET films for evaluation. The copper substrates, as before, were used to assess which coatings best inhibited oxidation while the PET substrates were inspected for cracking and subjected to tape peel tests to assess adhesion. While zirconia-based coatings did greatly reduce oxidation on the

copper substrates, they had such poor adhesion on the PET that they did not seem likely candidates to perform well in the permeability testing. Alumina-based coatings had good adhesion and no visible cracking on the PET but only somewhat reduced the rate of copper oxidation relative to uncoated surfaces. Zinc-oxide based coatings exhibited the best adhesion on PET, although with some cracking, with the copper oxidation level falling between that of zirconia and alumina-based coatings.

Ultimately, five sets of two samples each were provided to Mocon, Inc. for testing. Samples consisted of 2 mil thick PET film that was taped to a surface when coated, cured, and then cut to a 'stretched hexagonal' shape of ~4" x 6". After samples were coated, they were held to a flat surface with Kapton tape during curing to prevent the formation of residual stresses within the coating that would cause the film to significantly curl. The five samples of material that were tested are listed in Table 10. Sample 5 was uncoated PET film used to provide a baseline performance measurement. Samples 1, 2 and 4 were conventional coatings that included only one type of nanoparticle while sample 3 included a mixture of both Zinc Oxide and Alumina nanoparticles. This mixing of particles was included in the test to evaluate the potentially higher particle packing density that could theoretically be achieved due to the Zinc Oxide particles being approximately five times larger than the Alumina particles. Note that due to this difference in the size of the nanoparticles, the Alumina-based coatings tended to be more transparent than the Zinc Oxide-based coatings. Table 10 also includes a 'crack rank' that provides a relative indication of the degree to which the coatings appeared to have cracks with Sample 4 exhibiting the least cracking.

Table 10 Samples for Permeability Testing

Sample ID	Description	Crack Rank
1	2 microns of Zinc Oxide composite ASG coating on PET	2
2	4 microns of Zinc Oxide composite ASG coating on PET	3
3	4 microns of Zinc Oxide/Alumina composite ASG coating on PET	4
4	4 microns of Alumina composite ASG coating on PET	1
5	Uncoated PET	NA

Figure 43 shows images of samples prepared for two of the coatings (Samples 2 and 4). These pictures also include glass slides that were coated at the same time as the PET films and used to measure coating thicknesses. These were found to all fall within 0.2 microns of the target value.

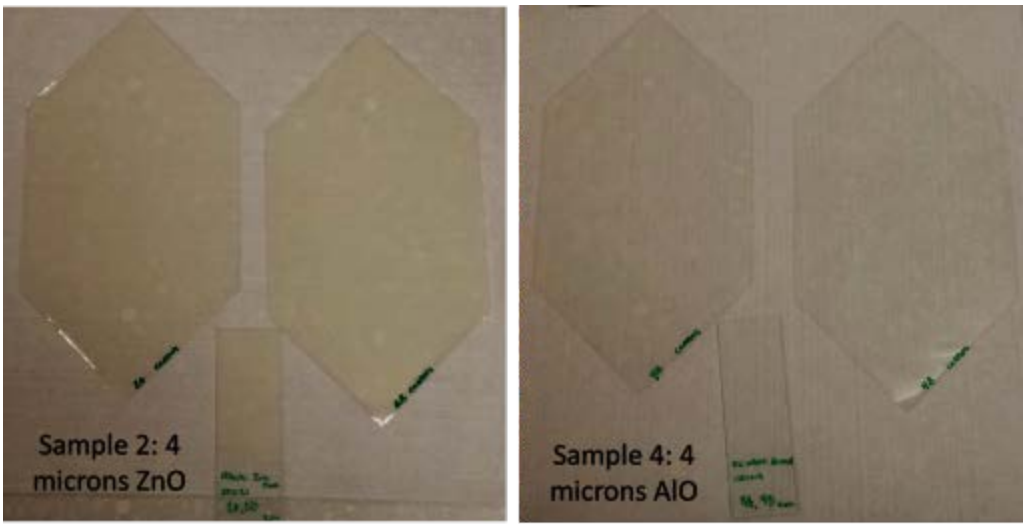

Figure 43 Samples Coated for Permeability Testing

Permeability testing of the coated films was conducted by Mocon, Inc. (Minneapolis, MN) using the protocol of the ASTM F 1249 test method, with modifications to improve resolution and temperature control. The fundamental approach of the test method is illustrated in Figure 44. Two streams of gas are in contact with the film under test. One stream enters the test block as dry nitrogen while the other stream has an inlet condition of nitrogen with a controlled level of Relative Humidity (RH). The RH, flow rates, and temperature of the sample can be adjusted for a given test. The exiting flow of the dry nitrogen stream is analyzed to determine the concentration of water within it, which is a function of the water permeability of the coated film.

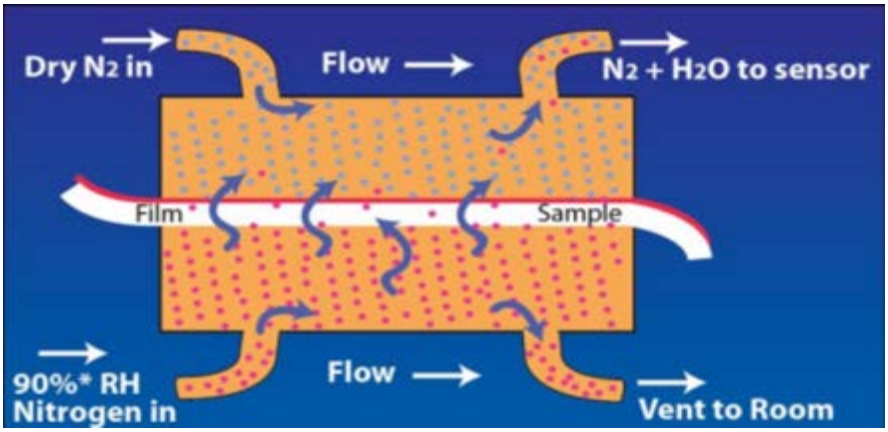

Figure 44 Conceptual Approach of Permeability Testing using ASTM F 1249 [22]

A Mocon Permatron-W 3/33 Water Vapor Permeability Instrument tested the coated TWICE samples with an inlet flow at 20°C and 40% relative humidity. Two samples of each coating combination were tested, with the resulting measurements shown in Table 11.

.

Table 11 Permeability Test Results

Sample ID	Description	Sample 1 (g/100 in^2 day)	Sample2 (g/100 in^2 day)
1	2 µm of Zinc Oxide / ASG coating on PET	0.109	0.108
2	4 µm of Zinc Oxide / ASG coating on PET	0.120	0.124
3	4 µm of Zinc Oxide/Alumina / ASG coating on PET	0.080	0.086
4	4 µm of Alumina / ASG coating on PET	0.116	0.115
5	Uncoated PET	0.112	0.105

Results from the permeability testing were surprising in that they showed very little impact of the ASG coating on the permeability to water vapor transmission. Discussions with Mocon are ongoing to better determine the test measurement accuracy for the conditions used in this testing. Since the PET film is more dense than materials typically evaluated with this measurement system, it is possible that an excessive flow rate of dry nitrogen may have been used. This would have led to a minimum detection level higher than the actual permeability of the samples. In addition, the returned test samples had an unexpected physical appearance that suggested that they may not have been adequately sealed during the tests. Evaluation of these results are ongoing and, if deemed necessary, this permeability testing may need to be repeated.

NPL Testing

The TWICE program had the opportunity to include the alumina nanocomposites ASG coating in a large tin whisker investigation being conducted by the National Physical Laboratory (NPL). The NPL has developed a unique test vehicle that allows for real time monitoring for electrical shorting due to tin whisker growth. A custom surface mount component with an internal daisy chain was plated with a bright acid tin that is a known tin whisker producing finish, coated with the ASG coating and subjected to standard laboratory temperature/humidity conditions. The internal daisy chain circuit (see Figure 45) allows for real time monitoring to detect when a tin whisker shorts adjacent leads. The testing methodology avoids the issue of potentially impacting a test component by removing it from its conditioning environment and subjecting it to SEM analysis.

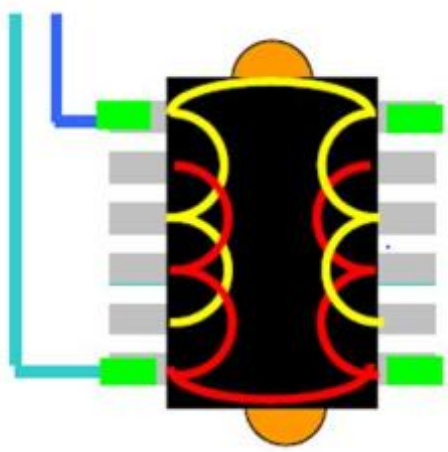

Figure 45 NPL Custom Surface Mount Component Internal Daisy Chain Configuration

Figure 46 illustrates tin whiskers growing between leads on the NPL control samples. The TWICE program test boards have accumulated a total of 12 months (8760 hours) of testing at NPL with no tin whisker shorting. The NPL Control (uncoated) samples developed multiple shorts due to whiskers within approximately two weeks. While tin whiskers have occurred on samples with many of the coatings included in the study, the results demonstrate that coatings can effectively insulate (electrically) a surface and greatly reduce, but not eliminate, the likelihood of a tin whisker induced failure. A separate publication by the NPL researchers will document details of that study and its conclusions.

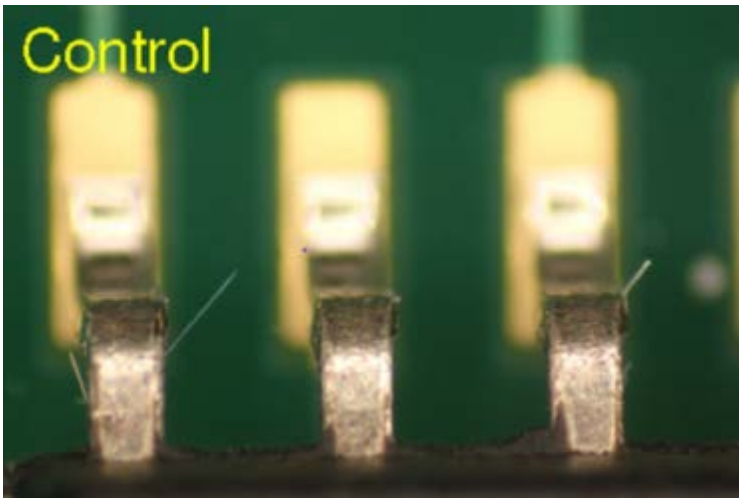

Figure 46 NPL Tin Whisker Control Test Sample (Courtesy of NPL, Dr. Chris Hunt)

Impact on RF Characteristics

Mitigating tin whiskers on Radio Frequency (RF) electronics can be more challenging than on digital or power electronics. This is due to the greater sensitivity of RF components and interconnect to the dielectric properties of adjacent materials. Traditionally, conformal coatings are not applied to many RF devices due to their impact on the device's functional operation. This is particularly true of harsh environment electronics that may be exposed to moisture and other contaminants; when organic coatings absorb these materials, their dielectric properties will change. This can de-tune RF circuits and cause them to operate out of specification and/or with significantly reduced efficiency.

ASG coatings are not organic, so they will not absorb moisture that would alter their dielectric properties. Moreover, since these coatings are extremely thin, their impact to the performance of any RF devices to which they are applied is expected to be minimal. Therefore, these materials may provide a tin whisker mitigation method that is simply not available from any currently used conformal coating, including Parylene.

<u>Initial Evaluation</u>

As part of the TWICE Phase 2 study, initial testing of conformal coatings was conducted on printed wiring boards (PWBs) designed to assess RF signal integrity. These PWBs, referred to as RF_TV1, were designed for evaluating the effect of surface finish on RF signal integrity and included a 10 cm long, microstrip transmission line with 50 Ω characteristic impedance in the 1-9GHz bandwidth. The RFTV_1 PWBs were fabricated with two different RF laminates: Rogers

6010 (D_k = 10.2, $\tan_d$ = 0.0023) and Rogers 4350B (D_k = 3.48, $\tan_d$ = 0.0031). Boards were tested by mounting them in an Anritsu Universal test fixture and measuring insertion loss though the transmission line from 10 MHz to 26.5 GHz with calibrated cables and connectors using an Agilent N5242A Network Analyzer.

Figure 47 RF_TV_1 RF Signal Integrity Test Boards

An RF_TV_1 test board that had been coated with 4 microns of an ASG4A composite with 10nm alumina is shown in Figure 48. Prior to being coated, short regions of each end of the trace were masked so that the board could then be correctly probed during subsequent RF testing. This figure also shows a region on the test board that was subjected to a tape-peel test to verify that the coating had adequate adhesion to the substrate. The image shows adhesive from the adhesive tape that remained on the test board during that test.

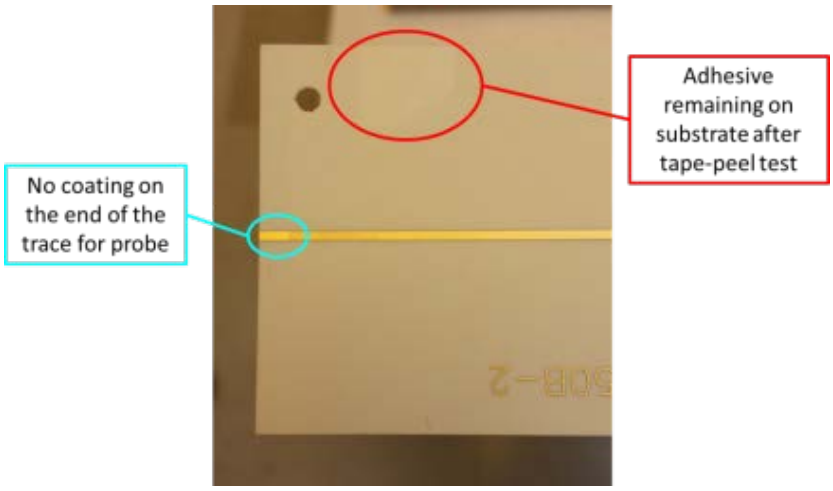

Figure 48 Coated RF_TV_1 Test Board

Figure 49 shows plots of the measured loss in multiple RF_TV_1 test boards fabricated with Rogers 4350B and 6010 materials. Test boards were coated with either ASG4A or Humiseal 1B31 acrylic coating. Two uncoated test boards with Rogers 4350B were also tested. These results showed that the coatings did not have a significant impact on the loss to the microstrip

structure. At higher frequencies (>15GHz), the loss was consistently higher in the boards with acrylic coating than those with ASG coating.

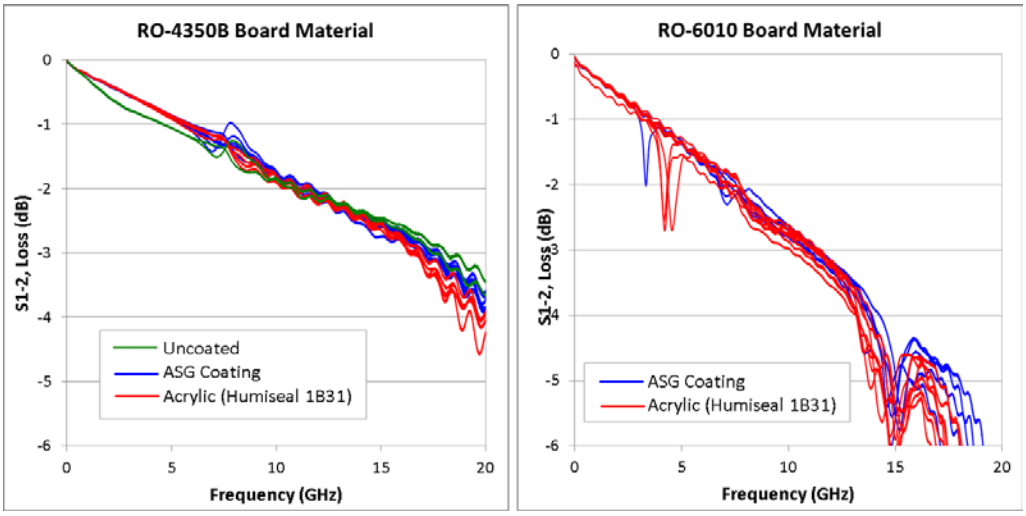

Figure 49 Loss (S_{1-2}) in Test Boards (uncoated, ASG coated, and Acrylic coated)

Figure 50 shows the results of simulations conducted with ANSYS HFSS (High Frequency Structural Simulator) software to predict loss in the RF_TV_1 test board for various coatings. The substrate in these simulations used the material properties of Rogers 4350B. Results show that both the acrylic and ASG coatings will not have significant impact on the RF loss, although the acrylic coating does introduce approximately 0.1dB more loss than the ASG. The simulations did not include the effects of test connectors, so the predicted losses are ~0.25dB less than measured. The plot also shows the predicted impact of a thin layer of water on the circuit board. This moisture would be expected in acrylic coating in circuit card assemblies that have been exposed to high humidity. However, since the ASG is inorganic, it should not absorb moisture and therefore its dielectric properties are not expected to change after exposure to humidity.

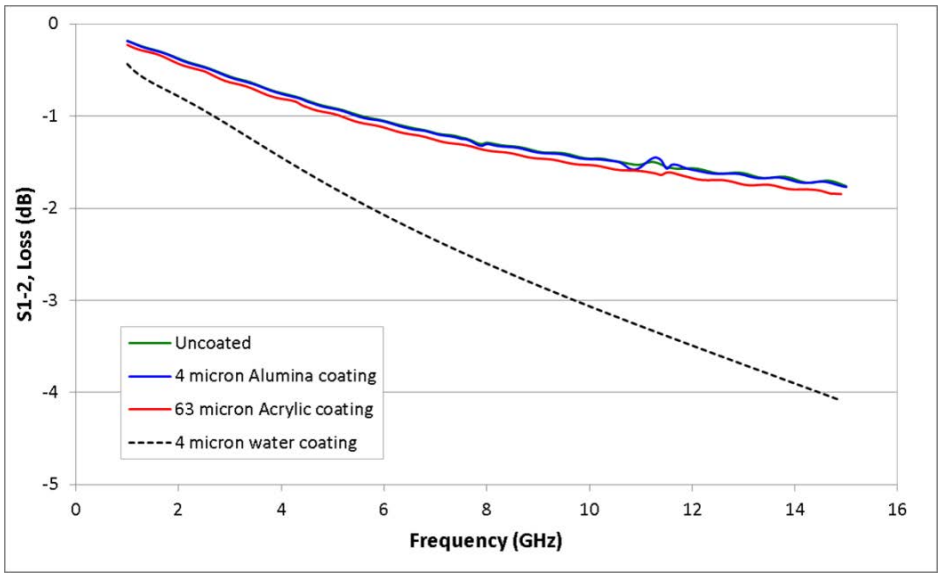

Figure 50 Simulated Loss in RF_TV_1 Test Boards

Follow-on Evaluation

The initial evaluation for the impact of conformal coatings on RF materials was somewhat limited by the geometry of the test vehicle and the test fixture used to characterize it. Subsequent to the initial evaluation, a follow-on study used smaller and better-controlled test vehicles to characterize the RF effects of the coatings at higher frequencies. To differentiate these tests from the initial evaluation, the test boards used for the follow-on testing are referred to as RF_TV_2 boards.

The RF_TV_2 boards were 0.75" x 1.25" x 13.3 mil thick and made of Rogers 4350B (D_k = 3.48, $\tan_d$ = 0.0031) material. A total of five of these test boards were evaluated. Boards 1 and 2 were coated with 63 microns of Humiseal 1B31 acrylic conformal coating; boards 3 and 4 were coated with a 4 micron thick layer of ASG4A (4:1 alumina nanoparticles, 120:1 dilution ratio, cured at 125°C for 1 hour); and board 5 was a control (uncoated) test board. Figure 51 shows images of the test boards before and after coating was applied. The image of the uncoated board shows the masking material applied to the test board connector areas. The mask was removed after coatings were applied to ensure adequate electrical contact between the connectors and the test board. The image of the uncoated board shows that test boards were kept in plastic bags prior to the coating process, in order to minimize oxidation and contamination.

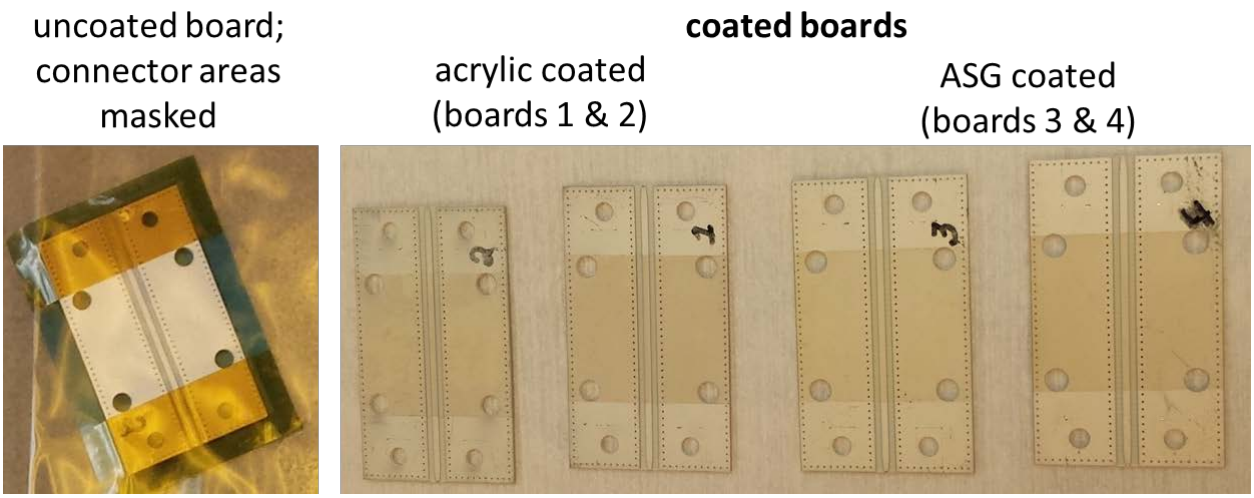

Figure 51 RF-TV_2 Test Boards Prior to Humidity Conditioning

Measurements were made to determine the RF loss (S_{1-2}) of the test board 50Ω stripline before and after the boards were coated. Following this characterization, the boards were subjected to 85°C/85% humidity for a minimum of 160 hours before being removed for post-humidity RF characterization.

Figure 52 shows images of the RF_TV_2 test boards after extended exposure to 85/85 humidity. The uncoated board test board had been used in a prior test and stored while mounted in a test fixture for an extended period, prior to this testing. The most severe oxidation on the uncoated board corresponds to those areas that were not covered by the test fixture or connectors. In addition, the uncoated board exhibits some localized tarnishing that is likely due to finger oils from handling. The other test boards in this study were only handled with gloves and do not show this type of local tarnish. The acrylic coated board shows some oxidation under the coating while the ASG coated board does not appear to show any tarnish.

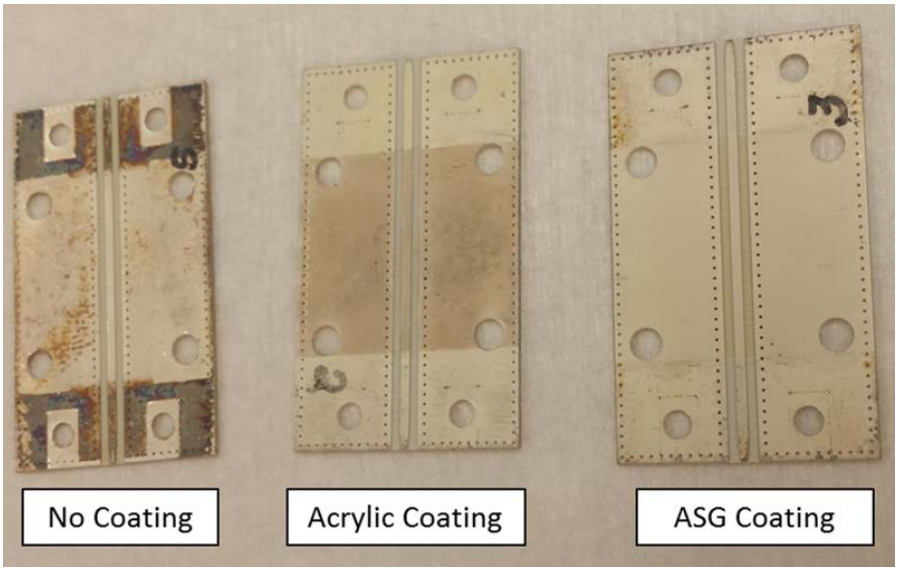

Figure 52 RF_TV_2 Test Boards after 160 hours of 85/85 Conditioning

Figure 53 compares the loss ($S_{1\text{-}2}$) of the five RF_TV_2 test boards for three conditions: before any boards were coated, after boards were coated and as quickly as possible after the test boards were removed from the humidity chamber. Due to the time needed to transport test boards between the two labs in which the humidity chamber and the RF test equipment were located, as well as the time required to place the board within the test fixture, RF testing could not be done immediately after test boards were removed from the humidity chamber. Instead, the initial post-humidity RF tests were conducted 7 minutes after the boards were removed from humidity.

Figure 53 shows very little variation in the RF loss among the test boards before coating, after coating and after humidity exposure. The ASG coated boards (in red/pink) may have slightly more loss (larger negative number) after humidity exposure than the other samples tested. However, the extremely small difference (~0.01dB) is within the variability associated with connecting the test board to the test fixture and is therefore not considered to be statistically significant.

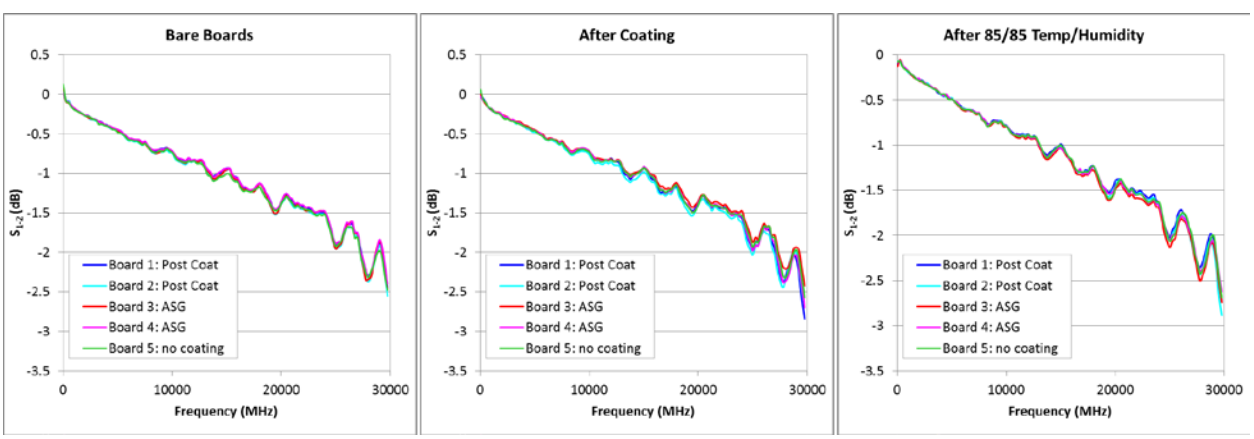

Figure 53 Comparison of RF_TV_2 Test Board Characterizations

Figure 54 directly compares the loss measurements for three individual test boards and shows that the loss slightly increased after exposure to humidity (the green lines in the left hand plots).

The right hand images in this figure show test data taken at times ranging from 7 to 60 minutes after removal from humidity. The change for each board in humidity is quite consistent and the values of S_{1-2} after removal from humidity remain relatively constant. These suggest that the humidity affected the board material, which would have a longer time constant for moisture diffusion, and not the thinner coatings. Regardless, the small changes in loss indicate that the presence of coatings would not substantially affect the performance of RF circuits.

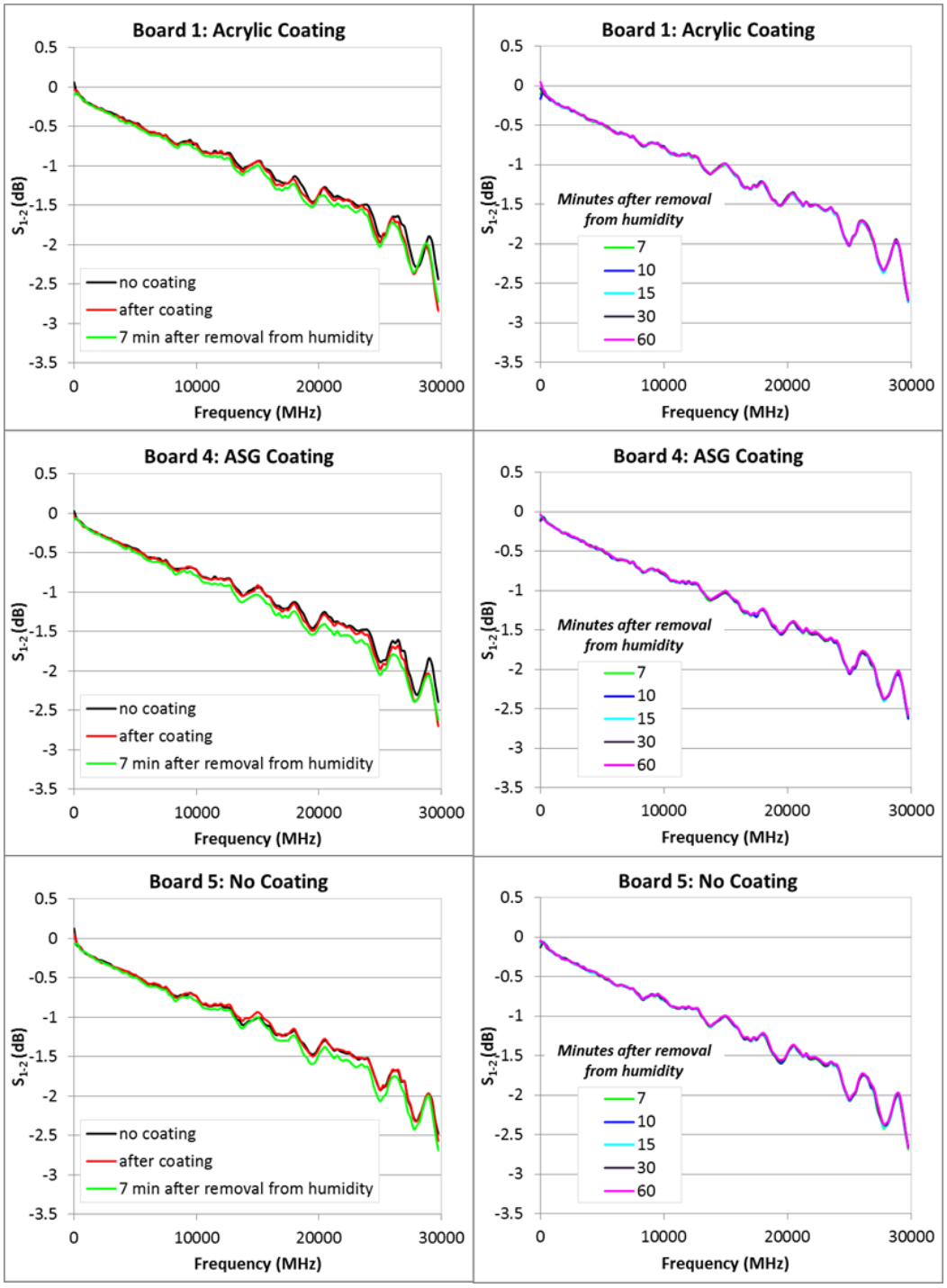

Figure 54 Loss in RF_TV_2 Test Boards: Effects of Humidity Conditioning

E.3 Discussion

TWICE has demonstrated that Alkali Silicate Glass coatings can influence how tin whiskers can form on tin surfaces, although in some cases this impact was surprising in that some coatings actually promoted, rather than inhibited, tin whisker growth. The goal of this study was not simply to prevent tin whiskers, but also to provide a deeper understanding of their genesis as well as to develop tools to control their formation. Therefore, the wide ranging effects of different ASG coatings on tin whisker formation is encouraging in that it suggests that variations in the formulation and deposition of ASG directly alter the mechanisms that lead to whisker formation. Understanding how to control these mechanisms is a critical step in understanding how to prevent tin whiskers.

In general, the coatings with the smallest particles (10nm) were more effective at inhibiting the growth of tin whiskers, presumably because they are better able to fill cracks and crevices within the coating and the tin plating. Filling these volumes should help to minimize the stress concentrations that are generally recognized as the initiation mechanism. Smaller particles could provide even further improvement, although procuring, handling and mixing/suspending particles that are 10nm or smaller in size can be challenging.

At the end of Phase 1 testing, all but one of the ASG coatings led to higher average whisker density than the Acrylic coating. The samples coated with the 4 micron thick composite formulation with small alumina nanoparticles and ASG4A material had approximately the same whisker density as the samples coated with Acrylic material. While the whisker density for that ASG material was similar to that of the Acrylic, there was a clear difference in character of the whiskers formed under the two coatings. Unlike those that form on ASG coated surfaces, whiskers on surfaces with Acrylic coating eventually emerged from the material relatively unscathed and continued growing to tens of microns, or more, in length.

ASG materials may ‘lose the battle’ of preventing the appearance of tin whiskers while winning the war to prevent them from substantially impacting the system reliability. The process of penetrating through the ASG coating clearly disrupts its normal growth process and leads to a ‘mushroom’ whisker that is only a few microns in length. Some studies [12, 20] have suggested an inverse correlation between whisker length and density such that there is a relatively fixed total volume of whisker material. In other words, a surface may have fewer, longer whiskers or more short whiskers. The tendency of ASG coatings to prevent whiskers from growing to full length may lead to the observation that more whiskers are then produced. From a system reliability perspective, the total number of whiskers produced on a surface is somewhat irrelevant; only the number of whiskers that grow long enough to cause a problem is important.

Testing showed that the specific formulation of the ASG-based coatings significantly affected how they influenced tin whisker growth. High-strength, brittle glass formulations appeared to induce stresses on the tin surfaces and accelerate tin whisker growth while the relatively softer ASG materials were more effective at inhibiting tin whiskers. Nanoparticle filler played a critical role in which the smaller particles improved the ability of a material to prevent long whiskers from growing. Deposition processes for these materials were also critical; the best results were seen when multiple layers of thin coatings were applied to build up comparatively thick (~4 micron layers). This deposition process led to coatings with fewer cracks that could produce stress concentrations that accelerate whisker growth. The use of an ultrasonic spraying head

allowed these thin coatings to be applied much more quickly than what could be achieved with the piezoelectric spraying head.

Of all the coatings evaluated in this study, at the end of Phase 2 testing, surfaces coated with Parylene were shown to have the fewest tin whiskers. This test result is in agreement with other published data [17, 18]. However, Parylene will never be the 'end-all' solution for tin whisker mitigation. This study, as well as the Woodrow investigation [16], demonstrated that tin whiskers could penetrate and erupt through a Parylene coating in a similar fashion to traditional conformal coatings. The deposition processes for Parylene are time consuming, expensive and the resulting coating is difficult to rework. While Parylene is certainly well suited for many markets, it is not suitable for many others – primarily due to cost and reworkability. In addition to cost and reworkability challenges, Parylene, like other conformal coatings, is not typically viable for direct coating of many RF devices that include structures such as air-bridges. The dielectric constant of these materials will affect device performance and their ability to absorb moisture leads to changes in the dielectric properties of the materials. The inorganic ASG coatings are expected to absorb less moisture, which would reduce changes in RF performance over time.

The ASG material used in Phase 2 exhibited the best whisker mitigation of all the ASG formulations included in this investigation. This is likely due to the use of the smaller nanoparticles, which helped to fill cracks in the tin plating, and a relatively thick coating (of ~4 microns) that better contained any whiskers that were present. Moreover, the growth characteristics of any whiskers that did form under this coating, or any of the ASG coatings in Phase 2, were substantially altered such that they would not likely grow to be long enough to lead to any failures.

The relatively smooth transition of implementing ASG materials at Ruggedized Plasma Solutions is a good indicator that the application processes are stable and robust. The equipment at PRS was similar to that used by Rockwell Collins, but not an exact match. Despite this, PRS was able to implement the recommended coating methods and produce coatings with similar characteristics as those applied at Rockwell Collins. A manufacturing challenge associated with the extremely thin coatings produced with the ASG materials is that they are very difficult to inspect. The materials can be optically transparent and are not visible under conventional inspection methods such as under a black light. Further work is needed to identify methods for effectively inspecting these extremely thin ASG coatings in a production environment.

F. Conclusions and Implications for Future Research/Implementation

Conclusions

The ASG coatings selected for this study produced tin whisker growth behavior that ranged from higher whisker density than uncoated samples, when coatings had high residual stress, to a significant whisker reduction for lower stress coatings with small nanoparticle filler. In all cases, the ASG coatings disrupted the formation of tin whiskers such that they remained so short that they were unlikely to pose a reliability threat. In contrast, while the conventional coatings (acrylic and Parylene) did produce fewer tin whiskers than the ASG coatings, they did not alter whisker morphology and appeared to only delay the risk from tin whisker growth rather than eliminate it.

Successful application of coatings at two different locations (Rockwell Collins and Plasma Ruggedized Solutions) demonstrated that the material processing and application methods are sufficiently robust that the ASG coatings are well positioned to eventually be transitioned to the wider DoD electronics manufacturing community. Thermal cycle testing of coated boards indicated that ASG coatings are sufficiently robust for a wide range of military and avionics use environments.

Future Research/Implementation

The results of this study are encouraging in that they provide strong evidence that ASG-based coatings can offer an effective alternative to more conventional coatings for tin whisker mitigation. While the ASG-based coatings do not eliminate tin whiskers from at-risk surfaces, they do significantly disrupt the continued growth of whiskers. This greatly reduces the risks of electrical shorting typically feared from tin whiskers. Continued work is needed to assess the system impact to performance and reliability of ASG-coated surfaces, and to establish consistent coatings that lend themselves to effective documentation and inspection. This work would include more extensive testing of the robustness of the coating when used on circuit boards and components subjected to DoD operational environments. This testing would characterize the effects of dynamic loading (shock and vibration) on coatings as well as their resistance to harsh fluids and salt spray. In addition, the system impact of alternative coatings on factors such as thermal radiation and RF loss would also need to be quantified to provide information to designers of circuit boards that would be coated. These activities are described in some detail in Appendix 6.

Traditional conformal coating materials utilize UV fluorescing agents to aid in optical inspection of the coating coverage. The ASG4A coating is not currently compatible with that technology and the topic remains an area for future investigation. This work may include incorporating fluorescing nanoparticles into the composite formulations or developing alternate methods for inspecting coated surfaces.

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H. Appendices

Appendix	Title	Description
1	Background on Tin Whiskers	Brief overview of the tin whisker phenomenon and a discussion of the need for improved mitigation strategies.
2	Rockwell Collins ASG Coatings	Overview of Alkali Silicate Glass (ASG) material development work that conducted by Rockwell Collins.
3	Glass Slide Coating DOE Results	Detailed measurements of coating thickness and roughness resulting from different processing settings.
4	University of Maryland MVA Testing Final Report	Detailed description of test methods and results of Metal Vapor Arc testing with ASG coatings by sub-contractor University of Maryland.
5	Plasma Ruggedized Solutions Phase 1 Report	Report of Phase 1 application conditions and lessons learned by sub-contractor Plasma Ruggedized Solutions
6	Operational Use Environmental Testing of Alkali Silicate Glass Coatings	White paper provided to SERDP with information on follow-on testing necessary to transition the ASG coating technology to DoD systems (requested after April 2013 review).
7	Discussion on Alkali Silicate Glass Formulations	White paper provided to SERDP with ASG formulation details (requested after April 2014 review).
8	Nanoparticle formulations discussion	Detailed discussion of considerations into nanoparticle composites with ASG.
9	Plasma Ruggedized Solutions Phase 2 Report	Report of Phase 2 application conditions and lessons learned by sub-contractor Plasma Ruggedized Solutions.
10	List of Scientific/Technical Publications	Conference paper and presentations that describe the work conducted under the TWICE program

Appendix 1: Background on Tin Whiskers

The transition to lead-free electronics has generated a need for improved understanding of how fundamental physical mechanisms associated with lead-free materials impact reliability. One of these mechanisms is the phenomenon of tin whiskers. Tin whiskers are metallic filaments, which grow from pure tin surfaces, that have been shown to cause shorting and other failures in fielded systems. This phenomenon has been recognized for decades, but the need to fully understand the physics behind tin whiskers subsided once it was shown that they could be prevented by 'poisoning' tin with small amounts of lead. The adoption of lead-free electronics has eliminated this simple, if not fully understood, method for preventing tin whiskers, thereby provoking renewed interest in the physics behind their formation and mitigation. While there is debate regarding the precise mechanisms that lead to tin whiskers, there is general agreement that they are due to internal compressive stresses within the tin, which promote the formation of crystal structures [10]. This has led to a number of theories to describe the kinetic growth mechanisms [11], but the issue is far from settled and further work is needed to understand the phenomenon.

A number of investigations have demonstrated that internal stresses in tin plating promote the initiation and growth of tin whiskers. Tin whisker investigations at Boeing [12] have provided a key advance in the understanding of tin whisker kinetics. The investigation monitored two separate non-radioactive tin isotopes (Sn^{120} and Sn^{118}) to demonstrate that tin atoms can diffuse through the tin grain structure predominately along tin grain boundaries over long distances, to enable tin whisker growth. This process is shown conceptually in Figure 1. Examination of tin whisker crystals produced in this study revealed that no visible local tin source (i.e. voids, pits, reduction of the tin plating layer at the whisker root, etc.) was present.

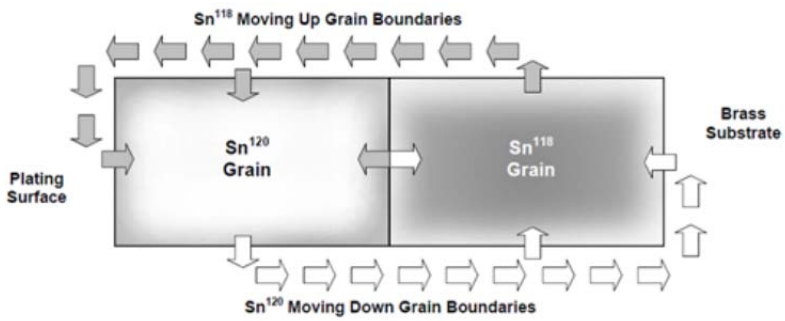

Figure 1 Tin Atom Diffusion Path Options [12]

Another critical parameter in understanding tin whisker formation is the initiation mechanism. The industry consensus, that internal stresses generate the driving forces to move tin atoms along the tin grain boundaries, is valid provided there is a vacancy well in the tin plating structure for tin atoms to fill. A recent publication that investigated the effect of creep on the growth of tin whiskers [6] postulated that the movement of tin atoms along tin grain boundaries could be restricted by intermetallic phases, contaminates (such as hydrogen or carbon) and corrosion. The resulting inability of tin atoms to move along these grain boundaries generates internal stresses that may be relieved by creep or through tin whisker growth. As shown in Figure 2, the tin plating grain size and temperature dictate whether this stress relief is likely to occur through creep or whisker growth.

An additional illuminating study [7] has found that ionic contamination from flux chemistries on a tin surface increased eventual tin whisker density and tin whisker length. Rockwell Collins has demonstrated similar results using ionic contamination due to salt exposure of bright acid tin plated test samples [13]. Both of these investigations indicated that alteration of the tin oxide species can create an initiation point for possible tin whiskers.

Combining the results of these investigations provides a physical picture of how tin whiskers initiate and grow. When tin atoms are pinned and unable to move along the tin grain boundaries, the tin plating has no mechanism to relieve internal stresses. Any break in the tin oxide layer will create an avenue to relieve these internal stresses by forming a tin whisker that is fed with tin atoms moving along available tin grain boundaries, as shown in Figure 3. These breaks in the tin oxide layer are inevitable and exacerbated by the effects of ionic contamination, which promotes localized corrosion of the tinned surfaces and thereby leads to the higher tin whisker growth and density that has been observed [7, 13].

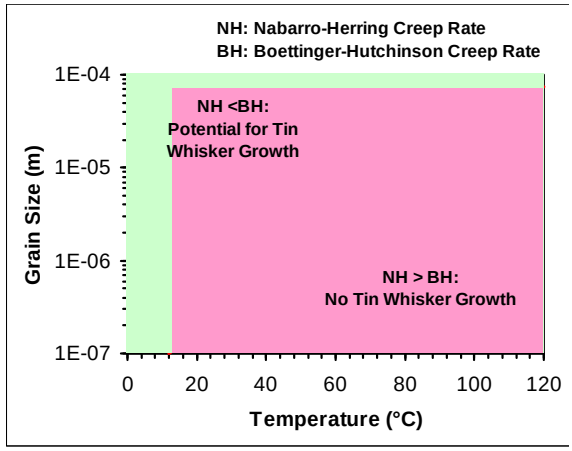

Figure 2 Creep Rate Impact on Tin Whisker Growth, adapted from [4]

Recognizing this as the possible mechanism that ultimately leads to tin whiskers provides significant insight regarding what mitigation paths will be most effective. The data in [11] suggests that tin whisker initiation could theoretically be prevented by controlling grain size (i.e., tin atom kinetics). However tin plating production processes and the effects of tin grain recrystalization dictate that grain size control is not a practical method for eliminating tin whiskers. Furthermore, while ionic contamination in production soldering processes can be prevented through consistent manufacturing procedures and process material selection, in-service exposure of fielded equipment and the use of COTS components will inevitably introduce conditions that can promote tin whiskers. Since the conditions that lead to tin whiskers can not be avoided (in pure tin finishes), the most practical approach for preventing their effects is to reduce their initiation by minimizing breaks in the tin oxide layer and impeding the growth of tin whiskers that are generated.

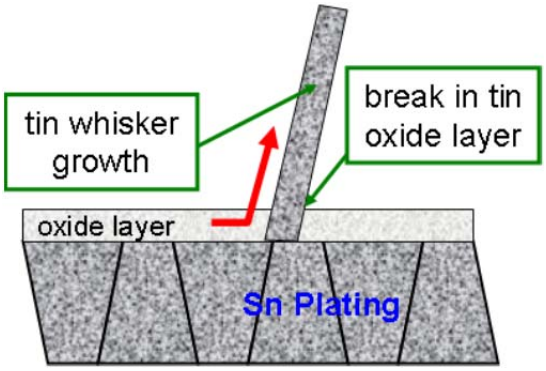

Figure 3 Proposed Tin Whisker Growth Mechanism, adapted from [12]

The most viable method for achieving that goal is to coat the tin surfaces with a material that ideally features the following characteristics:

- The coating would be impervious to moisture to prevent corrosion of the tin oxide layer.
- The coating would bond extremely well to the tin oxide layer. This would provide two benefits: it would inhibit tin corrosion by minimizing contact with moisture and also allow the coating to strengthen the tin oxide layer to reduce the formation and growth of cracks in the tin oxide.
- The coating would have a high modulus of elasticity and hardness so that any tin whiskers that do form would not be able to penetrate through it.

- The coating would be sufficiently compliant to minimize the formation of cracking due to strains induced by thermal excursions, mechanical flexing and stress concentrations. The material also must be sufficiently ductile such that any cracks that do form will not grow.
- The coating would fully cover tinned surfaces, including difficult-to-access regions including the undersides and bends of leaded components.
- Costs of the coating, including material costs, required production equipment, processing requirements and cure times/temperatures, etc. would be compatible with industry needs for DoD and other harsh environment electronics.

Conventional conformal coating materials are typically organic materials, in part because they are relatively easy to apply and cure on electronics. Inorganic coatings, such as glass, tend to have superior properties with respect to moisture permeability and hardness but are not obvious choices due to their normal processing requirements and potential brittleness. The Tin Whiskers Inorganic Coating Evaluation (TWICE) program introduces an inorganic coating that can be formulated and processed to have the characteristics described above.

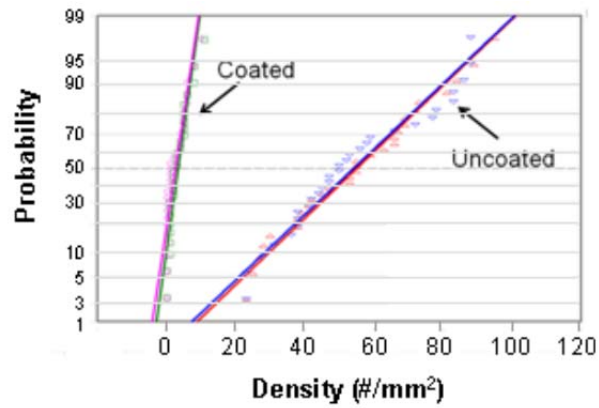

Figure 4 Impact of Urethane Coating on Tin Whisker Growth [17]

The recognition that oxidation [14], corrosion [15] and ionic contamination [4] can initiate and exacerbate tin whisker initiation/growth has led to investigations on the use of conformal coatings to mitigate tin whiskers. A study by Boeing has in fact shown that conformal coatings were able to delay the formation of tin whiskers on bright acid tin surfaces [16]. That work included a number of coatings including Parylene, acrylic and urethane. None of these completely eliminated the tin whisker phenomenon. The work did find that Parylene, which had the lowest oxygen and water vapor permeability as well as the highest modulus of elasticity of the coatings evaluated, was generally the most effective at mitigating tin whiskers. However, there was no strong correlation between coating moisture permeability or stiffness and tin whisker growth, as other coatings with vastly different stiffness and permeability produced similar results to the Parylene coating. An 11 year NASA investigation on the effects of urethane conformal coating as a tin whisker mitigation strategy provided additional insight into how conformal coating impacts tin whisker behavior [17]. The NASA investigative team found that the urethane conformal coating inhibited tin whisker growth from tin plated test sample surfaces. Once the urethane conformal coating was removed from samples, significant initiation and growth of tin whiskers was observed (Figure 4).

The results from [16] and [17] are encouraging in that they showed that conformal coating, which can be applied by manufacturers to ruggedize lead-free components against tin whiskers, do disrupt tin whisker formation and growth mechanisms. However, since none of the conformal coatings investigated in those studies eliminated tin whiskers, it is clear that further work is needed to develop a material that can sufficiently mitigate tin whisker risk.

Appendix 2: Rockwell Collins ASG Coatings

Over the past four years, Rockwell Collins has investigated the use of Alkali Silicate Glass materials in electronics. These materials are applied and cured at relatively low temperatures (typically ~120°C). Rockwell Collins has developed formulations of ASG suitable for extremely thin coatings that can be selectively applied to regions on packaged die. For example, Figure 5 shows 1 mil (24.4 micron) diameter wirebonds on an integrated circuit that have been coated with an ASG material to inhibit corrosion. In addition, ASG formulations have been developed for use as the matrix of a composite thermally conductive encapsulant [18] currently used in a military electronics system.

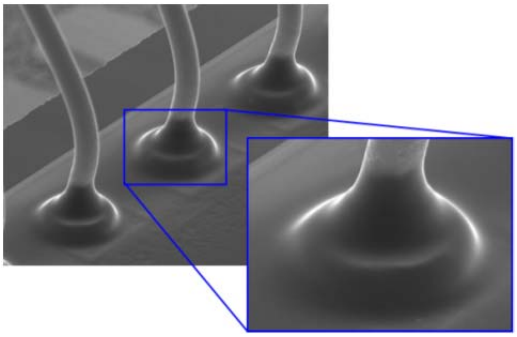

Figure 5 ASG Coated Wirebonds

The moisture permeability of ASG is significantly lower than that of Parylene. The effect of this permeability difference is clearly demonstrated in Figure 6, which shows a sample of copper that was coated with both ASG and Parylene prior to being placed in an oxidizing environment. Only the left half was coated with ASG while only the lower half was coated with Parylene. The discoloration on the right half of Figure 6, regardless of whether the quadrant was Parylene coated, shows a significant difference between how the two materials prevent oxidation in the underlying metal.

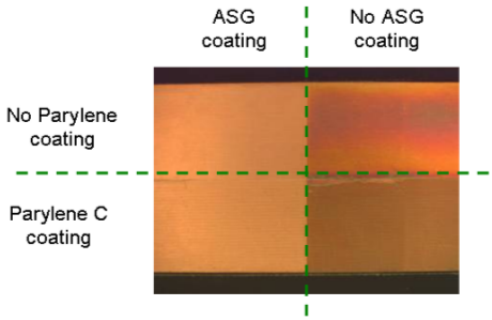

Figure 6 Parylene compared to ASG

In addition to moisture permeability, ASG materials exhibit a number of characteristics that can provide benefits as an electronics coating. The structural properties (hardness and modulus) of ASG are at least an order of magnitude higher than that of Parylene. Also, the dielectric strength of the ASG coating (>300 V/mil) can protect a surface against electrical leakage and shorting, such as that which could occur if a loose tin whisker were present on a surface.

Rockwell Collins has investigated methods for applying ASG coatings to a variety of surfaces using highly localized spraying of multiple thin layers of material. This approach enables extremely controlled deposition, in terms of both the location and thickness of a layer. It also allows for co-deposition of different materials to alter the layer properties and their impact to the surfaces to which they are applied. The essential keys to producing ASG coatings that will affect surfaces, such as those prone to tin whiskers, are a) the specific formulations of ASG with nanoparticle modifiers and b) processing for low stress cured materials.

Nanoparticle modifiers can be used to tailor the structure of the cured ASG material and control its properties. For example, work at Rockwell Collins has shown that the inclusion of zinc oxide nanoparticles can significantly improve the chemical resistance of the glass coatings. The effectiveness of a conformal coat to mitigate tin whiskers lies in its uniformity and completeness of coverage. Conventional conformal coatings tend to be thin on component termination corners, where residual stresses tend to initiate whiskers, and on the undersides of leads. In contrast, Figure 5 shows that ASG can be applied with consistent uniform coverage on die and wirebond surfaces that have an order of magnitude finer geometries than components.

Appendix 3: Glass Slide Coating DOE Results

Table 1 Glass Slide DOE: Samples with UVO Pre-treatment

RUN	# of passes	NEEDLE HEIGHT (in)	BARREL PRESSURE (psi)	COAX FLOW PRESSURE (psi)	RASTER SPEED (in/s)	DILUTION (DI:ASG)	COATING THICKNESS (um)	PEAK TO VALLEY (um)	RMS ROUGHNESS (um)
1	10	0.75	0.15	5	5	30	0.315	0.845	0.125
1	10	0.75	0.15	5	5	30	0.21	0.555	0.105
1	10	0.75	0.15	5	5	30	0.46	0.735	0.175
1	20	0.75	0.15	5	5	30	0.24	0.81	0.18
1	20	0.75	0.15	5	5	30	0.38	0.775	0.22
1	20	0.75	0.15	5	5	30	0.56	0.995	0.235
2	10	1.75	0.15	5	5	15	1.295	2.355	0.415
2	10	1.75	0.15	5	5	15	1.35	2.255	0.475
2	10	1.75	0.15	5	5	15	1.75	1.49	0.285
2	20	1.75	0.15	5	5	15	2.02	2.895	0.605
2	20	1.75	0.15	5	5	15	3.165	4.045	1.09
2	20	1.75	0.15	5	5	15	2.83	3.625	0.795
3	10	0.75	0.5	5	5	15	3.81	1.775	0.335
3	10	0.75	0.5	5	5	15	3.175	2.585	0.6
3	10	0.75	0.5	5	5	15	2.795	2.05	0.425
3	20	0.75	0.5	5	5	15	6.59	5.075	1.135
3	20	0.75	0.5	5	5	15	6.02	5.4	1.285
3	20	0.75	0.5	5	5	15	5.78	4.475	1.285
4	10	1.75	0.5	5	5	30	0.98	1.18	0.35
4	10	1.75	0.5	5	5	30	1.175	1.42	0.235
4	10	1.75	0.5	5	5	30	1.315	1.775	0.47
4	20	1.75	0.5	5	5	30	1.7	2.225	0.705
4	20	1.75	0.5	5	5	30	1.315	1.865	0.41
4	20	1.75	0.5	5	5	30	1.315	2.285	0.455
5	10	0.75	0.15	15	5	15	3.13	3.145	0.81
5	10	0.75	0.15	15	5	15	3.62	2.44	0.445
5	10	0.75	0.15	15	5	15	3.67	3.54	0.725
5	20	0.75	0.15	15	5	15	13.32	5.85	1.465
5	20	0.75	0.15	15	5	15	14.85	5.93	1.095
5	20	0.75	0.15	15	5	15	11.13	4.74	0.955
6	10	1.75	0.15	15	5	30	0.625	1.09	0.225
6	10	1.75	0.15	15	5	30	0.455	0.83	0.205
6	10	1.75	0.15	15	5	30	0.67	0.925	0.34
6	20	1.75	0.15	15	5	30	1.045	1.47	0.325
6	20	1.75	0.15	15	5	30	0.875	1.33	0.295
6	20	1.75	0.15	15	5	30	0.815	1.04	0.22
7	10	0.75	0.5	15	5	30	0.775	1.01	0.21
7	10	0.75	0.5	15	5	30	0.8	1.05	0.185
7	10	0.75	0.5	15	5	30	0.895	1.085	0.29
7	20	0.75	0.5	15	5	30	1.79	2.32	0.48
7	20	0.75	0.5	15	5	30	1.565	1.73	0.41
7	20	0.75	0.5	15	5	30	1.42	1.655	0.335
8	10	1.75	0.5	15	5	15	5.125	2.875	0.635
8	10	1.75	0.5	15	5	15	4.82	23.28	0.35
8	10	1.75	0.5	15	5	15	4.45	2.455	0.51
8	20	1.75	0.5	15	5	15	7.175	2.65	0.535
8	20	1.75	0.5	15	5	15	8.625	4.14	0.715
8	20	1.75	0.5	15	5	15	7.575	3.505	0.62

RUN	# of passes	NEEDLE HEIGHT (in)	BARREL PRESSURE (psi)	COAX FLOW PRESSURE (psi)	RASTER SPEED (in/s)	DILUTION (DI:ASG)	COATING THICKNESS (um)	PEAK TO VALLEY (um)	RMS ROUGHNESS (um)
9	10	0.75	0.15	5	10	15	0.65	1.695	0.29
9	10	0.75	0.15	5	10	15	0.495	1.16	0.205
9	10	0.75	0.15	5	10	15	0.8	1.395	0.315
9	20	0.75	0.15	5	10	15	1.395	2.02	0.51
9	20	0.75	0.15	5	10	15	1.475	2.58	0.59
9	20	0.75	0.15	5	10	15	1.47	2.755	0.625
10	10	1.75	0.15	5	10	30	0.21	0.49	0.115
10	10	1.75	0.15	5	10	30	0.25	0.48	0.095
10	10	1.75	0.15	5	10	30	0.215	0.57	0.15
10	20	1.75	0.15	5	10	30	0.395	0.93	0.19
10	20	1.75	0.15	5	10	30	0.335	0.745	0.145
10	20	1.75	0.15	5	10	30	0.335	0.87	0.17
11	10	0.75	0.5	5	10	30	0.37	0.675	0.12
11	10	0.75	0.5	5	10	30	0.23	0.5	0.13
11	10	0.75	0.5	5	10	30	0.305	0.765	0.125
11	20	0.75	0.5	5	10	30	0.91	2.18	0.505
11	20	0.75	0.5	5	10	30	0.615	2.06	0.37
11	20	0.75	0.5	5	10	30	0.65	1.1	0.245
12	10	1.75	0.5	5	10	15	1.625	2.365	0.605
12	10	1.75	0.5	5	10	15	1.495	2.975	0.505
12	10	1.75	0.5	5	10	15	2.37	2.995	0.675
12	20	1.75	0.5	5	10	15	3.34	4.78	1.3
12	20	1.75	0.5	5	10	15	3.57	4.59	1.115
12	20	1.75	0.5	5	10	15	3.61	3.12	0.78
13	10	0.75	0.15	15	10	30	0.31	0.655	0.115
13	10	0.75	0.15	15	10	30	0.32	0.535	0.125
13	10	0.75	0.15	15	10	30	0.235	0.575	0.1
13	20	0.75	0.15	15	10	30	0.475	0.74	0.14
13	20	0.75	0.15	15	10	30	0.515	0.66	0.175
13	20	0.75	0.15	15	10	30	0.605	0.91	0.22
14	10	1.75	0.15	15	10	15	2.365	1.885	0.41
14	10	1.75	0.15	15	10	15	2.41	1.705	0.33
14	10	1.75	0.15	15	10	15	2.475	1.825	0.345
14	20	1.75	0.15	15	10	15	4.33	1.835	0.345
14	20	1.75	0.15	15	10	15	3.855	1.535	0.39
14	20	1.75	0.15	15	10	15	4.54	1.655	0.315
15	10	0.75	0.5	15	10	15	2.03	1.89	0.245
15	10	0.75	0.5	15	10	15	2.12	1.36	0.275
15	10	0.75	0.5	15	10	15	1.975	1.12	0.21
15	20	0.75	0.5	15	10	15	3.76	1.98	0.39
15	20	0.75	0.5	15	10	15	2.715	1.52	0.305
15	20	0.75	0.5	15	10	15	3.65	1.48	0.295
16	10	1.75	0.5	15	10	30	0.685	1.185	0.2
16	10	1.75	0.5	15	10	30	0.515	1.17	0.185
16	10	1.75	0.5	15	10	30	0.65	1.335	0.295
16	20	1.75	0.5	15	10	30	1.03	1.115	0.22
16	20	1.75	0.5	15	10	30	1.04	1.89	0.44
16	20	1.75	0.5	15	10	30	1.26	1.575	0.31
17	10	0.75	0.15	15	5	60	0.36	0.41	0.085
17	10	0.75	0.15	15	5	60	0.385	0.56	0.1
17	10	0.75	0.15	15	5	60	0.32	0.345	0.08
17	20	0.75	0.15	15	5	60	0.695	0.745	0.155

RUN	# of passes	NEEDLE HEIGHT (in)	BARREL PRESSURE (psi)	COAX FLOW PRESSURE (psi)	RASTER SPEED (in/s)	DILUTION (DI:ASG)	COATING THICKNESS (um)	PEAK TO VALLEY (um)	RMS ROUGHNESS (um)
17	20	0.75	0.15	15	5	60	0.455	0.775	0.135
17	20	0.75	0.15	15	5	60	0.705	0.795	0.155
18	10	1.75	0.5	15	5	60	0.58	0.56	0.095
18	10	1.75	0.5	15	5	60	0.6	0.535	0.1
18	10	1.75	0.5	15	5	60	0.595	0.595	0.105
18	20	1.75	0.5	15	5	60	0.945	0.485	0.075
18	20	1.75	0.5	15	5	60	1.21	0.805	0.205
18	20	1.75	0.5	15	5	60	0.935	0.815	0.19
19	10	0.75	0.15	15	10	60	0.245	0.285	0.055
19	10	0.75	0.15	15	10	60	0.115	0.165	0.03
19	10	0.75	0.15	15	10	60	0.21	0.3	0.05
19	20	0.75	0.15	15	10	60	0.41	0.48	0.07
19	20	0.75	0.15	15	10	60	0.305	0.43	0.065
19	20	0.75	0.15	15	10	60	0.365	0.29	0.045
20	10	1.75	0.5	15	10	60	0.375	0.665	0.06
20	10	1.75	0.5	15	10	60	0.325	0.35	0.05
20	10	1.75	0.5	15	10	60	0.36	0.52	0.09
20	20	1.75	0.5	15	10	60	0.57	0.695	0.075
20	20	1.75	0.5	15	10	60	0.625	0.715	0.11
20	20	1.75	0.5	15	10	60	0.56	0.56	0.09
21	10	0.75	0.15	5	5	60	0.15	0.33	0.09
21	10	0.75	0.15	5	5	60	0.16	0.52	0.085
21	10	0.75	0.15	5	5	60	0.115	0.245	0.045
21	20	0.75	0.15	5	5	60	0.285	0.585	0.085
21	20	0.75	0.15	5	5	60	0.235	0.645	0.12
21	20	0.75	0.15	5	5	60	0.195	0.57	0.1
22	10	1.75	0.5	5	5	60	0.255	0.78	0.15
22	10	1.75	0.5	5	5	60	0.43	0.82	0.14
22	10	1.75	0.5	5	5	60	0.3	0.49	0.12
22	20	1.75	0.5	5	5	60	0.515	1.995	0.305
22	20	1.75	0.5	5	5	60	0.63	1.26	0.335
22	20	1.75	0.5	5	5	60	0.83	1.065	0.19
23	10	0.75	0.15	5	10	60	0.09	0.39	0.06
23	10	0.75	0.15	5	10	60	0.115	0.305	0.04
23	10	0.75	0.15	5	10	60	0.07	0.22	0.03
23	20	0.75	0.15	5	10	60	0.13	0.42	0.07
23	20	0.75	0.15	5	10	60	0.11	0.54	0.1
23	20	0.75	0.15	5	10	60	0.07	0.39	0.065
24	10	1.75	0.5	5	10	60	0.25	0.4	0.12
24	10	1.75	0.5	5	10	60	0.105	0.325	0.055
24	10	1.75	0.5	5	10	60	0.205	0.335	0.07
24	20	1.75	0.5	5	10	60	0.375	0.56	0.095
24	20	1.75	0.5	5	10	60	0.305	0.525	0.08
24	20	1.75	0.5	5	10	60	0.355	0.63	0.12

Appendix 4: University of Maryland MVA Testing Final Report

CALCE Report

Report Title: *Evaluation of Tin* Whisker Induced Arcing On Conformal Coated Conductor Surfaces

Principal Investigator: *Michael Osterman*

Abstract:

Testing was conducted to assess the impact of conformal coats on inhibiting tin whiskers from initiating metal vapor arc. The results indicate that selected conformal coat materials did not influence arc initiation when electrical contact is made. Interestingly, the 1B31 coating appeared to contain the arc and the coated bridge that formed over the whiskers remained intact after the arc test. While the test size was limited, the results were nearly identical to extensive testing CALCE has conducted previously on non-coated test specimens. Metal vapor arcs are highly likely to initiate when a cold current metric value is found to be greater than 5 A and unlikely to occur if the cold current metric is less than 3 A or undeterminable due to a measured open.

Revision History

Contributor	Date	Description
M. Osterman	4/17/2013	Initial Draft
Rockwell	4/23/2013	Review
M. Osterman	5/1/2013	Final

CALCE Contact:

Reviewed and Approved: _____ _____

(signature) (date)

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Examination of Mitigating Effect of Conformal Coating on Tin Whisker Induced Metal Vapor Arc Formation

Abstract

Tin whiskers which form on tin finished metal substrates present a known failure risk for electronic products. For electronic hardware, tin whiskers can create mechanical or optical obstructions, can cause unintended electrical shorts and lead to the formation of a metal vapor arc. Tin whisker induced metal vapor arcs, which operate at high extremely high temperatures, can melt surrounding metal and incinerate organic material. Conformal coatings have been identified for mitigating the electrical shorting tin whisker failure risk. Conformal coatings are dielectric materials that are applied over the surfaces which electrically insulated the surfaces. Several studies have been conducted on the effectiveness of various conformal coatings materials to contain tin whiskers and mitigation tin whisker induced failures. This study examined the ability of select conformal coating materials to prevent metal vapor arc formation. For this work, two separate tests were conducted. In the first test, tin whiskers bridging two electrodes were conformally coated and subjected to electrical conditions sufficient to induce a metal vapor arc. In the second test, a tin whisker was brought into physical contact with a conformally coated metal surface and subsequently subjected to an approximate 50 Volt step bias. Tests indicate that coated bridged whiskers would still initiate metal arcs with the coating able to contain the event. For the contacting whisker, metal vapor arcs were only initiated when electrical contact was achieved with sufficiently low resistances that arcing would be predicted.

Introduction

Tin whiskers are known to grow on thin tin films deposited on metal substrates. Tin whiskers can have diameters below a micrometer and above ten micrometers but are typically in the range of 2 to 5 micrometers. These whiskers can extend a few microns to several millimeters from the surface of the tin deposit on which they form. Despite decades of research there is no physical test that can be used to consistently predict the maximum whisker growth beyond the test period. For electronic equipment, the formation of tin whiskers is a concern since the structures are electrically conductive and can create unintended electrical circuits. Due to their small cross-sectional areas, whiskers that form electrical circuits can melt due to Joule heating brought on by conducting electrical current. However, if the current rises quickly enough and the voltage bias is sufficiently high, the tin may be vaporized and ionized. In these cases, a metal vapor arc may be initiated. In the case of a metal vapor arc, both an electrical short and a high temperature event in the location of arc are concerns.

Tin whisker induced metal vapor arc formation has been examined by Hada et al [1], Westerhuyzen, *et al* [2], Mason et al [3], and Han et al [4]. Hada et al defined a melting and fusing region based on current and atmospheric pressure. Westerhuyzen et al [2] simulated metal vapor arcs using gold wire. Mason et al [3] found 28 volts was sufficient to initiate a metal vapor arc with a tin wire. Han et al [4] established a cold current metric and threshold value for the formation of metal vapor arcs with tin whiskers.

Han et al [4] defined the cold current metric as the voltage bias applied the a whisker arc test

specimen divided by the total resistance (specimen resistance plus circuit resistance). The expression for the cold current metric is defined as:

$$Acc = \frac{V_{applied}}{R_{specimen} + R_{circuit}} \quad (1)$$

where $V_{applied}$ is the applied voltage bias, $R_{specimen}$ is the electrical resistance of the arc test specimen that includes the tin whisker, and $R_{circuit}$ is the resistance of the remainder of the circuit. The voltage bias was applied using a series of lead-acid batteries. The tin whisker arc specimen was placed under a vacuum jar and tests were conducted a various pressures. A schematic of the test system is presented in Figure 7.

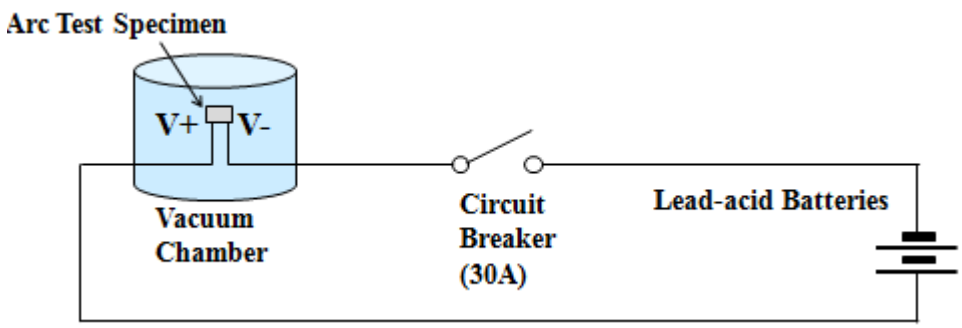

Figure 7 Schematic of Arc Test System

A plot of test results is presented in Figure 8.

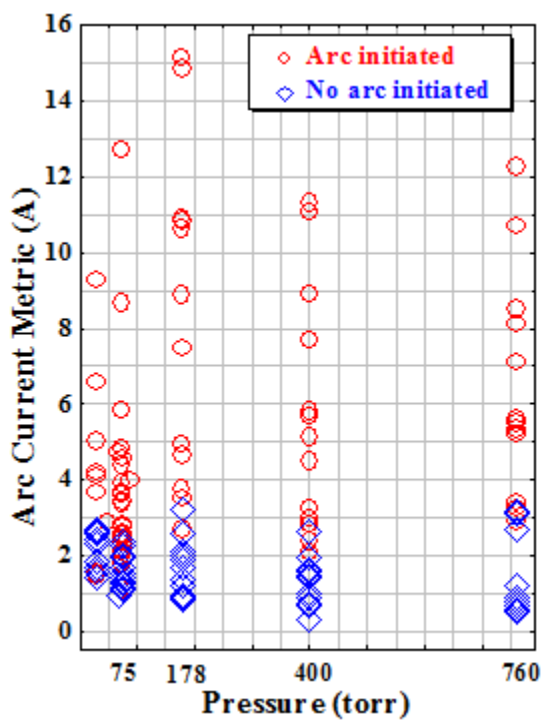

Figure 8 Arc Metric versus Pressure (Courtesy of CALCE)

In Han et al [4] tests, an arc was confirmed by light emission and the surface damage. The finding was that above a cold current metric value of 3 A arcing normally occurred and below 1 A arcing generally did not occur.

For the referenced studies, the ability of a conformal coating material to prevent metal vapor arc formation was not examined. This report examined the use of select conformal coating materials to prevent metal vapor arc formation.

Test Specimens

This study used the whisker bridging specimen design developed by CALCE to assess tin whisker induced metal vapor arc formation and reported by Han et al [4]. Each test specimen had two tin plated copper coupons attached to printed wiring boards with machine screw and nuts. As assembled, the tin plated copper coupons were separated with a gap span of approximately 0.6 mm. A tin whisker, which was detached from available whisker bearing samples, mechanically bridged the gaps and was secured to the coupons using a silver epoxy. A sample test specimen is depicted in Figure 9.

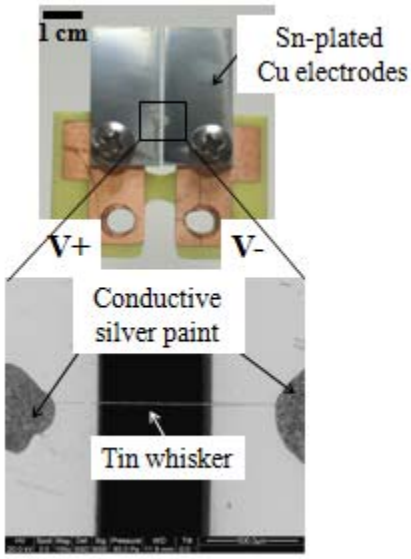

Figure 9 Arc Test Specimen

CALCE provided design information regarding the test specimen and Rockwell Collins produced tin plated coupons, test boards, and fasteners to create fifty test specimens. The test specimen materials were sent to CALCE where arc test specimens were created by attaching tin whisker samples. These test specimens were then shipped back to Rockwell where select conformal coating were applied. In addition to the arc specimens, twenty individual tin plated coupons were coated with select conformal coating materials. These treated coupons were used to assess the potential for whisker induced metal vapor arc formation when a tin whisker was brought into physical contact with the coated surface of a tin plated coupon. For the contact-induced whisker formation, the previously described test specimen was assembled with one conformal coated coupon. For the contact test specimens, the whisker was secured to the non-coated coupon using silver epoxy and was simply made to contact the surface of the adjacent coated tin coupon.

For this study, conformal coating materials included a commercial coating material identified as 1B31 and two specially blended materials formulated by Rockwell identified a 4A and 5A.

Test Specimens

In the following sections, the test specimens used for this study are documented. Test specimens include bridged test specimens and contacting test specimens. The bridged test specimens mechanically and electrically connected a whisker between two electrodes. The contacting test specimens mechanically attached the whisker to one electrode and physically brought the attached whisker in contact with the surface on the adjacent electrode. A description of the test specimens follows.

Bridged Test Specimens

For the bridged test specimens, in which the whisker was attached with silver epoxy to the two tin plated copper coupons mounted on the printed wiring board, thirty test specimens were prepared. For each test specimen, the tin plate coupons were mounted to the printed wiring board with machine screws with the coupons within approximately 0.6 mm of each other. Once the coupons were secured to the printed wiring board, a tin whisker was selected and placed in contact with the surfaces of the adjacent coupons and bonded to the coupons with silver epoxy. After the whisker was secured, the electrical resistance of the test specimen was measured using a digital multimeter. The electrical resistance measurement was used to confirm an electrical connection between the coupons through the tin whisker and was used to determine~~d~~ the initial whisker metal vapor arc cold current value. Prior testing had found that cold current values greater than 2 Amp were sufficient to induce metal vapor arcs. After establishing electrical contact, the whisker was documented using an environmental scanning electron microscope. Documentation included measuring the gap between the edges of the tin plated copper coupons, the length of the whisker between the points of silver epoxy attachment, and the projected diameter of the tin whisker under the assumption that the whisker cross-section was round. An example of the whisker length and coupon gap measurement is depicted in Figure 10. An example of the whisker diameter measurement is depicted in Figure 11.

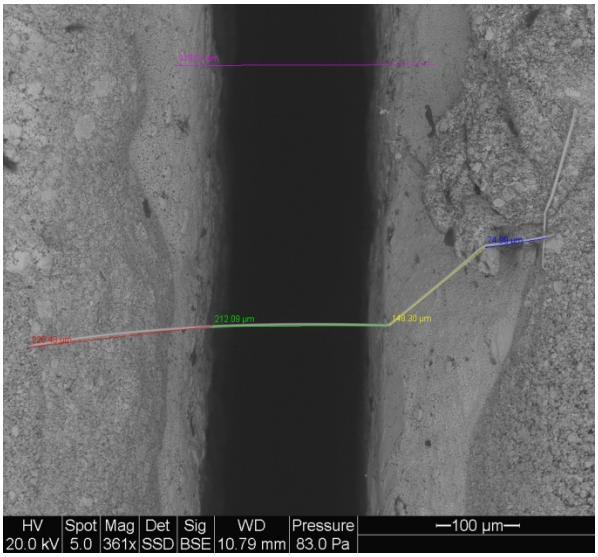

Figure 10 Example of Whisker Length and Coupon Gap Measurement

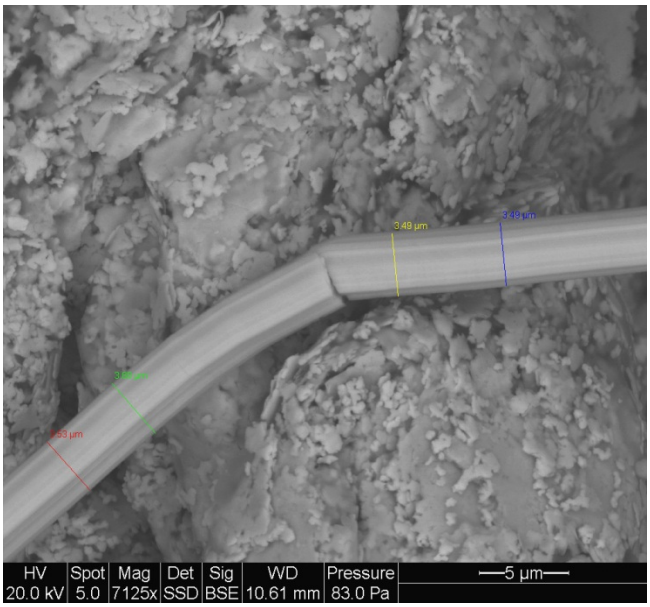

Figure 11 Whisker Diameter Measurement

After the test specimens were prepared, they were shipped to Rockwell Collins in a machined shipping frame. A picture of the shipping frame is presented in Figure 12.

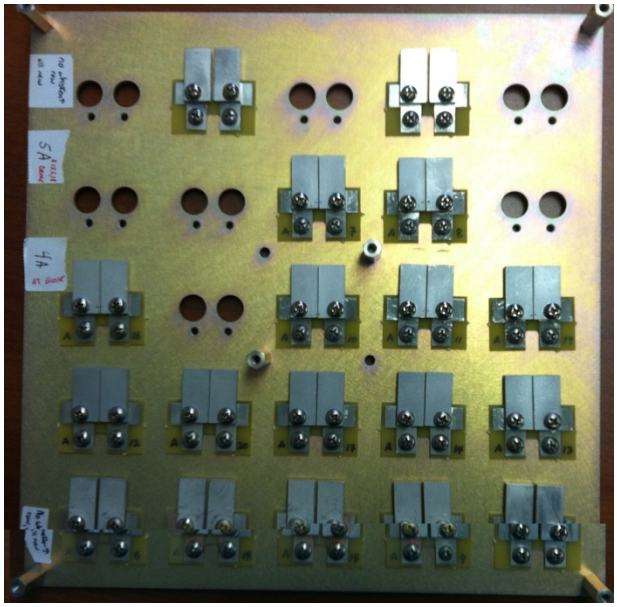

Figure 12 Tin Whisker Arc Test Specimens in Shipping Frame

At Rockwell Collins, the test specimens were removed from the shipping frame and select conformal coating materials were applied. The test specimens were then remounted on the shipping frame and returned to CALCE. The process was repeated three times. For each shipment, a number of test specimens lost electrical continuity. In the first shipment, three of five test specimens lost electrical continuity. In the second shipment, nine out of fifteen specimens lost continuity. In the third and final shipment, eight out of ten specimens lost continuity. In reviewing process, the application of conformal coat, specimen handling, and the

mounting process in the shipping frame were all suspected of playing a role in the low yield. With regards to handling and shipping frame, a thicker printed wiring board that would be more resistant to mechanical bend should be investigated. A example of one of the test specimens that was found to have lost electrical continuity after return from the coating process is depicted in Figure 13.

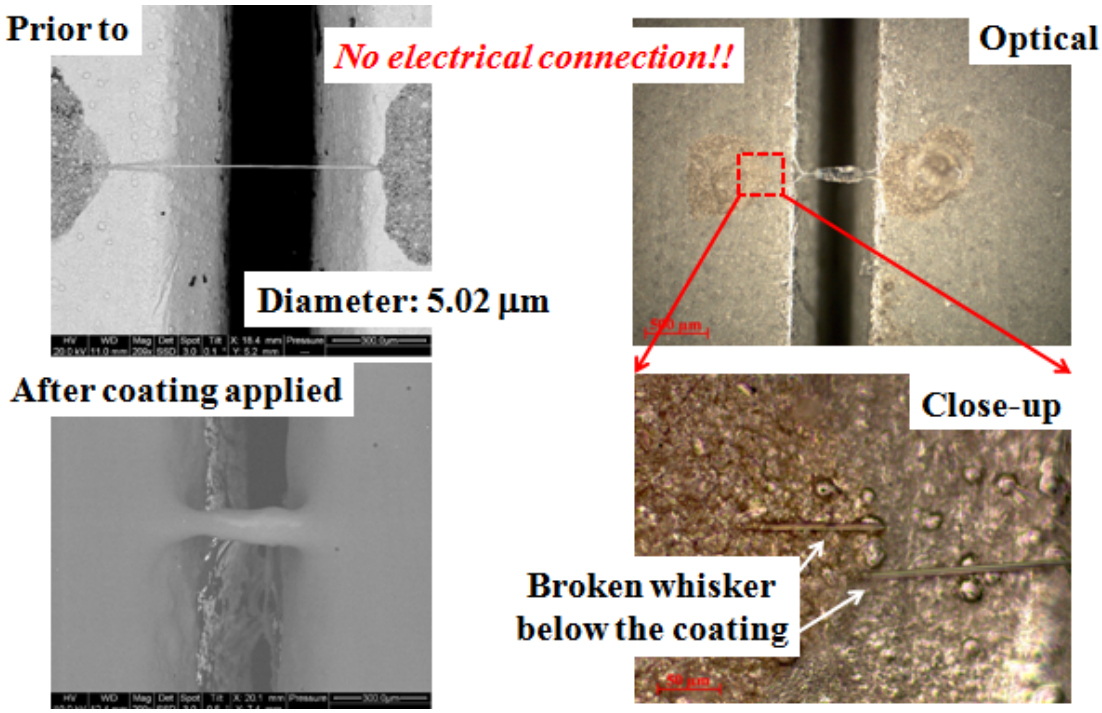

Figure 13 Identified Broken Whisker on Coated Arc Test Specimen

Contacting Test Specimens

In addition to creating bridging whisker specimens for the metal vapor arc formation tests, test specimens were also prepared for a whisker brought into contact with a coated surface. These specimens included the same material set with two coupons, a printed wiring board, machine screws and nuts, a tin whisker and silver epoxy. For these test specimens, Rockwell Collins provided sets of individual tin plated copper coupons with select conformal coatings. The list of coatings and specimen count are provided in Table 2.

Table 2 Coated Coupons for Contact Test

Coating	Count
Control (No Coat)	5
1B31	5
1H20AR1	5
4A	5
5A	5

The tin whisker arc test specimens for the contacting whisker test were constructed in the same manner as the bridging test specimens. The difference is that the whisker was not attached to the

coated coupon using silver epoxy. For the contacting whisker test specimen, the whisker was simply brought into contact with the coated surface. An example of one documented contact specimen is provided in Figure 14.

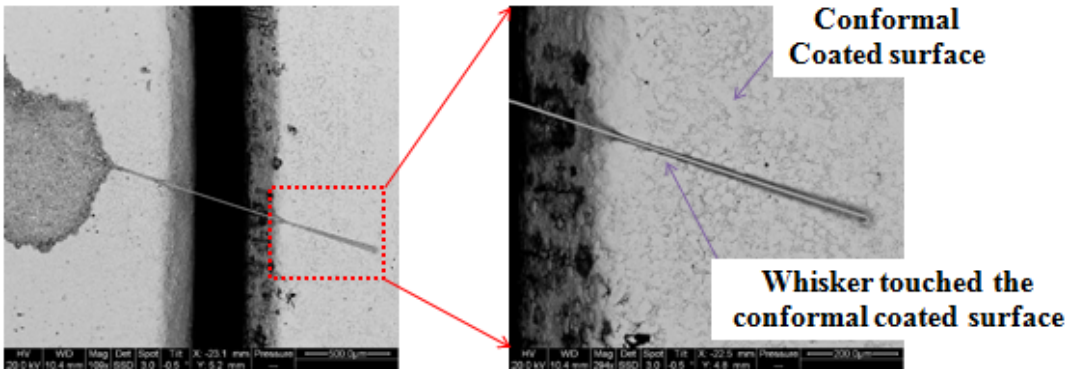

Figure 14 Example of a Contacting Whisker Specimen

Tests

The prepared test specimens were placed in the arc test system depicted in Figure 7. For all tests, the air pressure was reduced to approximately 35 torr. The battery bank provided a voltage bias of approximately 48 Volts. The work of Han et al [4] showed that air pressure had a negligible influence on arc initiation, but in some cases it was shown that under the low pressure condition sustained arcing with a single attached whisker could occur. The results of the tests for the bridged and contacting whisker specimens are provided in the following sections.

Bridged Whisker Specimens

For the bridged whisker specimens, three groups were created. The first group consisted of test specimens coated with 1B31 coating. The second group contained test specimens with 1B31, 4A and 5A coatings. The third group consisted of test specimens coated with 4A and 5A coatings.

For the first group created with 1B31 coating, only two out of five specimens were considered to be viable for testing after being returned from Rockwell Collins. A summary of these specimens is provided in Table 3.

Table 3 Bridged Whisker Test Group 1

Specimen	Coating	Resistance Prior to Shipping (ohms)	Resistance upon receipt (ohms)	Arc Metric	Finding
A-1	1B31	4.81	Open	N/A	Not Tested
A-2	1B31	11.21	Open	N/A	Not Tested
A-3	1B31	5.16	7.48	6.42	Arced
A-4	1B31	26.21	Open	N/A	Not Tested
A-5	1B31	10.42	9.57	5.02	Arced

For this group, the two test specimens that had electrical continuity were measured to have cold

current metrics that would indicate a strong likelihood for metal vapor arc formation. In both cases, metal vapor arcing was indicated by the light emission that occurred when applying the voltage bias. For these samples, despite the observed light emission, the coatings appeared to sustain little to no damage. Figure 15 provides a scanning electron microscope image of the coating before and after the arc test.

In both cases, the continuity was lost after the light emission.

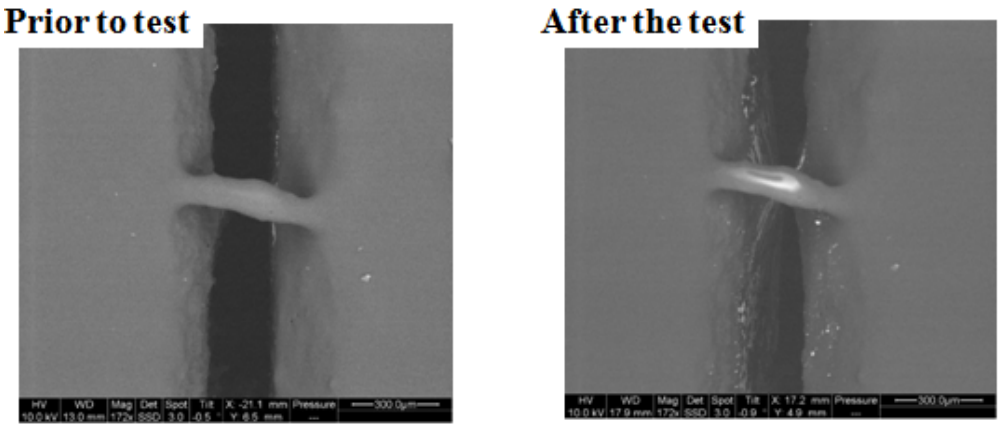

Figure 15 Before and After Arc Test Image of 1B31 Coated Specimen A-3

For the second set of bridged tests specimens, six of fifteen specimens were viable for arc testing after application of coating and shipping. This set included specimens with 4A and 5A coatings as well as the 1B31 coating. The complete list of set two specimens and test results are provided in Table 4. For the 4A and 5A specimens, the presence of the coating was not obvious under optical or electron microscopes. In Figure 16, specimen A19 is coated with the 4A formulated coating but the surfaces of the coupons and the whisker appear uncovered. In this image, you can see the silver epoxy regions that attach the whisker to the two coupons. In addition, the whisker does not appear to have coating. In contract, you cannot see the attach points or the whisker in Figure 9. In Figure 9, the presence of the whisker is based on the cylindrical coating the bridges between the two coupons.

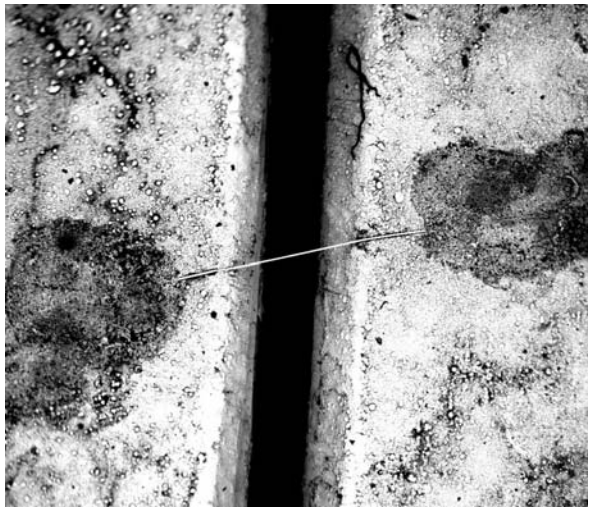

Figure 16 Bridged Whisker Specimen A19 Coated with 4A

For the six tested specimens, arcs were observed on three out of six specimens. These results are consistent with results found when testing of non-coated specimens. Specifically, metal vapor arcs were initiated at cold current arc metrics above 5 Amps and not below 3 Amps. As with the first set, the presence of the conformal coating material did not prevent arc initiation.

Table 4 Test Set Two for Bridge Specimens

Specimen	Coating	Resistance Prior to Shipping (ohms)	Resistance upon receipt (ohms)	Arc Metric (Amps)	Finding
A-6		7.65	Open	N/A	Not Tested
A-7	5A	20.97	22.58	2.13	No visible Arc
A-8	5A	11.63	Open	N/A	Not Tested
A-9		14.77	Open	N/A	Not Tested
A-10	4A	4.21	5.4	8.89	Arced
A-11	4A	32.47	Open	N/A	Not Tested
A-12	1B31	11.13	Open	N/A	Not Tested
A-13	1B31	33.14	16.18	2.97	No visible Arc
A-14	1B31	10.83	Open	N/A	No visible Arc
A-15		20.73	Open	N/A	Not Tested
A-16	4A	11.32	10.56	4.55	No visible Arc
A-17	1B31	9.61	Open	N/A	No visible Arc
A-18	0	25.43	Open	N/A	Not Tested
A-19	4A	5.25	4.59	10.46	Arced
A-20	1B31	4.63	15.56	3.08	Arced

An example of light emission indicating the initiation of a metal vapor arc is depicted in Figure 17.

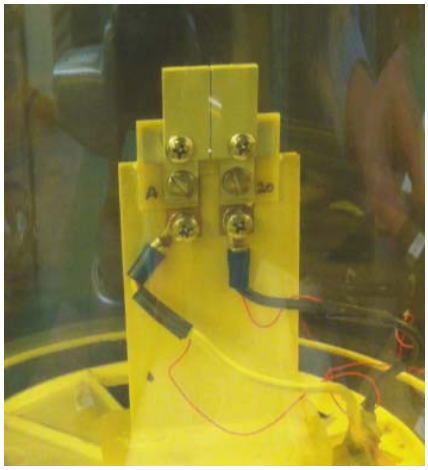

Figure 17 Light Emission Record For Specimen A20

For the specimens that exhibited an arc, surface damage was visible under an optical microscope.

Figure 18 shows the coupons of specimen A19 after the arc test.

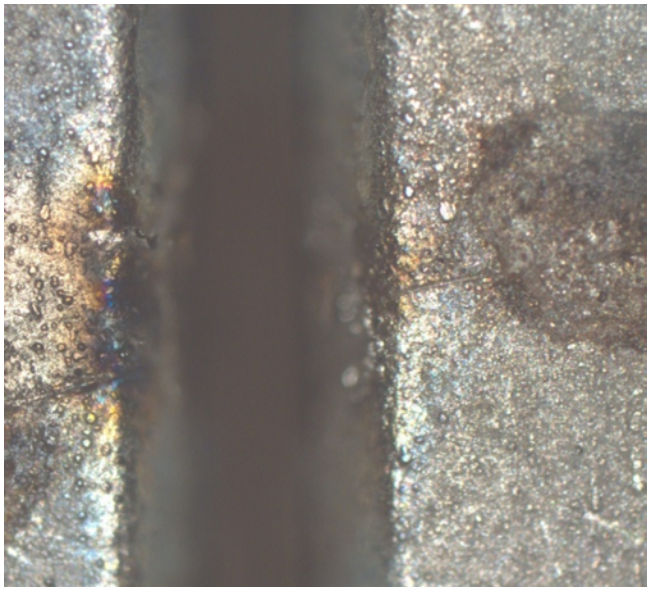

Figure 18 Arc burns present on coupons for specimen A19 after test

For the specimens that did not exhibit an arc, evidence of melted whiskers was found under inspection using an optical microscope.

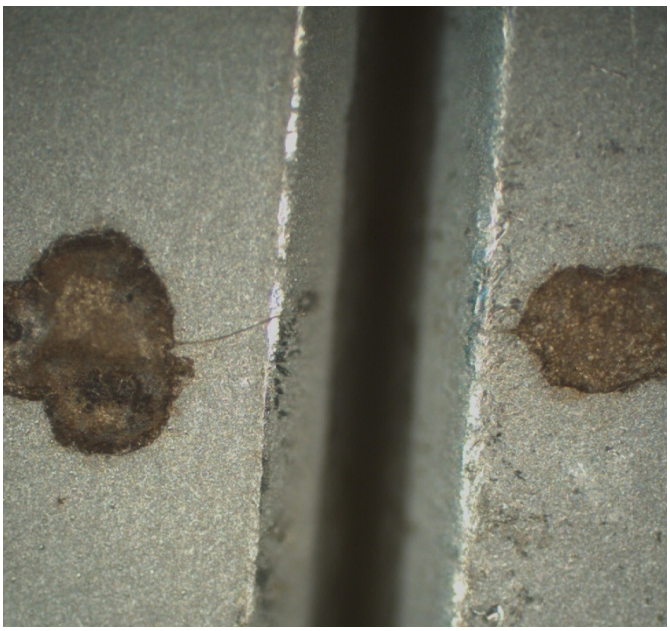

Figure 19 Melted Whisker on 4A Coated Specimen A16

For the final set of bridged specimens, another twenty specimens were prepared. However, seven viable specimens were lost over the several day period during which the whisker and specimen geometries were being documented for baseline conditions. As a result of the loss in specimens, twelve bridged specimens were sent to Rockwell Collins for conformal coat

application. After coating, only two specimens were viable. A list of the specimens for the third test set is presented in Table 5.

Table 5 Test Set Three for Bridged Specimens

Specimen	Coating	Resistance Prior to Shipping (ohms)	Resistance on Return (ohms)	Arc Metric (A)
A-15-III	5A	10.11	Open	NA
A-18-III	5A	10.23	Open	NA
A-21	5A	7.91	Open	NA
A-23	5A	12.1	Open	NA
A-24	4A	10.49	11.14	4.31
A-27	5A	0.35	Open	NA
A-28	5A	24.26	Open	NA
A-29	5A	9.18	Open	NA
A-31	5A	11.89	Open	NA
A-32	4A	17.89	14.78	3.25
A-33	4A	15.17	Open	NA
A-9-III	4A	6.06	Open	NA

Based on prior work, the two specimens fall into the region where arc initiation is possible but the probability is not particularly high. However, these specimens were not subjected to the arc test. Observations made by CALCE and Rockwell Collins raise suspicion that the attachment to the shipping fixture was the primary cause of the very low test specimen yield. For future work, a thicker printed wring board coupon holder may be better suited for preventing specimen loss.

The primary finding from arc tests of the bridged test specimens is that the tested conformal coatings do not prevent metal vapor arc initiation when a whisker mechanically and electrically bridges between adjacent conductors. Arcs were recorded for 1B31 and 4A coatings. The lack of a recorded arc for 5A should not be taken as an indication that the 5A coating provides some additional protecting not found with 1B31 and 4A coating. This result was due to the fact that not specimens with sufficient low enough resistance were available for test. Arc always initiated when the cold current metric was higher than 5 A and did not initiate when the metric was below 3 A. The results are consist with finding of non-coated bridged test specimens.

Contact Test Specimens

For the coated specimens, one tin plate coupon was coated with a conformal coat material. The coated coupon was connected to the mounting printed wiring board and a tin plated copper coupon was secured with an edges separated by a gap of approximately 0.6 mm. After the coupons were secured to the holder board with machine screws, a tin whisker was placed to bridge the gap between the two coupons and secured to the non-coated coupon using silver epoxy. In those cases in which the whisker made electrical contact, the electrical resistance of the specimen was documented. In other cases, no electrical contact was made. After the specimens were created, the specimens were examined under optical and in some cases electron

microscope. All test specimens were tested under 35 torr pressure and a 48 Volt bias.

For the specimens with electrical contact, the estimated arc metric with a 48 Volt bias were determined to be above 3 A. In all cases, arcs were detected where the arc metric indicated the high likelihood of an arc initiate. A summary of prepared and tested specimens is provided in Table 6. Figure 20 depicts the arc test specimen with 1B31 coating before and after the arc test. In this test, light emission was detected and surface of the anode shows evidence of tin deposits which have been documented in previous whisker arc tests.

Table 6 Contact Specimen Findings

Sample	Coating	Resistance	Arc Metric (A)	Arc Detected
1A-S1	1B31	Open	NA	No
1A-S2	1B31	6.11	6.95	Yes
2B-S1	1H20AR1	Open	NA	No
2B-S2	1H20AR1	12.45	3.86	Yes
4A-S1	4A	Open	NA	No
4A-S2	4A	7.02	6.84	Yes
5A-S1	5A	Open	NA	No
5A-S2	5A	Open	NA	No

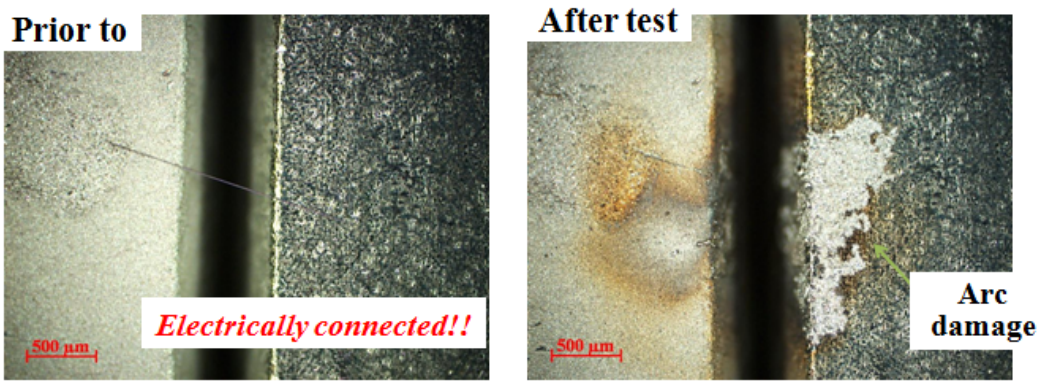

Figure 20 Contact Whisker Sample with 1B31 coating before and after Arc Test

From the contact tests that were conducted, its seems clear that any conformal coating that prevents electrical contact between adjacent conductor surfaces with sufficient bias and available current will prevent metal vapor arc initiation. Based on these results, no further testing was conducted.

Discussion

The tests conducted on this project found that the CALCE cold current arc metric was a good predictor of tin whisker metal vapor arc initiation. The test data plotted with the CALCE test data is presented in Figure 21. These results indicate that the selected conformal coating can prevent whisker induced metal vapor arcs when electrical contact is prevented. However, the coatings do not prevent arcs when electrical contact is made and the CALCE cold current arc metric is above 3 A. For future work, the test specimen design should be ruggized to prevent

whisker damage during shipping.

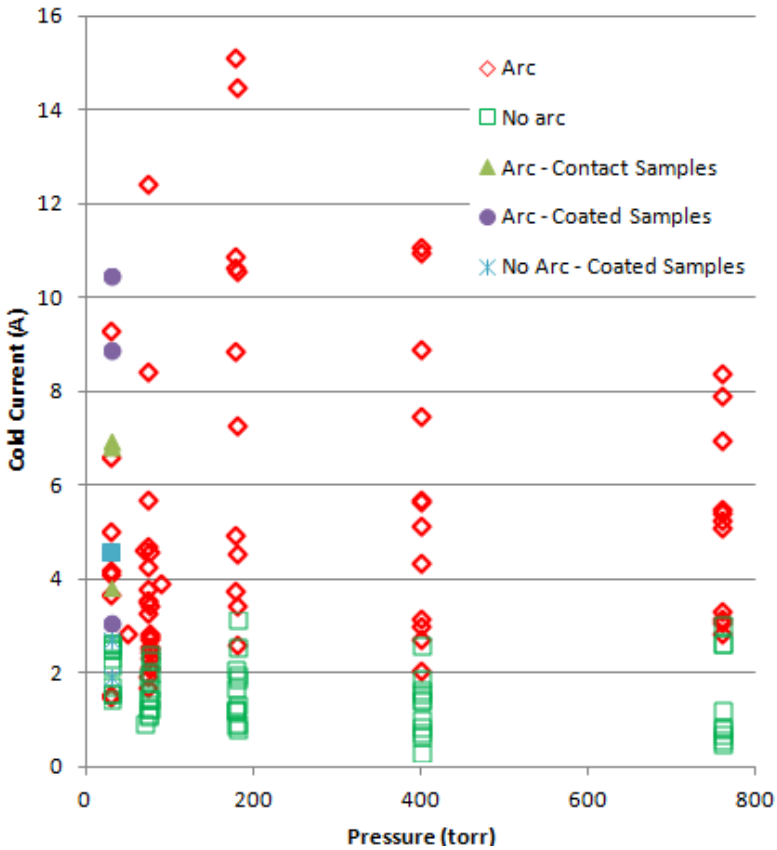

Figure 21 Plot of Test Results with CALCE Data for Tin Whisker Induced Arcing

Conclusions

The select conformal coat materials were examined for their ability to prevent metal vapor arc formation. For this study, a test specimen design and test procedure, previously used to examine the circuit requirements for tin whisker induced metal vapor formation, were used. Coatings included two custom coating materials identified as 4A and 5A and two commercial coatings identified as 1B31 and 1H20AR1. In this study, electrically and mechanically bridged whisker specimens as well as contacting whisker specimens were tested. For the electrically bridged specimens,1B31, 4A and 5A coatings were tested. For the contacting specimens, 1B31, 1H20AR1, 4A and 5A coatings were tested. Metal vapor arcs were detected in all cases where an electrical connection was measured and when the cold current metric was above 3A. These results are consistent with previous tests conducted without conformal coating.

The results indicate that selected conformal coat materials did not influence arc initiation when electrical contact is made. Interestingly, the 1B31 coating appeared to contain the arc and the coated bridge that formed over the whiskers remained intact after the arc test. While the test size was limited, the results were nearly identical to extensive testing CALCE has conducted previously on non-coated test specimens. Metal vapor arcs are highly likely to initiate when a cold current metric value is found to be greater than 5 A and unlikely to occur if the cold current metric is less than 3 A or undeterminable due to a measured open.

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4. S. Han, M. Osterman, M. Pecht, "Likelihood of Metal Vapor Arc by Tin Whiskers," IMAPS Advanced Technology Workshop on High Reliability Microelectronics for Military Applications, Linthicum Heights, MD, May 17-19, 2011.

Appendix 5: Plasma Ruggedized Solutions Phase 1 Report

Plasma Ruggedized Solutions

Global Provider of Custom Ruggedized Engineering Solutions across Industry

Tin Whisker Inorganic Coating Evaluation (TWICE) Program

Phase 1

Final Report

Date: 2 January 2013

Prepared for

Rockwell Collins, Inc.
Advanced Technology Center
400 Collins Road NE
Cedar Rapids, Iowa 52498

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Abstract

Plasma Ruggedized Solutions was contracted by Rockwell Collins Inc. to determine the viability of the Alkali Silicate Glass (ASG) material. This was done through the application of two types of conformal coating using ASG as a base coat or primer. In addition to proving that the material could be sprayed using industry standard equipment, the study was also to prove that the material could be sprayed within a given thickness range.

Statement of Work

1. Material Integration
Plasma Ruggedized Solutions (PRS) shall adapt processes the recommended by Rockwell Collins Inc. (RCI) for Alkali Silicate Glass (ASG) deposition to electronics devices for the PRS prototype production line. Results of this effort shall be documented in a summary report that describes relevant, non-proprietary processes and methods utilized by PRS to apply ASG coatings to electronic devices.

2. Sample Test Vehicle Coating

a. Initial ASG coating application
PRS shall apply ASG coatings, using the processes documented in 1.1.1, to devices on multiple samples of the RCI coating evaluation test vehicle. The quantity of samples to be coated is defined in Table 1.
b. Baseline coatings application
PRS shall apply baseline coatings to RCI coating evaluation test vehicles. These baseline coatings shall include at least one Parylene coating and at least one acrylic based coating. The quantity of samples to be coated is defined in Table 1.
c. ASG primer risk assessment
PRS shall apply acrylic coating to RCI coating evaluation test vehicles with ASG material used as the post coat primer. The quantity of samples to be coated is defined in Table 1.

3. Documentation
PRS shall document the results of Phase 1 activities for inclusion in the Phase 1 report and to provide the basis for making any necessary modifications to Phase 2 test plan. Required documentation is defined in Table 1.

4. Program Management/ Travel

a. PRS shall supply an administrative point of contact and oversight for the identified activities.
b. PRS shall provide sufficient support to meet all deliverables at appropriate times as designated in Table below: Deliverables & Meetings.
c. PRS shall provide quarterly status reports to Rockwell Collins, Inc.
d. PRS shall provide support for all meetings specified in Table below.

Commentary: The coating evaluation test vehicle will be designed and built during the early stages of the TWICE program. At this point in time it is envisioned to be a small, electrically non-functional, printed wiring board assembly (~1" x 3") that includes approximately ten leaded components such as SOICs. The test vehicle will be designed to allow portions of the circuit card assembly to be mechanically separated from the rest of the board so that individual components can be inspected to evaluate the coating coverage on the component leads and to identify the presence of tin whiskers.

5. Deliverables & Meetings

Item	Description	Due
1	Kickoff Meeting	August 31, 2012
2	8 Parylene coated Phase 1 test vehicles, 8 acrylic coated Phase 1 test vehicles	September 21, 2012
3	16 ASG Phase 1 test vehicles (8 each with 2 different ASG coatings)	October 26, 2012
4	16 Phase 1 test vehicles coated with acrylic coating with an ASG primer (8 each with 2 different ASG coatings)	November 23, 2012
5	Phase 1 Final Report	December 14, 2012

Background

Rockwell Collins has been awarded a research contract from the Department of Defense's Strategic Environmental Research and Development Program for the Tin Whiskers Inorganic Coatings Evaluation (TWICE) program. This research has the potential to mitigate the impact of tin whiskers on high-reliability, high-performance electronic systems caused by new lead-free alloys and finishes in the aerospace and defense supply chain and manufacturing systems.

The transition to lead-free electronics has changed some of the ground rules for designing reliable electronics for use in harsh environments. One of the most significant changes has been the need to address the phenomenon of tin whiskers, which can grow from the pure tin surfaces commonly used on lead-free devices. Tin whiskers are microscopic metal fibers that are thinner than a human hair capable of bridging great distances that can create short-circuits leading to equipment failures.

This project will lead to a better scientific understanding of the mechanisms by which tin whiskers form and how they can be controlled with conformal coatings. Rockwell Collins will develop materials and the necessary processes to generate coatings that mitigate tin whisker growth on a variety of surfaces over a wide range of environmental conditions.

Rockwell Collins is leading a team that includes Plasma Ruggedized Solutions and the University of Maryland Center for Advanced Life Cycle Engineering in this effort.

Source: Press Release posted on Rockwell-Collins web site

Objective

Plasma Ruggedized Solutions was tasked with the objective of effectively spraying the Rockwell Collins ASG materials alone and as a primer to other conformal coatings. In doing so, an additional objective was to maintain a final coating thickness of ~0.1-0.5 microns.

Procedures

Test Vehicles

Image 0 depicts the coating evaluation test vehicle "Tin Man" utilized in Phase 1 of the TWICE program. The test vehicle measured 3 inches wide by 3 inches high. Each test vehicle consisted of a single sided (non-PTH) FR-4 circuit card assembly with 4 bright tin plated copper lead frame parts (simulated SOIC-16) selectively attached on approximately 1 inch center-to-center spacing uniformly distributed.

A total of 48 coated test vehicles were produced during Phase 1:

Baseline Coating (Acrylic and Parylene)

- 8 test vehicles were coated with Humiseal 1B31 (Acrylic).
- 8 test vehicles were coated with Galxyl Parylene type C.

Alkali Silica Glass (ASG) Coating

- 8 test vehicles were coated with ASG 4A.
- 8 test vehicles were coated with ASG 5A.

Acrylic Coating with Alkali Silica Glass (ASG) Primer

- 8 test vehicles were coated with ASG 4A (as primer) followed by Humiseal 1B31 (as post coat).
- 8 test vehicles were coated with ASG 5A (as primer) followed by Humiseal 1B31 (as post coat).

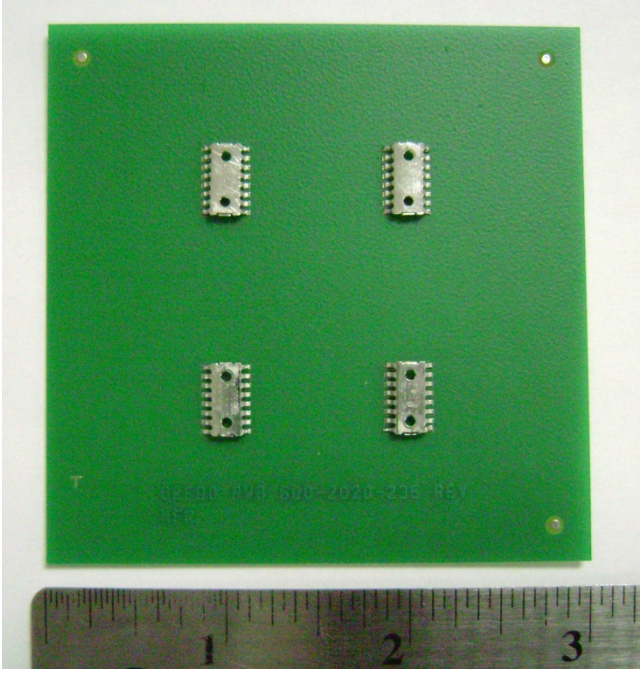


Image 1: Test Vehicle "Tin Man"

Test Component

Images 1 and 2 show the bright tin plated copper lead frame parts designed to simulate an SOIC-16 package with a high propensity for growing tin whiskers. The component was selectively attached at pins 1, 8, 9, and 16 to allow for ease of removal as needed by Rockwell Collins for inspection of tin whisker growth.

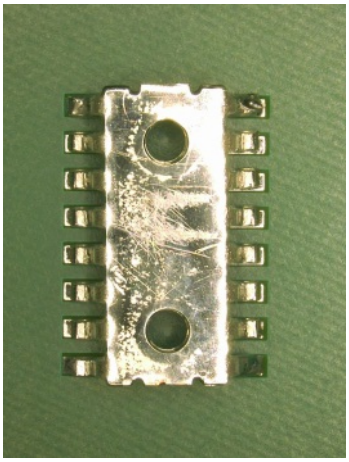


Image 2: "Tin Man" Test Vehicle

Coupons and Additional Test Substrates

Single Sided Copper Clad Laminates were used by PRS primarily to evaluate the effectiveness of the plasma treatment and behavior of the ASG material.

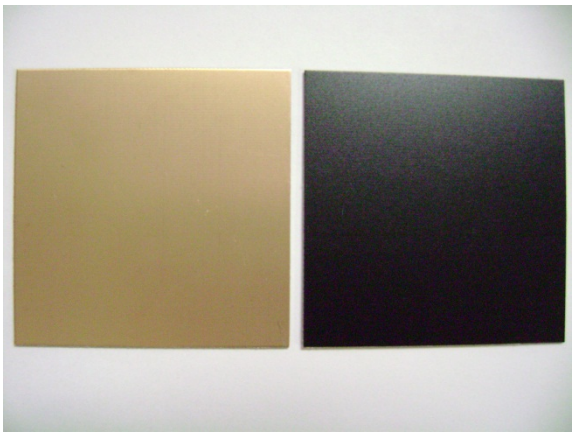


Image 3: Copper Clad Laminate Test Substrate

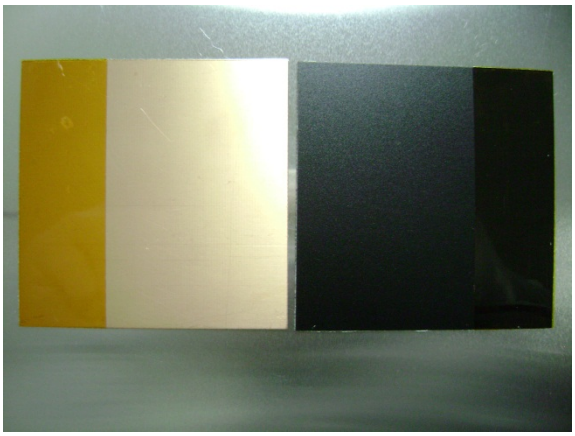


Image 4: Copper Clad Substrates (as masked)

Glass Microscope Slides: used throughout the entire process

A standard American made (from Swiss glass) glass microscope slide which measured 75 mm x 25 mm x 1mm was utilized as the primary validation substrate.

Image 5: Glass Slide (as masked)

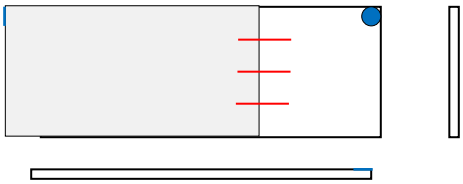


Figure 1: Illustration of masking of glass slide (described below)

The slides were coated on one side only; the coating encompassed the lower 2/3 of the glass slide (approximately a 50 mm x 25 mm area) with the remaining 1/3 masked to create the step height to be measured. The coated side was marked with a dot and/or indelible markings identifying the specifics details for each slide. Measurements were made at 3 differing locations across the coating transition per slide. A minimum distance of travel prior to the coating edge transition was incorporated to use as a zero reference of the glass surface. The glass slides allowed for

measurements to be taken which provided the nominal thickness of coating (excluding the random peaks associated with debris and/or large particles), and the overall roughness of the coating. These coupons also served as cross-hatch adhesion test samples as well as samples for evaluating the effectiveness of plasma treatment.

Familiarization and Discovery

A period of ASG material familiarization and discovery was initiated during the initial weeks of Phase 1. Material behavior related to its inherent properties as well as process compatibility was paramount to producing a uniform quality film; as such a greater understanding of how conventional coating techniques, surface compatibility, and simple masking materials would impact the coating quality was necessary to determine further process guidelines.

This period of initial testing allowed for development of process procedures designed to work with the specific equipment utilized while providing a common knowledge base for use with any existing set of equipment.

Plasma: 2 minute etch cycle followed by a 10 minute oxygen clean cycle.

Manual Application

Manual hand spraying of the ASG coatings was initiated during Phase 1 to determine the probability of utilizing off the shelf spray equipment to produce a high quality consistent finish at the desired thickness on a repeatable basis.

The process for applying the ASG materials was a standard box coat application in which the items to be coated were sprayed in alternating directions covering all four sides and a vertical downward coat consisting of 5 total passes per box coat. The coating thickness was built up to the desired level by adjusting the total number of box coats, and increasing the spray volume slightly as the number of box coats increased.

Image 6: DeVilbiss DAGR ® DGR-501

Automated Application

The automated application of the ASG materials was adapted from the recommended Rockwell Collins processes which were provided to Plasma Ruggedized Solutions Inc. (PRS). An automated Asymtek Dispensemate 585 dispense system was selected from PRS inventory and modified to spray the ASG materials using the original programs developed at Rockwell Collins **- HTC Spray PWB 6X4 5 Pass 10-15-12.fmw** - with an equivalent hardware configuration. The system format of the Asymtek Dispensemate D-585 coating system is very similar to the Asymtek Spectrum S-820 utilized with the major difference in the D-585 system being a table top version without an enclosure.

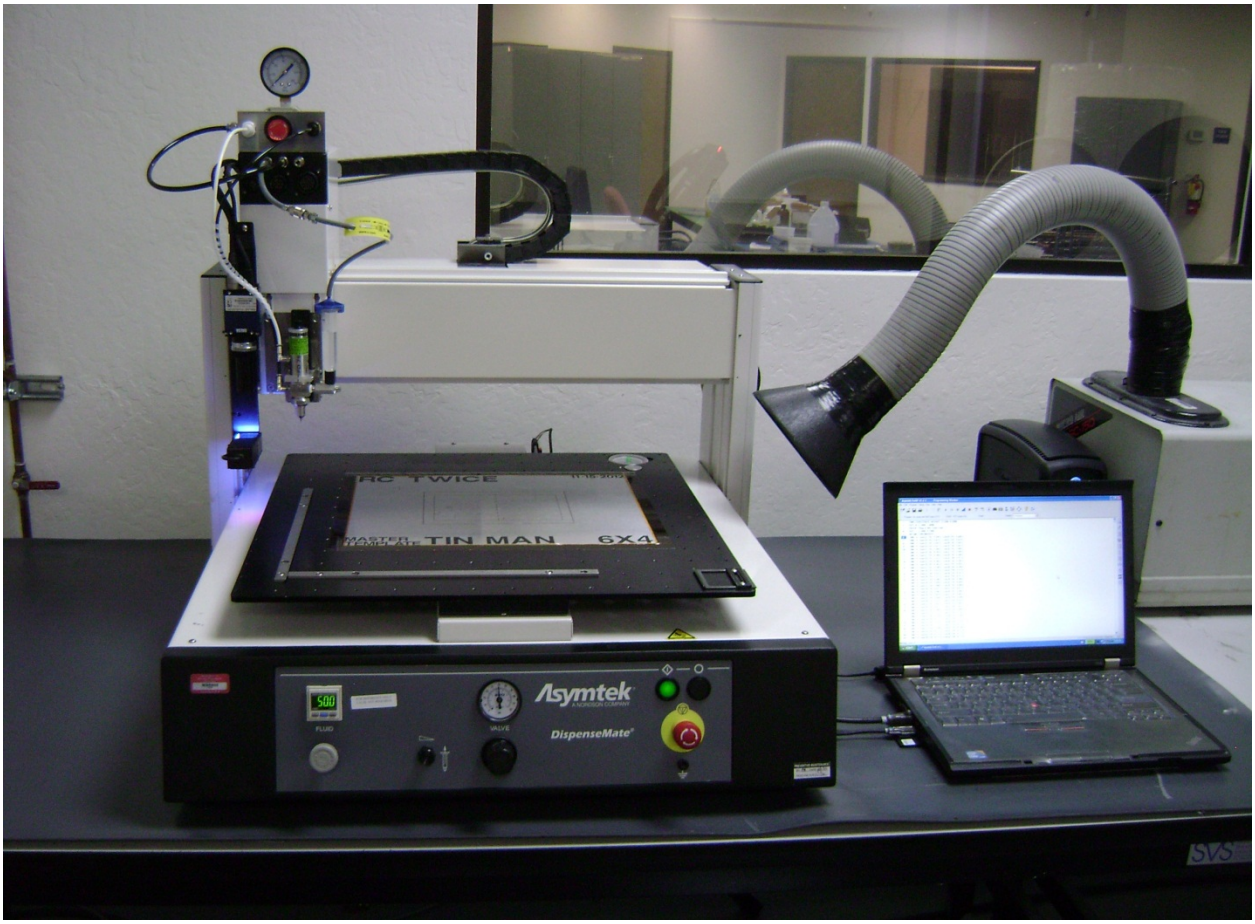


Image 7: Asymtek Dispensemate D-585 with ASG Spray Configuration

Automated Deposition Equipment

- Asymtek Dispensemate D-585; S/N 31260 DOM 11/08
  - Running PC based Windows XP with Fluidmove® software.
  - Using an EFD 787MS-SS Micro Spray LVLP Precision Valve.
    - Utilizing an EFD 32 Gauge, 0.5 inch long Precision Dispense Tip, P/N 7024648.
    - Fed by an EFD 10 CC Barrel and adaptor.
    - Filtered by a CAMEO 0.22 micron x 1 inch diameter luer lock Nylon particulate filter.
  - Operating under Program Recipe HTC Spray PWB 6X4 5 Pass 10-15-12.fmw
    - 10 mil steps
    - 4 inches per second travel speed
    - 0.25 psig nominal fluid (barrel) pressure. Note constant air pressure delivered by a remote dual stage filtered regulator system.
    - 15 psig nominal atomizing spray air (coax) pressure
    - 50 psig nominal valve pressure
  - Residual vapor extraction provided by a Micro Air SC-150 HEPA fume extractor
- Test Vehicle Pre-treatment.
  - IPA cleaning followed by a 2 hour dehumidification bake at 77°C.
  - Plasma treatment; 2 minute etch cycle followed by a 10 minute oxygen clean cycle.
- ASG materials.
  - ASG 4A (30:1), October 1, 2012 date of manufacture.
  - ASG 5A (30:1), October 1, 2012 date of manufacture
- Final coating thickness: 0.1 to 0.5 microns.
- Cure: Samples cured per TDS guidelines with the addition of a ramp cycle from the ambient segment to the 80°C thermal segment and the addition of a hold (retain) temperature upon completion of the cure cycle.
  - 20 minute dwell at ambient (25° nominal)
  - 20 minute ramp from ambient (25°C) to 80°C followed by a 30 minute dwell at 80°C
  - 60 minute ramp from 80°C to 125°C followed by a 60 minute dwell at 125°C
  - 60 minute ramp from 125°C to 165°C followed by a 180 minute dwell at 165°C
  - 60 minute ramp from 165°C to 38°C, hold at 38°C until unloaded.

Image 8: Despatch Lab Oven Model LAC 1-38A-6

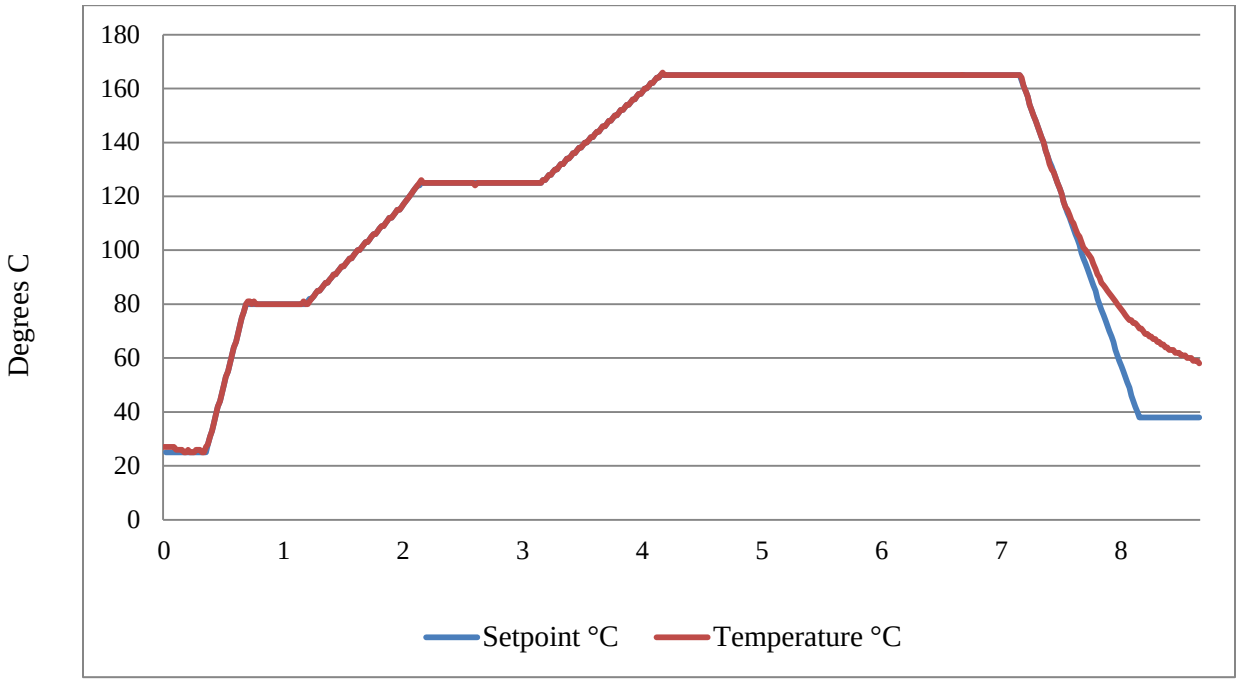


Image 9: Cure Schedule Data Log: ASG4A and ASG5A

Materials and Thicknesses

Acrylic: Humiseal 1B31 was applied (without ASG material as a primer), using a manual spray application. Measured thickness averaged 1.45 mils on the bottom of coupon and 1.8 mils on the top of the coupon.

Image 10: DeVilbiss Model JGHV 531

Image 11: Plasma Spray Booth

Parylene: Galxyl C was distributed using an automated vapor deposition process. Measured thickness averaged 0.97 mils, top and bottom of the coupons.

Image 12: Parylene chamber in clean room at Plasma Ruggedized Solutions San Jose

Glass Slides

Plasma processed 4 glass slides utilizing the automated application of the ASG 4A and ASG 5A materials, two of each. This was again done using the original programs developed at Rockwell Collins **- HTC Spray PWB 6X4 5 Pass 10-15-12.fmw**.

After processing, the slides were sent to an outside lab for measurements.

ASG 4A: 0.25 microns, average

ASG 5A: 0.13 microns, average

Once we confirmed that the glass slides were within the required thickness, we commenced production of the Tin Men test vehicles.

Analysis

Measurement

Validation of thickness

Roughness

Uniformity

The analysis used a stylus profilometer to characterize the thickness of films deposited on different glass coupons.

Profilometry of the samples was performed using a Bruker Dektak XT system. The Dektak XT produces a height profile by lightly tracing the stylus across the sample surface.

Table 1: Operating Conditions of the Dektak XT Profilometer

Parameter	Description or Setting
Stylus Shape	Diamond tip, 2 micrometer radius, 60 degree shank angle
Short wave cut-off	Default
Long wave cut-off	Disabled (no filter)
Trace Length	3000 micrometers
Scan Speed	300 micrometers per second
Stylus Force	3 milligrams
Sampling Rate	300 hertz
Horizontal Resolution	1.0 micron
Vertical Range	6.5 microns

Each coupon was measured multiple times to acquire the desired data. The test measurement traces were 3mm in length and acquired parallel to each other in the specified area of each 25mm wide coupon running across the edge of the deposited film. The traces were located so that 1mm of the trace was on the bare glass surface, and the following 2mm located on the film. Adjacent traces on the same coupon were separated by approximately 6mm to 7mm and located a minimum of about 6mm from the edges of the coupon. A limited number of repeat traces were acquired. The repeat traces were displaced along the film edge some tens of microns from the original trace locations.

Visual Inspection: Material was inspected under high magnification (50x) for any cracking of the material; none was found.

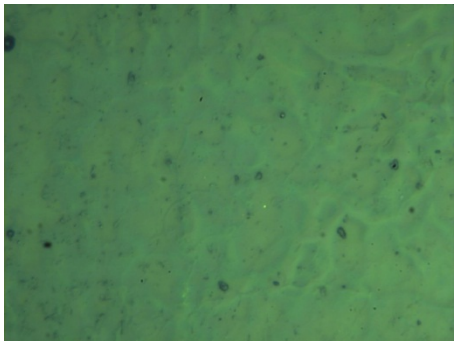


Image 13: ASG 4A coupon at 50X magnification

Adhesion Test: Tape adhesion tests were performed. The results were negative; there were no adhesion issues.

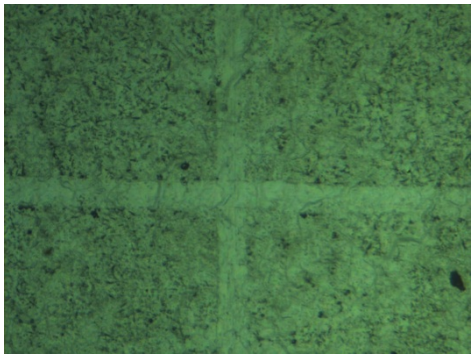


Image 14: ASG 4A coupon post cross-hatch adhesion test at 100x magnification (view of cross section of the score lines)

Conclusions

Results of the profilometry measurements indicate that the conformal coating film of ASG 4A and 5A materials were successfully applied to the test vehicles at the prescribed thickness. The results also showed that the application can be achieved by manual or automated deposition processes.

PRS found that applying the material manually was very user friendly. The difficulty in this process is having someone who is well-trained, who can meet these tight tolerances with repeatability.

On the other hand, the automated process was also user friendly; however, it took approximately 15 times as long as the manual process.

No matter which process is used, the difficulty is in the measurement of the thickness, and finding an outside vendor that has the capability and the willingness to measure the coupons.

Recommendations

1. Determine a process that improves the coverage, perhaps a dip with spray process to insure maximum coverage ; as part of the Phase II study, consider adding an additional study group that uses dip with spray as a way to get a more complete coverage
2. As part of the Phase II Study group, offer a low temperature alternate cure for the material.
3. To make the process more friendly, modify the material to have a more conventional thickness (1/2 mil and up).
4. Inspection is difficult; if possible, a UV indicator would be helpful.

Acknowledgements and References

DoD SERDP

RC Rockwell Collins

AEP

Bruker: Stylus and Optical Metrology Nano Surfaces Division

Evans Analytical Group (EAG): Metrology Services Division

KLA Tencor: Stylus and Optical Metrology Nano Surfaces Division

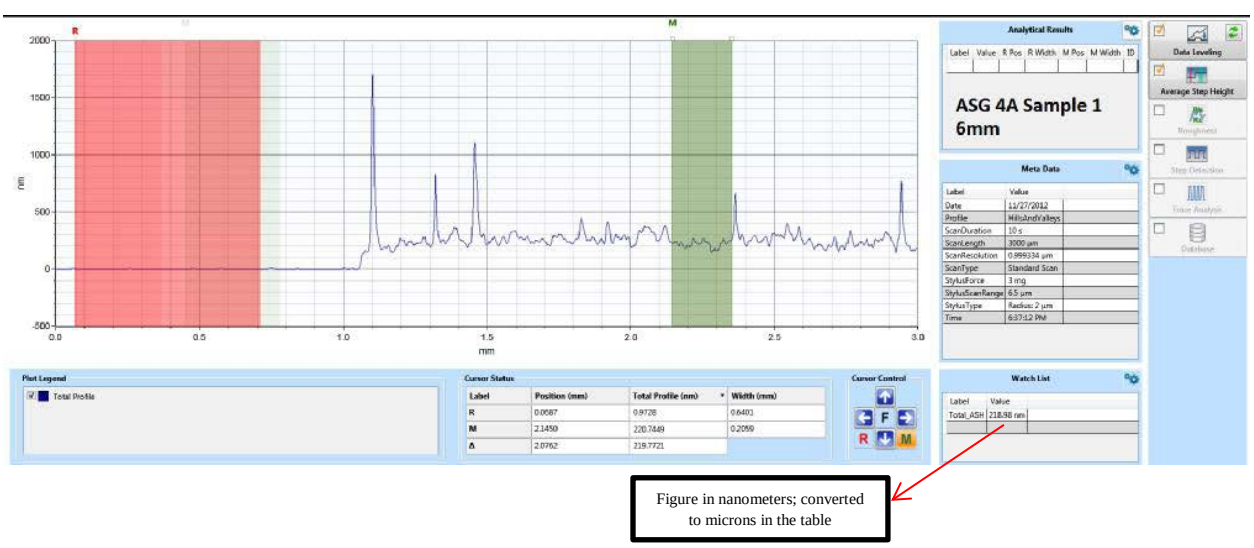
Nordson-Asymtek: Technical Support Services

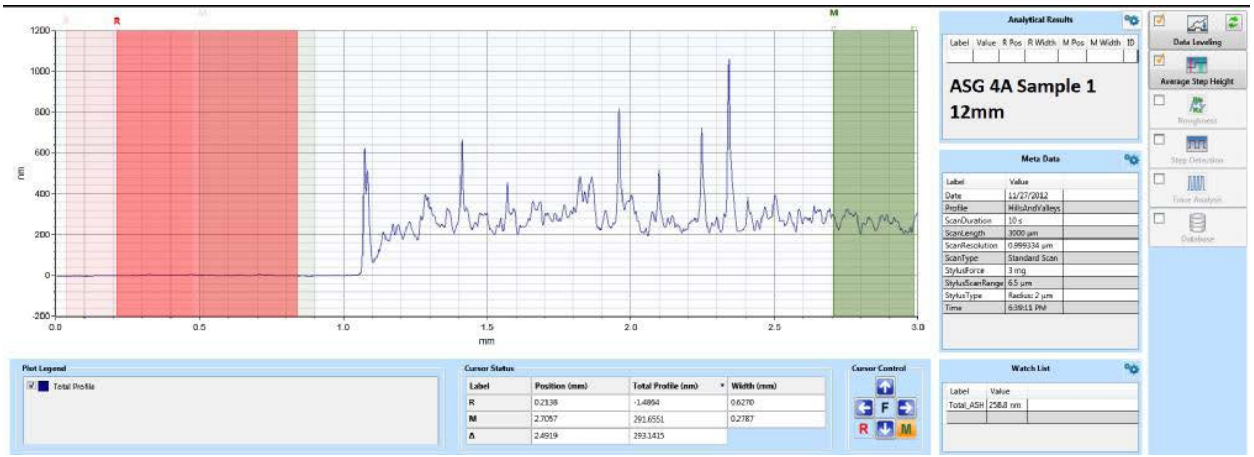
Appendices

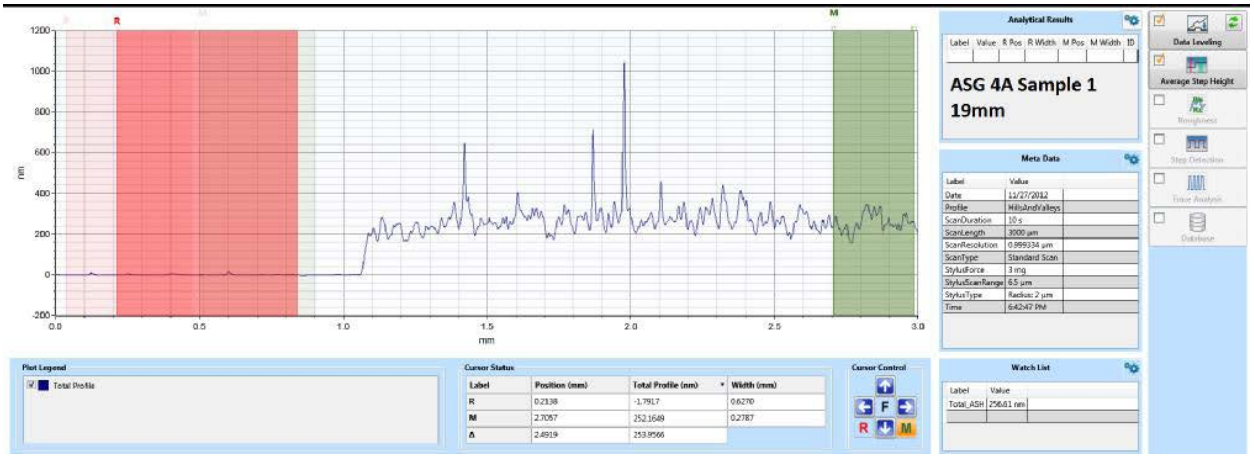
Material	Sample #	Location	Thickness (microns)
ASG 4A	1	6 mm	0.21898
ASG 4A	1	12 mm	0.25880
ASG 4A	1	19 mm	0.25461
ASG 4A	4	6 mm	0.26464
ASG 4A	4	6 mm (repeat)	0.25938
ASG 4A	4	12 mm	0.26236
ASG 4A	4	12 mm (repeat)	0.28137
ASG 4A	4	19 mm	0.25716
ASG 5A	1	6 mm	0.11976
ASG 5A	1	12 mm	0.14962
ASG 5A	1	19 mm	0.15235
ASG 5A	4	6 mm	0.12772
ASG 5A	4	12 mm	0.12242
ASG 5A	4	19 mm	0.09181

Table 2: Summary of Thickness Measurements from 2 samples of both ASG materials

Sample 4 of the ASG 4A material was repeated at the 6mm and 12 mm positions to help validate the actual test equipment and processes, and to insure we were within the spec limits of 0.1 – 0.5 microns. Actual data results follow below.




Analytical Results
ASG 4A Sample 1
12mm
Meta Data
Watch List
Plot Legend
Total Profile
Cursor Status
Cursor Control
Data Levelling
Average Step Height
mm
nm


Analytical Results
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19mm
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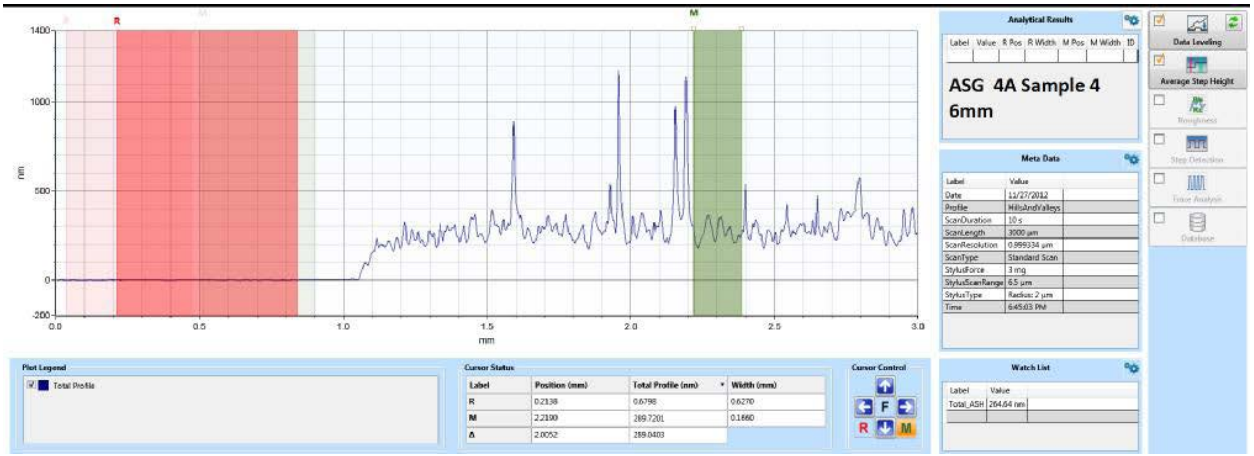
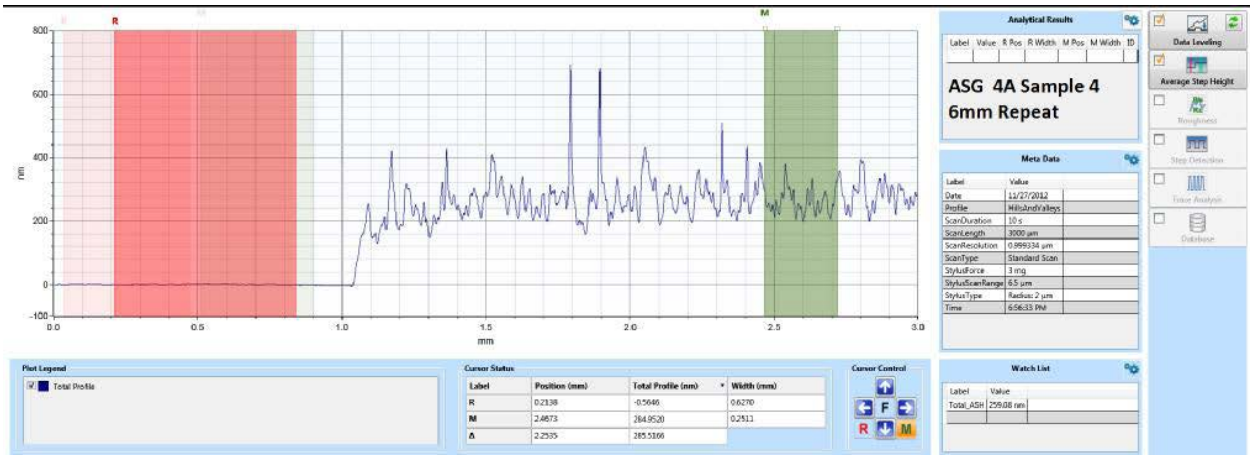
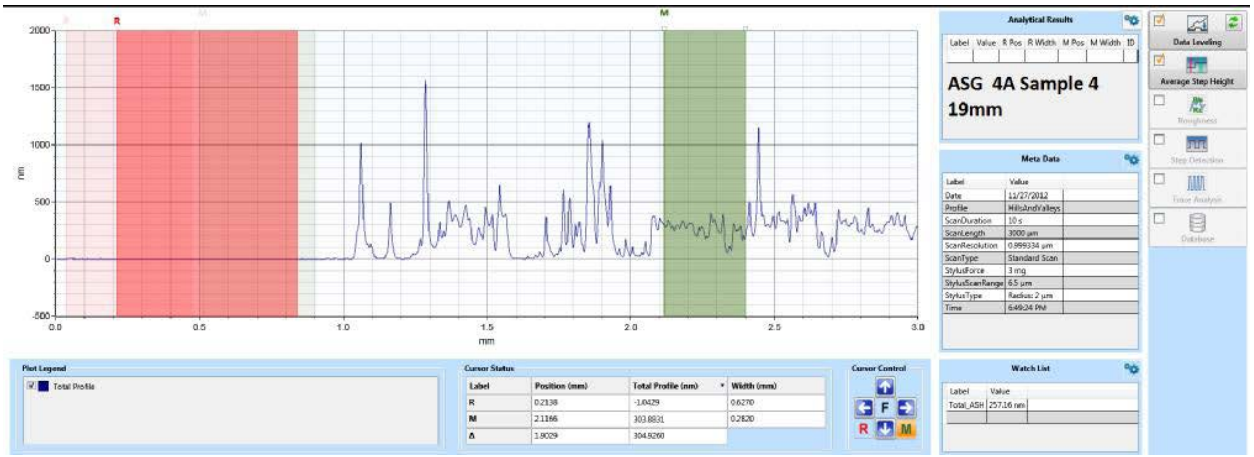
Watch List
Plot Legend
Total Profile
Cursor Status
Cursor Control
Data Levelling
Average Step Height
mm
nm


Analytical Results
ASG 4A Sample 4
6mm
Meta Data
Watch List
Plot Legend
Total Profile
Cursor Status
Cursor Control
Data Levelling
Average Step Height
mm
nm

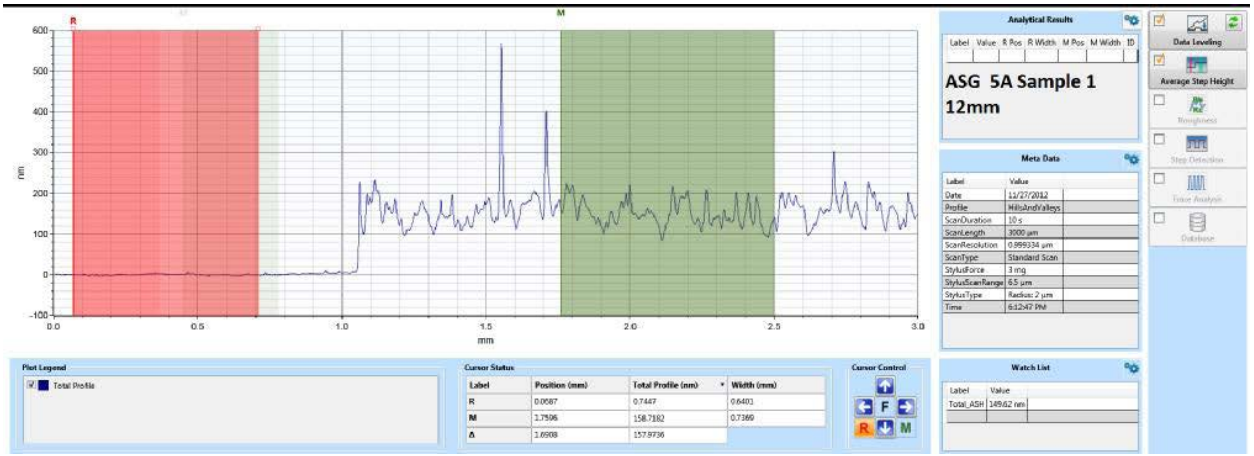

ASG 4A Sample 4
6mm Repeat

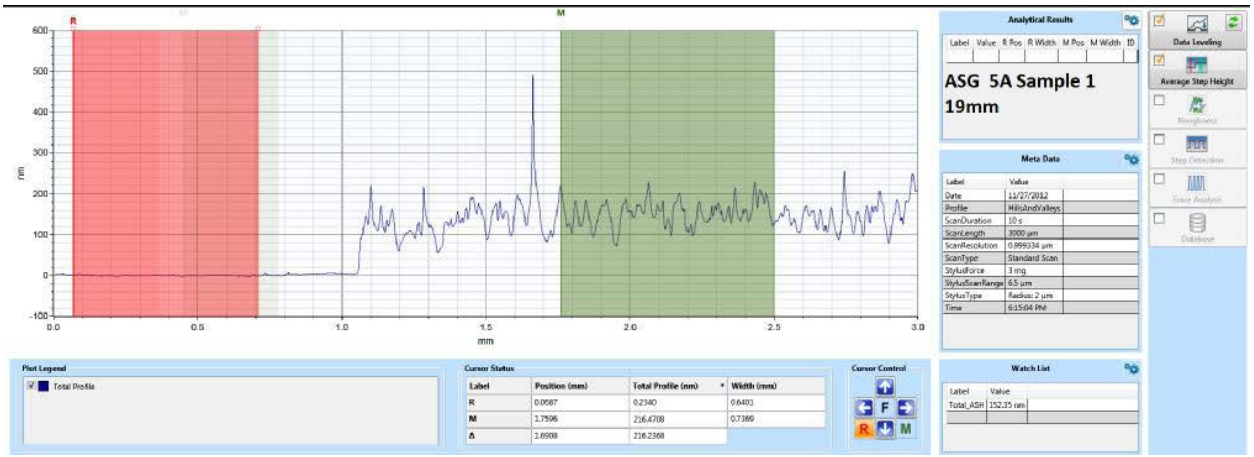
ASG 4A Sample 4
12mm

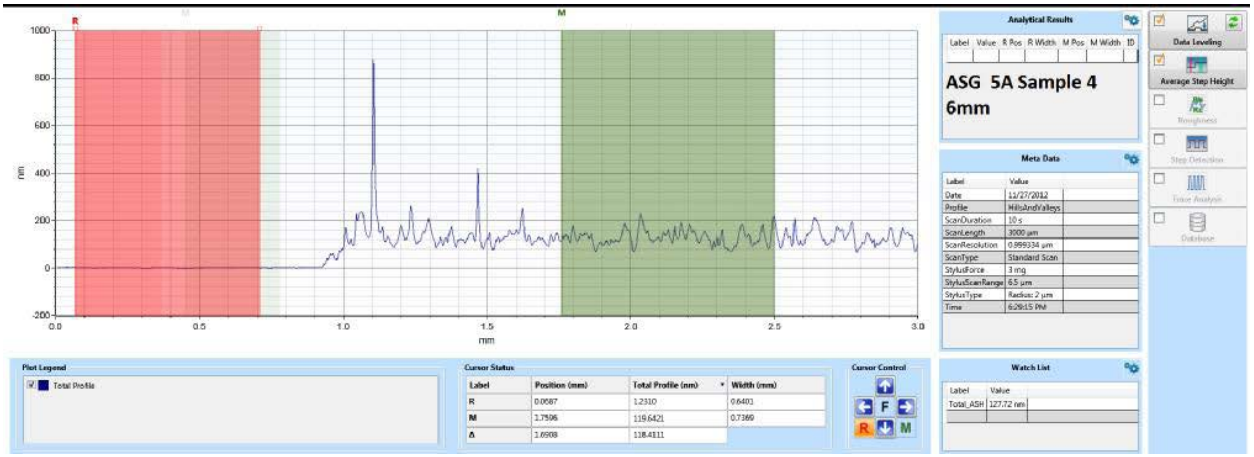
ASG 4A Sample 4
12mm Repeat


ASG 4A Sample 4
19mm

ASG 5A Sample 1
6mm


ASG 5A Sample 1
12mm


ASG 5A Sample 1
19mm
Analytical Results
Meta Data
Watch List
Total_ASH 152.35 nm
Plot Legend
Total Profile
Cursor Status
Cursor Control
Data Leveling
Average Step Height
mm


ASG 5A Sample 4
6mm
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Meta Data
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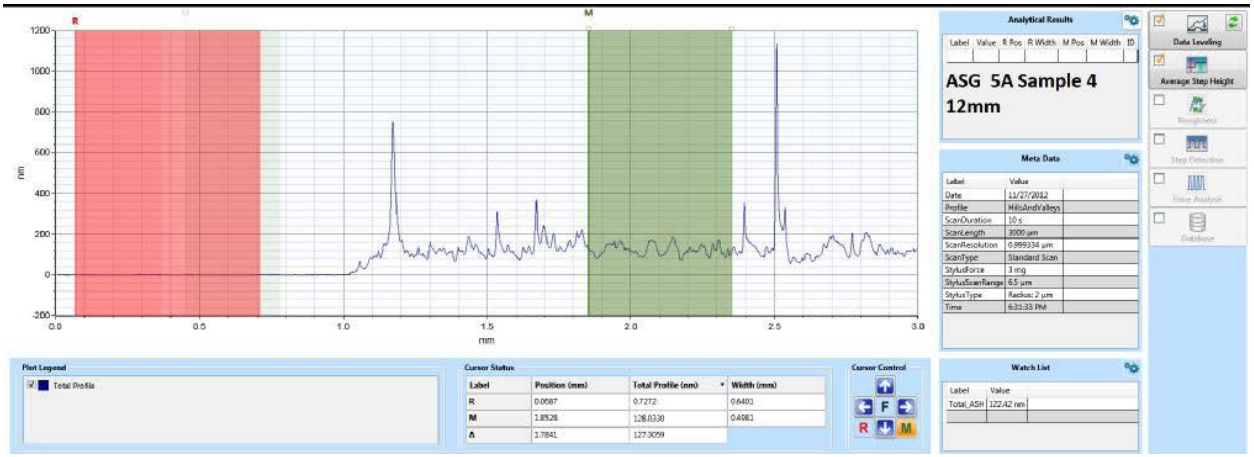
Plot Legend
Total Profile
Cursor Status
Cursor Control
Data Leveling
Average Step Height
mm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Total Profile
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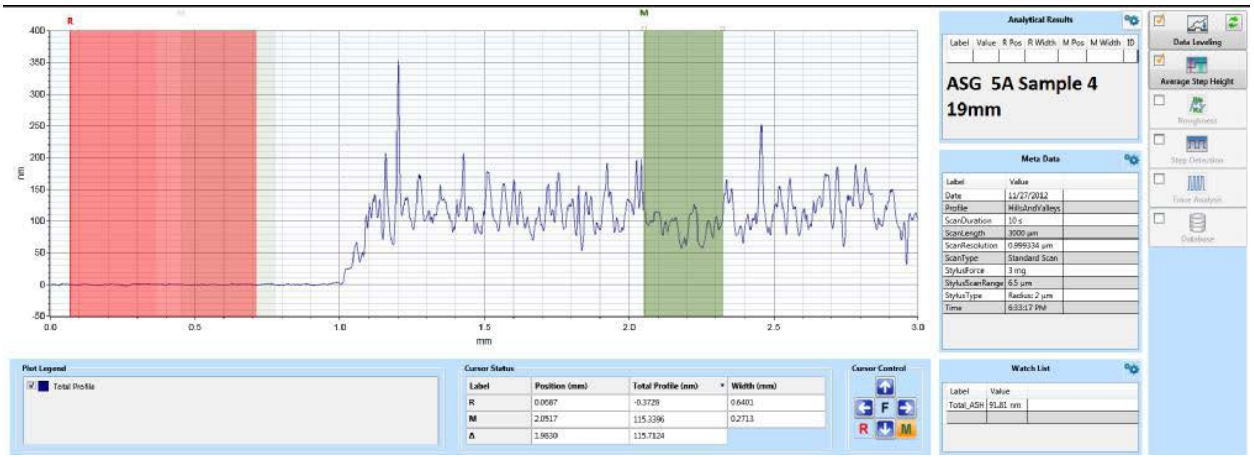
Cursor Control
Data Leveling
Average Step Height
mm


R
M
400
350
300
250
200
150
100
50
0
-50
nm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
mm
Analytical Results
Label
Value
R Pos
R Width
M Pos
M Width
ID
ASG 5A Sample 4
19mm
Meta Data
Label
Value
Date
11/27/2012
Profile
HillsAndValleys
ScanDuration
10 s
ScanLength
3000 µm
ScanResolution
0.999034 µm
ScanType
Standard Scan
StylusForce
3 mg
StylusScanRange
6.5 µm
StylusType
Radius: 2 µm
Time
6:33:17 PM
Data Leveling
Average Step Height
Roughness
Step Detection
Trace Analysis
Database
Plot Legend
Total Profile
Cursor Status
Label
Position (mm)
Total Profile (nm)
Width (mm)
R
0.0087
-0.3728
0.6401
M
2.0517
115.3396
0.2713
Δ
1.9830
115.7124
Cursor Control
F
R
M
Watch List
Label
Value
Total_ASH
91.81 nm

Appendix 6: White Paper on Operational Use Environment Testing of Alkali Silicate Glass Coatings

Prepared by: Dave Hillman and Ross Wilcoxon

Submitted June 28, 2013

Executive Summary

Alkali Silicate Glass (ASG) coatings have been developed by Rockwell Collins for enhancing the robustness of electronics used in harsh environments and to mitigate the risk of tin whiskers. To finalize transition of this technology to the military electronics industry, the system-level capabilities of ASG materials must be demonstrated through materials and robustness testing such as vibration, fluids susceptibility, etc. This white paper describes the recommended testing to be conducted and provides an estimate on the time and cost required.

Background

The transition to lead-free electronics in consumer electronics has led to renewed interest in tin whiskers, which are metallic filaments that can grow from the pure tin surfaces commonly used as surface finishes on components (Figure 1). Tin whiskers can cause shorting and other failure mechanisms in electronics; they were first reported decades ago. Historically, the risk of tin whiskers was mitigated by 'poisoning' the tin with small amounts of lead. However, the adoption of lead-free electronics has eliminated this simple, if not fully understood, method for preventing tin whiskers. While the precise mechanisms that lead to tin whiskers are not completely understood, there is general agreement that they are due to internal compressive stresses related to tin plating processes as well as environmental exposures. Because consumer electronics generally see less severe environmental conditions and have shorter product lifetimes, tin whiskers ares typically of less concern for these products than in the long-life systems commonly used in military and other avionics systems.

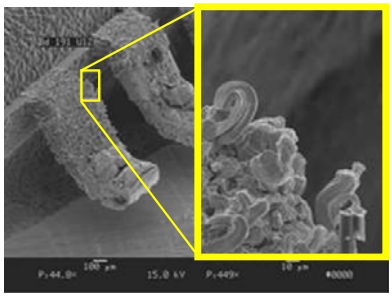


Figure 1: Example of Tin Whiskers on Component Lead

Under a combination of internal and external funding[1], Rockwell Collin has developed Alkali Silicate Glass (ASG) coatings that are targeted at mitigating tin whiskers in Department of Defense (DoD) electronics. These coatings are of interest primarily due to the fact that they can be processed at temperatures that are compatible with conventional electronic packaging materials. Work to date has focused on developing formulations that can reduce the tin whisker

[1] Tin Whisker Inorganic Coating Evaluation (TWICE) program under the Strategic Environmental Research and Development (SERDP) WP-2212

risk in harsh environment electronics and comparing the effectiveness of these coatings to more conventional conformal coatings. These conventional conformal coatings include Parylene and acrylic, which are commonly used to help ruggedize circuit card assemblies (CCAs) against corrosion, shorting from moisture and, more recently, to help mitigate the risk of tin whiskers. Ongoing work is implementing ASG coatings with nanoparticles on a variety of electronic components on a representative CCA. That work will establish the ability of ASG coatings to mitigate tin whiskers and demonstrate that the materials can be transitioned into a production environment in which they can be applied to harsh environment electronics. That work is scheduled to be completed by June of 2014.

While the ASG coatings are projected to be validated for tin whisker mitigation and factory-transitioned in 2014, they will not be product-transitioned until their system-level impact has been demonstrated. This will require testing that demonstrates robustness in harsh environments and that these coatings do not adversely affect the performance of electronics.

Proposed Solution

This white paper describes activities needed to complete the overall technology transition of ASG coatings for ruggedizing military and other harsh-environment electronics against tin whiskers. Technology transition activities will include A) characterization of coatings for their robustness in operational environments and B) materials characterization of coatings to provide guidelines to designers.

A. Operational Testing for Environmental Robustness

Military and aerospace systems currently use a wide variety of coatings to protect electronics. These coatings, such as Parylene, urethane, acrylic, etc., tend to be very mechanically compliant relative to the surfaces that they coat (metal leads, circuit boards, copper traces, etc.). Prior to their use in a system, coatings are subjected to environmental testing to verify their robustness and performance benefits to the CCA. The inorganic ASG coatings tend to be stronger, stiffer and less permeable to moisture than other coatings. While these attributes are generally positive for coatings targeted at protecting a surface, testing is required to demonstrate robustness in their use environment as well as to verify their compatibility with other aspects of a system's design.

Vibration

Vibration imposes high cycle stresses on circuit boards; these stresses are in turn transferred to any coatings applied to those assemblies. The stiffness and comparatively more brittle nature of the glass-based ASG coatings may lead to a greater susceptibility to these vibration stresses than would be experienced by organic coatings. Initial research by Rockwell Collins has indicated that, because ASG coatings are extremely thin, they are relatively unaffected by vibration-induced stresses. Standard board-level testing can be used to verify this observation. The industry standard for vibration testing is MIL-STD-810F (Test Method Standard for Environmental Engineering Considerations and Laboratory Tests) Method 514.5 (Vibration).

The MIL-STD-810F vibration test method will be adapted for evaluating ASG coatings to determine a) if the coatings are sufficiently robust to withstand vibration stresses and b) whether the presence of the coatings adversely affect the reliability of components on the circuit cards. Typically in vibration testing, the electrical continuity of circuits on the board under test is monitored and either a 'step-stress' vibration level approach or a "resonant frequency" vibration approach is employed to cause circuit assembly failures. Both testing approaches have positive

and negative characteristic test results. Typically, step-stress testing can be conducted in a shorter amount of time; however it also introduces greater uncertainty due to the fact that test vehicles are subjected to multiple levels of stress. It is proposed that for the TWICE coating evaluation, the resonant frequency approach be utilized. In resonant frequency vibration testing, the assembly under test is instrumented with strain gauges and accelerometers and subjected to a 1G sine sweep input. Data collected from the strain gauges and accelerometers can be used to determine the resonant frequencies of the test vehicle, the amplitudes, and estimates of damping. **Figure 2** shows an example of a sine sweep acceleration response of a circuit board with a first resonant frequency of ~70Hz. The primary resonant frequency and a specific vibration input can then be selected as vibration test parameters.

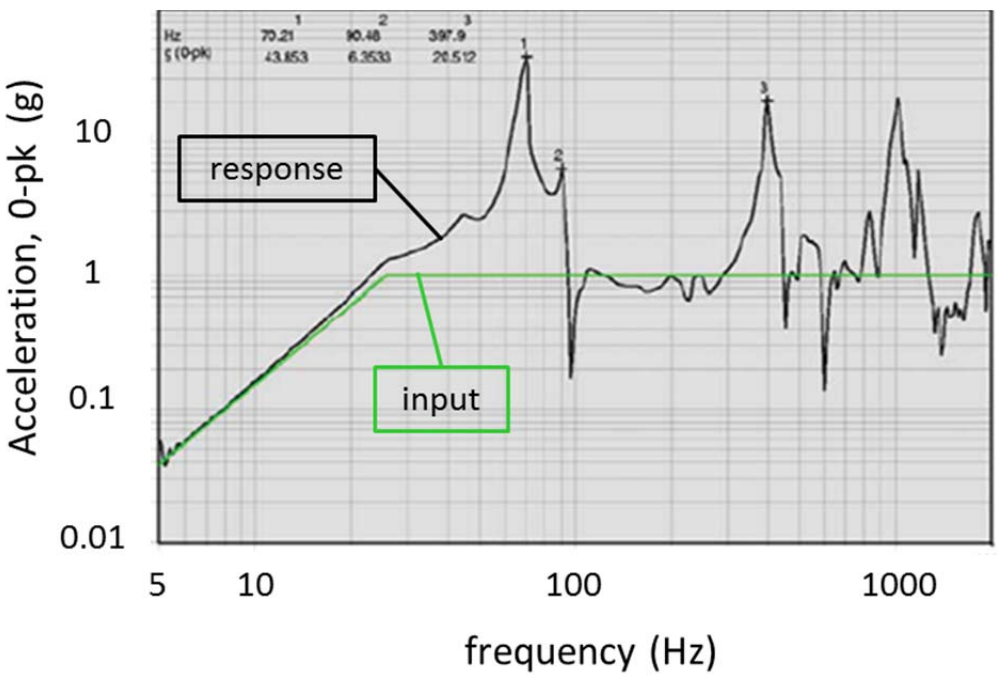


Figure 2 'Resonant Frequency' Sine Sweep Response

Testing will be conducted with ASG coated circuit boards (both populated and unpopulated), uncoated reference boards, and test coupons. Selected boards would be removed from the overall population after a specified time interval for coating assessment testing while some of the populated boards would remain on the test fixture throughout testing so that component continuity can be measured. The population of test vehicles would be divided into groups that are each subjected to a fixed amplitude of vibration testing at the resonant frequency. Samples would be removed from testing at specified time intervals and assessed for coating damage. The fixed amplitudes at the resonant frequency establish specific peak stress (S) levels and the test time multiplied by the resonant frequency defines the number of cycles (N). These data would be used to generate 'S-N' curves that characterize damage relative to stress conditions.

The circuit cards removed from testing after each sample interval will be assessed to determine if the coating has been adversely affected by the accumulated vibration cycles. This assessment will include (1) visual inspection to determine if the coating has cracked or peeled away from the circuit card and (2) conventional tape test methods used to determine if the coating adhesion has

degraded. In addition, test coupons with copper will be included in the testing. The copper will be acid cleaned before it is coated so that the surface is not oxidized. If the coating cracks during vibration testing, oxygen will contact the copper and cause it to oxidize, particularly when the samples are placed in an oven at 100°C for one hour. The level of oxidation will be an indication of the permeability of the ASG coating and the degree to which it degrades during vibration.

Drop Shock

Drop shock testing has traditionally been used to assess the resistance of board level interconnects to board strain induced by dynamic bending that result from a sudden impact. The root cause of failures that occur in this testing is typically a combination of excess strains due to process issues, weak interconnects due to soldering issues or the quality of incoming components/boards. Drop shock testing has not been commonly used in the past to evaluate coating materials; however as electronics assemblies become smaller and more complex this test methodology is finding greater utility in evaluating coating integrity. A drop shock test can identify limitations of coatings with respect to the coating material application consistency and adhesion on complex coating configurations. In a similar fashion to the proposed vibration testing and using the same test vehicles, groups of circuit cards will be subjected to different levels of drop-shock and assessed after each impact to determine if the coating has been adversely affected. This assessment will include visual inspection to determine if the coating has cracked or peeled away from the circuit card and conventional tape test methods to determine if the coating adhesion has degraded.

Fluids Resistance Testing

Electronics systems used in harsh environments are often exposed to fluids that can cause damage. Conformal coatings are often included in designs to help mitigate this damage; to be effective the coatings themselves must be tolerant of the fluids. MIL-STD-810F test methods are widely used to assess the effects of many aviation fluids and are widely used by the high performance electronics industry. Testing will be conducted by subjecting coated test samples to three exposure levels: 'Occasional' (a one-time exposure to a fluid), 'Intermittent' (exposure to a fluid once per hour over an 8 hour period) and 'Extended' (continuous exposure to a fluid for 24 hours). Fluids against which coatings should be tested include Kerosene (jet fuel), Skydrol (hydraulic fluid), Lubricating Oil (3 in 1 Oil), Polypropylene glycol, Isopropanol (IPA), Alkaline Cleaner (27% Aquanox SSA solution), Toluene, Xylene and Detergent (10% Alconox solution).

To assess the impact of fluids, test coupons will be inspected for visible attack of the coating by the fluid, in which visible attack is defined as bubbling or blistering of the conformal coating. If the fluid causes loss of surface gloss of the coating, but does not bubble the conformal coating, then the coating will be considered to be resistant to the fluid. In addition, the adhesion of the coating will be assessed for degradation by placing test boards into a thermal cycle chamber for 100 cycles between -55C and +125C, with an 8-10°C ramp rate and 15 minute soaks at either extreme, and examining for signs of delamination.

Salt Spray Testing

The electronics industry utilizes salt spray testing to characterize the interaction of a coating material and the printed circuit assembly against a harsh product use environment. Marine and polluted industry smog product use environments contain chloride compounds, which can degrade product integrity. Salt spray testing is conducted per ASTM B117 with a 5% salt

solution for a 24 hour cyclic exposure. This test will demonstrate the resistance of the ASG coating to a corrosive product use environment and permit high performance electronic programs to compare the results to existing product applications.

The following table summarizes the testing to be performed:

Test	Test Method	Procedure	Samples	Assessment
Vibration	Adapted from MIL-STD-810F	Determine resonant frequency of test board and determine maximum amplitude of board displacement for 1G sinusoidal input. Subject coated boards to a fixed amplitude of vibration testing at the resonant frequency. Remove samples from testing at specified time intervals and assessed for coating damage.	Populated circuit boards Unpopulated circuit boards Copper test coupons	Monitor electrical continuity of components Visual inspection, adhesion testing, high temperature exposure to reveal copper oxidation in cracked coating
Shock	JEDEC Standard JESD22-B110A	Shock testing will be conducted in the -Z direction. 40G peak input, 25ms pulse duration, Remove part of test population after a series of shock pulses.	Populated circuit boards Unpopulated circuit boards Copper test coupons	Monitor electrical continuity of components, visual inspection, adhesion testing, high temperature exposure to reveal copper oxidation in cracked coating
Fluids	MIL-STD-810F	Subject coated boards to single exposure, once per hour for 8 hours, and 24 hour continuous exposure of fluids. Fluids: Kerosene, Skydrol, Lubricating Oil, Polypropylene glycol, Isopropanol, Alkaline Cleaner, Toluene, Xylene, Detergent and none (baseline sample).	Populated circuit boards	Visual inspection for bubbling and blistering of coating as well as inspection for delamination following temperature cycling
Salt Spray	ASTM B117	5% salt solution, two cycles of 24 hour exposure, followed by 24 hours dryout.	Populated circuit boards	Visual inspection for bubbling, blistering, delamination of coating or corrosion of metals

B. Design Impact Characterization

Thermal and electrical properties of coatings can affect the performance of the materials onto which they are coated. For example, coatings have been shown to alter the thermal emissivity of a surface, which in turn affects its radiant heat transfer. Thermal radiation can be a significant contributor to overall heat transfer in natural convection cooled electronics, particularly at high altitudes. Also, the dielectric properties of coatings can alter the electrical performance of active and passive RF devices. Properties such as these must be determined for coatings being

considered for use in many DoD electronics systems. Materials characterization testing will include measurements of the thermal conductivity and emissivity of coatings as well as measurements of the dielectric constant and loss tangent of coatings over a frequency range from 100 MHz to 60GHz.

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Appendix 7: White Paper: Discussion on Alkali Silicate Glass Formulations

Submitted to SERDP: June 6, 2014

Background on Alkali Silicate Glass

Material Overview

Alkali silicate glasses belong to a family of materials that have seen wide use in applications that include the production of ceramics, constituents in paints, protecting pipes and other systems with fluid flow from corrosion and even as an egg preservation agent. Given this extreme breadth of applications, it is somewhat surprising that these materials have not been used in electronics, but reviews of the literature show that this appears to be the case. One likely reason that these materials have not seen wider use in electronics is the fact that off-the-shelf alkali silicate materials tend to have high ionic mobility and poor durability that would lead to corrosion. Also, many conventional formulations of these materials can exhibit undesirable properties, such as brittleness and poor adhesion. Through careful formulation however, the properties of these materials can be tailored by optimizing the silicate ratios (silicate to alkali), the mixture of alkalis, and the use of nanoparticles to modify the glass network and thereby make them suitable for use in electronics packaging.

ASG materials are water based (dissolved in aqueous solutions); they look like water and cure when water is removed by evaporation, leaving a solid glass material. Thus, they can be applied under atmospheric pressure, in a variety of methods, and processing temperatures can be as low, or lower than, the cure temperature of many conventional organic materials. Once cured, the glass layer can be quite robust and impermeable to moisture.

It is well known that diffusion and ionic conductivity of binary alkali silicate glasses increases with increasing ion concentration [1]. For this reason, high alkali containing glasses are generally avoided for use in electrically insulating applications. However, ion mobility can be drastically reduced by exploiting the “mixed alkali effect” [1]. While there is no universally accepted theory that explains the mixed alkali effect, it is recognized that the use of multiple alkali, especially those with a larger mismatch such as potassium and lithium, can reduce the ionic mobility of alkali silicate glasses by five orders of magnitude or more [2]. For this reason, the ASG material development work at Rockwell Collins has focused on such mixed alkali formulations.

Alkali Silicate Glass System

The basic building block of silicate glass is the covalently bonded tetrahedral silicon dioxide (SiO_2). In covalent bonding, electrons are shared between atoms in such a way that each atom has its outer *sp* orbital filled. Silicon has a valence of four and shares electrons with four oxygen atoms, thus giving a total of eight

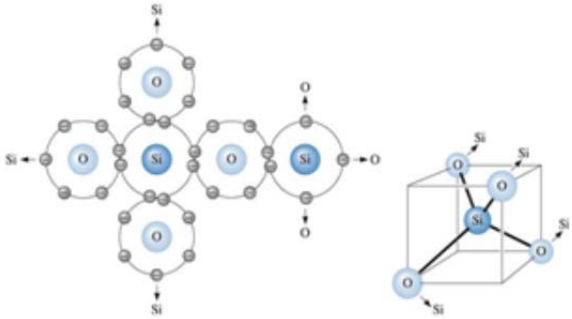

Figure 3 Tetrahedral structure of silica ($Si0_2$)

electrons for each silicon atom. However, oxygen has a valence of six and shares electrons with two silicon atoms, giving oxygen a total of eight electrons. Figure 3 illustrates this fundamental silica structure. Pure SiO_2 glass is considered to be fully polymerized, as every oxygen atom bridges two silicon atoms. This fully crosslinked structure is very strongly bound and gives pure SiO_2 glass the highest known intrinsic strength of all glasses, up to 14 GPa [3]. The addition of alkali to a SiO_2 network, results in a breakdown of the strong bridging oxygens into charge balancing nonbridging oxygens (NBO), as depicted in Figure 5. Every alkali ion addition creates one new non-bridging oxygen.

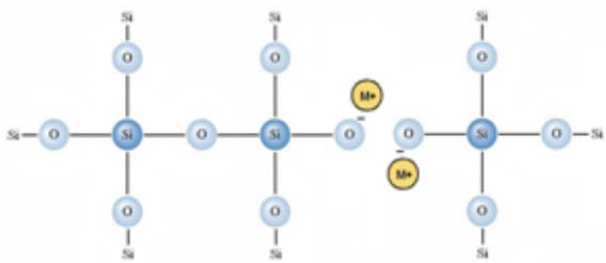

Figure 5 NBO formation in SiO_2 due to alkali ions

The addition of alkali increases ion density, as the ions 'fill holes' in the silicate network as depicted in Figure 4. This tends to both increase the material density as well as decrease its strength, elastic modulus (stiffness), and brittleness [21]. The properties of alkali silicate glass depend on the field strength (z/r_c^2) of the modifying cation, i.e. the alkali type. Therefore, lithium NBO bonding is stronger than sodium, which is stronger than potassium, which is stronger than cesium. It follows that the stronger bonding leads to increased modulus, strength, transition temperature (Tg), and durability.

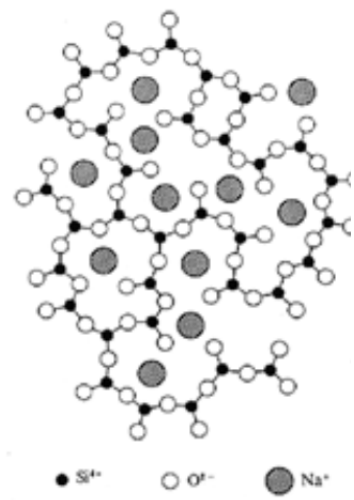

Figure 4 Structure of a binary sodium silicate glass [4]

Aqueous silicate solutions

Alkali silicate solutions are composed of a mix of silicate anions. The fundamental building block of silicate solutions is the tetrahedral silicate anion with a silicon atom at the center of an oxygen cornered four sided pyramid. In aqueous solutions, each oxygen atom is typically associated with one hydrogen (H+) or alkali atom (M+), or it may be linked to other silicon atoms through tetrahedral coordination.

Liquid alkali silicate solutions are commercially available in a variety of SiO_2 / M_2O ratios where M_2O as an alkali oxide of lithium, potassium or sodium. The molar ratio of silica to alkali is known as the R-value and strongly influences the properties of the material. Highly siliceous (high R-value) liquid alkali silicate solutions tend to air dry rapidly, are the most refractory (high melting temperature), and are the most resistant to acids and corrosion. These silica rich liquid solutions tend to contain more water than the alkaline rich solutions and thus undergo greater shrinkage while curing. Low ratio, alkaline rich, solutions tend to have greater elasticity, lower brittleness, and less shrinkage but exhibit poor corrosion resistance. These low ratio coatings also dry more slowly because their alkali content creates a greater affinity for water. Many chemically resistant cements and mortars are produced using high ratio (R ~ 3.22) alkali silicate solutions. In order for the silicate coatings to become impermeable and relatively insoluble,

water must be completely removed. Air drying alone is usually not adequate for coatings which will be exposed to weather or high moisture environments. For these applications heat curing is often needed. Curing temperatures between 95 and 100°C are often sufficient for adequate dehydration.

Micro- and Nanoparticle Composites

Adding the appropriate nano- and microfiller particles to silicate solutions can provide many benefits to the final silicate glass composite. Nanoparticle fillers, however, can provide additional unique benefits over microparticle fillers alone. The properties of most materials, in general, tend to change as particle size is reduced. For example, grain structure can be significantly smaller in nanoparticles (or non-existent) resulting in higher elastic modulus, improved durability, improved electrical characteristics, and enhanced magnetic properties. Nanoparticles have a significant surface area to volume ratio as compared to microparticles, thus providing a high fraction of surface atoms which can lead to increased reactivity, exhibit quantum confinement characteristics, superparamagnetism, extreme hardness, etc. It often only takes a small fraction of nanoparticles to significantly modify the properties of a composite. Because nanoparticles are so small, the stress concentrations that that they produce within a composite are often are far less than what would be contributed by microparticles or extrinsic defects (scratches and defects from handling, processing, corrosion, etc.).

Reduced diffusion and corrosion susceptibility, as well as antimicrobial, non-wetting, and self-cleaning characteristics can also be achieved with nanoparticles composites. The use of nanoparticle filler can be critical for ASG-based materials in some circumstances. While glasses are generally considered to have good chemical durability in water and other solvents, some glasses may quickly degrade in low or high pH solutions. In general, silicate glasses rapidly corrode when pH < 1, and pH > 9. Adding alumina (2% to commercial compositions) tends to improve neutral pH durability, but is provides little benefit in low pH solutions. Zirconia is often used to improve high pH resistance, while zinc oxide will improve resistance to acids. There are many other inorganic additives that can be used to control glass durability in both high and low pH environments and when these additives are in the form of nanoparticles, their extremely high surface to volume ratio allows a small amount of additive material to provide a significant impact to the bulk material durability.

One of the challenges associated with creating nanoparticle composites is achieving high particle loadings. Because of the large surface area of nanoparticles, a significantly greater volume of liquid is required to wet the surface of the particles. As a result, viscosity is often significantly higher in nanoparticle solutions, which can create difficulties in applying and curing the materials (i.e. high viscosity and high shrinkage). Another challenge is keeping nanoparticles from clustering and behaving like microparticles, thereby losing the benefit of the nano-size. Van der Waals' forces, which are interatomic attractive forces between particles, tend to cause nanoparticles to cluster and prevent dispersion and suspension in composite solutions. In some cases ultrasonics, mechanical mixing, and/or the use of surfactants or other chemical additives can help to disperse nanoparticles. Anionic dispersants have shown to be very effective at dispersing aqueous nanoparticle solutions. In some cases, as little as 0.25 wt% anionic dispersant relative to the solids is sufficient [5]. Often times, material vendors can provide nanoparticles in deionized water suspensions for little additional cost. These solutions can sometimes be carefully added to alkali silicate solutions to create the nanoparticle composites.

Specific Applications To SERDP TWICE Program

ASG Formulation Details

Two formulations of ASG materials were used in the TWICE program; these were referred to as 4A and 5A. The specific formulations of the base materials are proprietary to Rockwell Collins; the information in Table 1 provides an overview of the differences between the two materials. In both cases, the formulations were produced by combining one or more commercially available alkali silicate solutions with deionized water to achieve a target R-value, mixed alkali ratio and solid (non-water) fraction.

Table 1 ASG Formulations used in TWICE

ASG Formulation	Alkali Constituents	R-Value (M%) (silica/alkali ratio)	% Solids
ASG 4A	Lithium, Sodium, Potassium	2.77	24.8
ASG 5A	Lithium, Potassium	4.00	24.7

To formulate the materials that were coated onto the TWICE test vehicles, these base materials were further diluted with deionized water (to allow them to be sprayed) and, in the composited formulations, mixed with mixed with nanoparticles prior to spraying. Phase 2 formulations were diluted with a ratio of 240:1 dionized water to ASG formulation. Composite materials were generally designed to have a 4:1 ratio (by weight) of nanoparticles to solid glass after the applied materials had been fully cured.

Nanoparticle Formulation Details

The nanoparticles used in the TWICE formulations are shown in Table 2. Adhesion between the glass matrix and the nanoparticles, as well as to the tin surface finish on the test components, is expected to primarily be due to covalent bonding between the ASG and oxides on the surfaces of the solids. These bonds are extremely strong, which leads to excellent cohesive strength within the composite material and, with proper pre-treatment of the surfaces to ensure good adhesion of their oxide layers, adhesive strength between the ASG composites and the surfaces to which they are coated.

Table 2 Nanoparticles used in TWICE

Nanoparticle	Size (nm)	Hot Water Adhesion Test*	High Temp Oxidation Resistance+	Notes
Alumina	10	Good	Poor	stable suspension
Alumina	30-60	NA	NA	suspension and deposition challenges
Titania (Rutile)	5-15	Poor	Poor	stable suspension
Titania (Anatase)	5-15	Poor	Poor	stable suspension
Zirconia	45-55	OK	Best	stable suspension
Zinc Oxide	35	NA	NA	suspension and deposition challenges

Whisker Growth Behavior on ASG-Coated Surfaces

It is industry consensus that the initiation and growth of tin whisker structure morphology occurs as a result of stress reduction in the component pure tin surface finish [6-11]. Tin whisker crystallographic structures grow through the diffusion of tin atoms, which is driven by high local stresses in the pure tin surface finish. Tin whiskers formation is very different from that of dendritic crystallographic structures, which are caused by corrosion mechanisms. The initiation of these dendritic structures requires three primary inputs: a potential (voltage) difference, an electrolyte and an ionic material. Tin whiskers only require tensile or compressive stress in the component pure tin surface finish. Figure 6 illustrates both tin whisker and dendritic crystallographic structures.

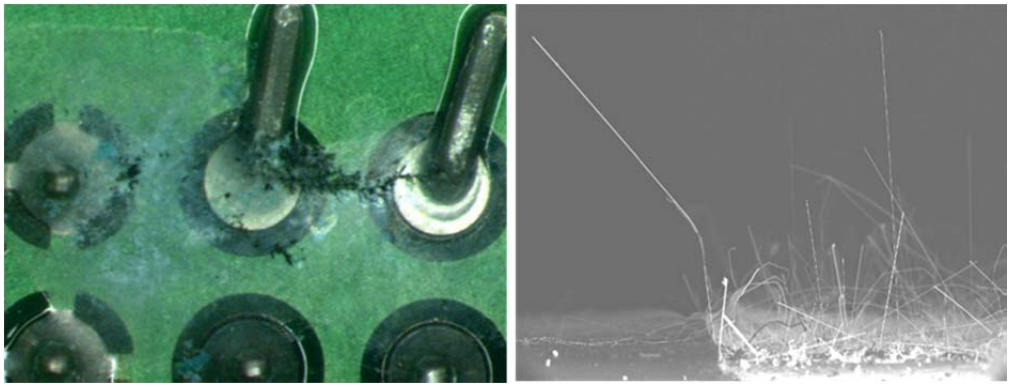

Figure 6 Crystallographic Structures: Left - Dendrite Formation due to Corrosion, Right - Tin Whisker Formation due to Diffusion

An understanding of how the tin whiskers form their crystallographic structures is key to developing successful tin whisker mitigation and elimination strategies. How the tin atoms diffuse through the tin plating and build a tin whisker has been the subject extensive industry investigative efforts. Singh and Ohring [12] deposited Sn^{119m} atoms on thin Sn film stripes so that they could be diffusion traced using auto radiographic techniques. They concluded that the tin atoms diffused along grain boundaries first and then into the tin crystalline lattice. A more recent investigation conducted by Woodrow [13] significantly advanced the understanding of tin atom diffusion interaction with tin whisker growth. In his study, two non-radioactive tin isotopes, Sn^{120} and Sn^{118}, were deposited on a test coupon as shown in Figure 7. The tin atom diffusion was traced using time-of-flight secondary ion mass spectroscopy (TOF-SIMS). Characterization of the two Sn^{120} and Sn^{118} tin isotopes provided a measure of the tin diffusion speed and relative origination location for the tin plating surface and the tin whiskers observed on the tin plating surface. The TOF-SIMS analyses revealed that the tin atoms diffused along the grain boundaries and then into the tin grains (see Figure 8). A series of surface/depth profiles analyses showed that the tin atom diffusion occured over large distances (i.e. 3000 microns), thus providing on possible mechanism for a tin whisker growth source. Woodrow also investigated the tin whisker internal and surface composition in terms of the two Sn^{120} and Sn^{118} tin isotopes. The internal tin whisker composition was similar to the tin grain boundary composition in which the tin whisker originated. However, the surface tin whisker composition was consistent over the length of the whisker and had a different isotropic signature in comparison to the internal whisker composition. Surface diffusion of tin atoms along the whisker length was proposed as the root cause of the composition differences.

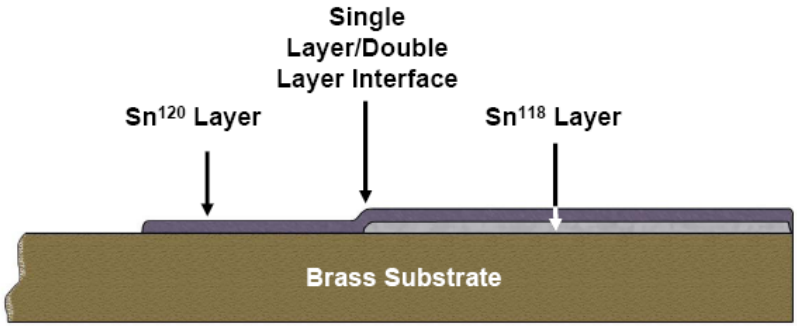

Figure 7 Tracer Diffusion Test Coupon [8]

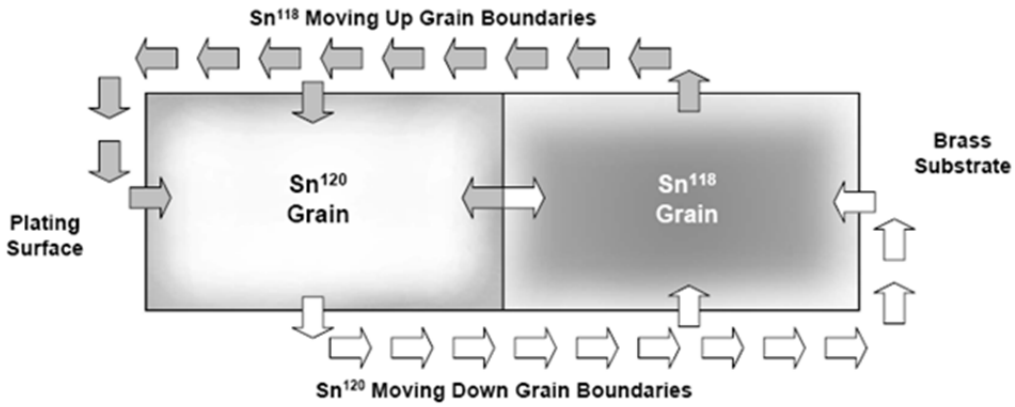

Figure 8 Proposed Tin Isotope Movement Patterns [8]

Woodrow's investigation suggests that the initiation and growth of a tin whisker is a material characteristic of tin. Efforts to eliminate tin whiskers should be focused along either of two approaches: (1) Changing the composition or grain structure of the component pure tin surface finish to disrupt the diffusion kinetics; and (2) Changing the interface surface of the component pure tin surface finish to disrupt the crystallographic structure formation. Since OEMs such as Rockwell Collins cannot control component surface finishes, the TWICE program has focused on modifying the interface surface to alter the tin whisker crystallographic structure. The use of the alumina nanoparticles in the ASG coating results in a significant change in the pure tin surface finish. However, coatings do not eliminate the presence of stresses in the surface finish, which will tend to relax over time and thereby initiate and grow tin whiskers. Inspection of TWICE test vehicles have shown that control (uncoated) samples will typically grow relatively long, blade-like, structures that are randomly distributed at points in the surface finish at which stress has been relieved and there is no longer a diffusion driving force (Figure 9, Left image). On the TWICE program ASG coated samples inhibit continued growth at a given location. This disrupts the growth of the tin whisker and results in a short, button-like structure. Since the coating prevents continued growth of the whisker, stress is not sufficiently relieved and whiskers will initiate at other nearby locations. This results in high density patches of whiskers that cumulatively relieve the stresses and ultimately eliminate the diffusion driving force (Figure 9, Right image). Even when the ASG coatings do not prevent the formation of whiskers, they do provide a controlled, engineering solution to prevent the formation of the long tin whisker crystallographic structures and thereby greatly reduce the probability of a tin whisker leading to electrical shorting.

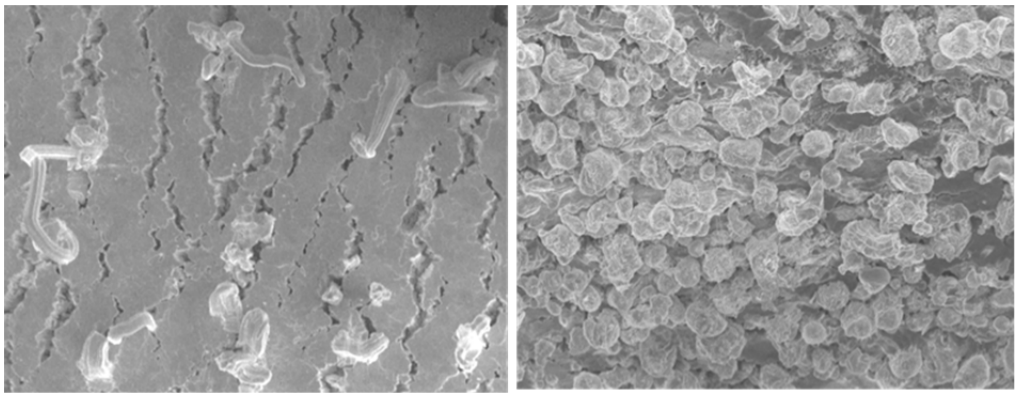

Figure 9 Tin Whisker Crystallographic Structures: Left - Blades, Right - Button

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Appendix 8: Nanoparticle coating formulation details

Table 1 shows all of the nanoparticle materials procured as liquid/particle suspensions that were evaluated in this study while Table 2 shows materials that were procured as dry powders. Development of the coatings used for the permeability testing included a number of nanoparticles that were not utilized in the earlier tin whisker evaluation. This was in part due to the need to limit the number of combinations, due to budget and schedule, that could be in evaluated for tin whisker growth. In addition, as the project matured, it became apparent that the ultrasonic sprayer, which was not available until part way through Phase 2, provided significant opportunities for applying coatings that could not be effectively deposited with the conventional spraying head that was first used. For example, prior development work on ASG-based encapsulants that are dispensed from a syringe rather than sprayed as a coating, found that including powdered Zinc Oxide in the composite improved their robustness. These nanoparticles would not remain in suspension when used with the conventional spraying head but could be successfully deposited with the ultrasonic spraying head.

Table 3 Liquid/Nanoparticle Suspensions

Nanoparticle Material	Particle Density (g/cc)	Weight % Solids	Size (nm)	Suspension
Zirconium Oxide (Zirconia), ZrO2	5.68	20%	45-55	Water
Zirconium Oxide (Zirconia), ZrO2	5.68	15%	5-20	NH4, Water
Aluminum Oxide (Alumina, Gamma phase), Al2O3	3.95	20%	10	Water
Cerium Oxide (Ceria), CeO2	7.65	18-20%	15-25	NH4, Water
Tin Oxide, SnO2	6.95	15%	10-15	NH4, Water
Zinc Oxide	5.61	30%	50-90	NH4, Water
Titanium Oxide (Titania, Rutile phase), TiO2	4.2[2]	15%	5-15	Water
Titanium Oxide (Titania, Anatase phase), TiO2	3.9[2]	15%	5-15	Water

Table 4 Dry Power Nanoparticles

Nanoparticle Material	Particle Density (g/cc)	Size (nm)
Calcium Carbonate	2.71 - 2.83	70
Zinc Oxide	5.61	55
Alumina	3.95-4.10	<50
Cerium oxide	7.22	

[2] Density of particles was not reported for these suspensions; this density value corresponds to nanoparticles of the same material that are available from the same manufacturer (US Research Nanomaterials, Inc.).

One of the mechanisms by which nanoparticles are able to effect changes in material properties, is their extremely large surface area for a given volume of nanoparticles. This surface area can alter the net forces and reaction rates between constituants in a mixture. While this can be beneficial, it can also lead to challenges in handling and processing nanoparticles. Attractive forces related to the surfaces of these particles can be larger than their weight. This will lead to particles agglomerating into macroparticles that have significantly less exposed area than the individual particles and therefore less influence on the composite material to which they are added. Commercially available nanoparticles are subjected to surface treatments and/or held in specific liquid suspensions to prevent this agglomeration. When these nanoparticles are then mixed into a matrix material, such as ASG, these surface treatments or the the suspension liquid may prevent good bonding to the matrix material or simply be incompatible with it. Acetic acid, or example, is commonly used to stabilize nanoparticles but is not compatible with ASG materials as it will prevent proper curing. The ammonia (NH4)-stabilized solution with Zinc Oxide was found to be compatible with ASG, but other nanoparticle suspensions with NH4 stabilizer led to non-robust coatings, presumably due to poor adhesion of the ASG to the particles. Efforts to react out the NH4, such as exposure to ultraviolet (UV) radiation followed by mixing with hydrogen peroxide, did improve the robustness of the resulting ASG composites, but not to the degree needed for this application.

The samples for permeability testing consisted of 2 mil thick PET films that were coated with various ASG formulations and thicknesses. Ensuring adequate adhesion to these films proved to be a greater challenge than it had been with other materials that had been coated in this study, such as glass, copper, plated tin, circuit boards, etc. Unlike these other materials, the use of plasma treatments on the PET films did not sufficiently improve adhesion; however UV ozone treatment did. After a number of iterations, a standard pre-treatment schedule of Argon plasma at 100W for 3 minutes, followed by a 10 minute UVO treatment was established as a suitable standard treatment that would ensure adequate adhesion on circuit boards as well as films.

Appendix 9: Plasma Ruggedized Solutions Phase 2 Report

Plasma Ruggedized Solutions

Global Provider of Custom Ruggedized Engineering Solutions across Industry

Tin Whisker Inorganic Coating Evaluation (TWICE) Program

Phase 2
Final Report

Date: 20 December 2013

Prepared for

Rockwell Collins, Inc.
Advanced Technology Center
400 Collins Road NE
Cedar Rapids, Iowa 52498

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Abstract

1. Test Vehicle DOE

A mix of standard coatings, ASG as primer and ASG alone were processed in this phase as outlined in Table 1 of this document. In total, 32 samples of five varieties were produced.

2. Material Application

Plasma Ruggedized Solutions (PRS) has used processes developed as a result of work in Phase 1 and recommended by Rockwell Collins Inc. (RCI) for Alkali Silicate Glass (ASG) deposition to electronics devices for the PRS prototype production line. Results of this effort are documented in this report that describes relevant, non-proprietary processes and methods utilized by PRS to apply ASG coatings to electronic devices. Standard processes for application of Acrylic and Parylene are also summarized.

3. Measurements

Thicknesses of coatings were verified by measuring coupons that accompanied all test vehicles through the process.

4. Documentation

PRS shall document the results of Phase 2 activities for inclusion in the Phase 2 report.

Background

Rockwell Collins has been awarded a research contract from the Department of Defense's Strategic Environmental Research and Development Program for the Tin Whiskers Inorganic Coatings Evaluation (TWICE) program. This research has the potential to mitigate the impact of tin whiskers on high-reliability, high-performance electronic systems caused by new lead-free alloys and finishes in the aerospace and defense supply chain and manufacturing systems.

The transition to lead-free electronics has changed some of the ground rules for designing reliable electronics for use in harsh environments. One of the most significant changes has been the need to address the phenomenon of tin whiskers, which can grow from the pure tin surfaces commonly used on lead-free devices. Tin whiskers are microscopic metal fibers that are thinner than a human hair capable of bridging great distances that can create short-circuits leading to equipment failures.

This project will lead to a better scientific understanding of the mechanisms by which tin whiskers form and how they can be controlled with conformal coatings. Rockwell Collins will develop materials and the necessary processes to generate coatings that mitigate tin whisker growth on a variety of surfaces over a wide range of environmental conditions.

Rockwell Collins is leading a team that includes Plasma Ruggedized Solutions and the University of Maryland Center for Advanced Life Cycle Engineering in this effort.

Source: Press Release posted on Rockwell-Collins web site

Objective

After effectively spraying ASG materials to circuit boards as defined in Phase 1, Plasma Ruggedized Solutions (PRS) was tasked with the objective of working with RCI to develop a design of experiments using a variety of conventional conformal coatings in conjunction with ASG and then executing the application of those coatings according to that DOE. PRS was to use the knowledge of applying the material gained in Phase I as a basis for applying the ASG as specified. That application process and the DOE used in Phase 2 are defined in detail in this document.

Design of Experiments

A total of 32 coated test vehicles were produced in five different variations during Phase 2 (details are outlined below in Table 1):

1. Parylene C
2. Acrylic Humiseal 1B31
3. Coating (Acrylic and ASG)
4. Alkali Silica Glass (ASG) Coating 4A
5. Alkali Silica Glass (ASG) Coating 4A Combo Mix A-Z

Table 1

Description	Quantity	Target Thickness	Date Produced
Parylene C	4	0.0010”nominal	October 10, 2013
Acrylic Humiseal 1B31	8	0.003”+/- 0.002”	October 11, 2013
ASG 4A Combo Mix A + Humiseal 1B31 (Acrylic)	4	2 microns 0.003”+/- 0.002”	November 7, 2013
ASG 4A Combo Mix A	8	2 microns	November 11, 2013
ASG 4A, Combo Mix A-Z	8	2 microns	November 13, 2013

Procedures

Test Vehicles

Image 1 depicts the coating evaluation test vehicle utilized in Phase 2 of the TWICE program. The test vehicle measured 5 3/8 inches wide by 3 7/8 inches high. Each test vehicle consisted of a double sided FR-4 circuit card assembly populated on one side with a variety of parts including one “tin man” (simulated SOIC-16).

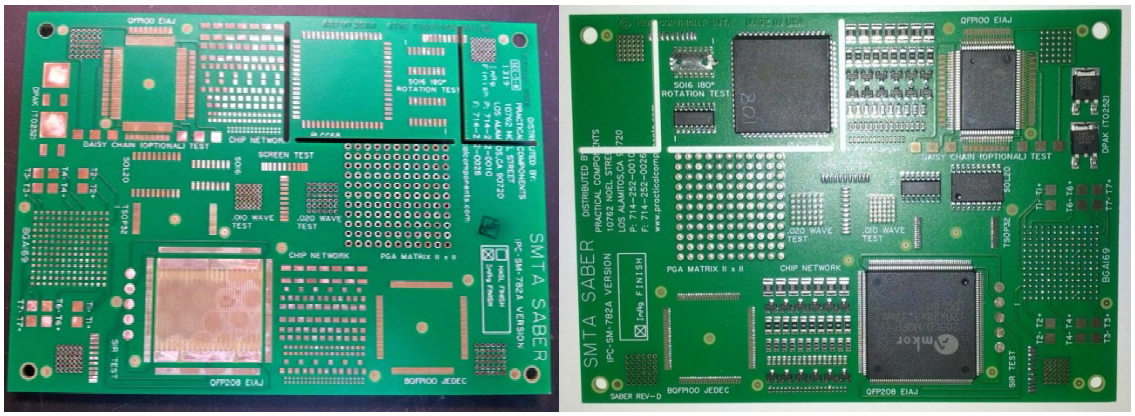


Image 1 Test Vehicle

Test Component

The component Image 2 shows the bright tin plated copper lead frame parts designed to simulate an SOIC-16 package with a high propensity for growing tin whiskers. This component is common to Phase 1 and Phase 2 test vehicles; it was selectively attached at pins 1, 8, 9, and 16 to allow for ease of removal as needed during post coating application inspections.

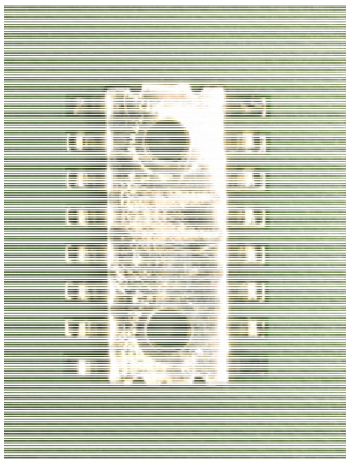


Image 2

Coupons

Plasma processed a glass slide with each test vehicle. The slides were placed within the spray pattern along with the test vehicle to get the exact coating application as the board.

Glass Microscope Slides: A standard American made (from Swiss glass) glass microscope slide which measured 75 mm x 25 mm x 1mm was utilized as the primary validation substrate.

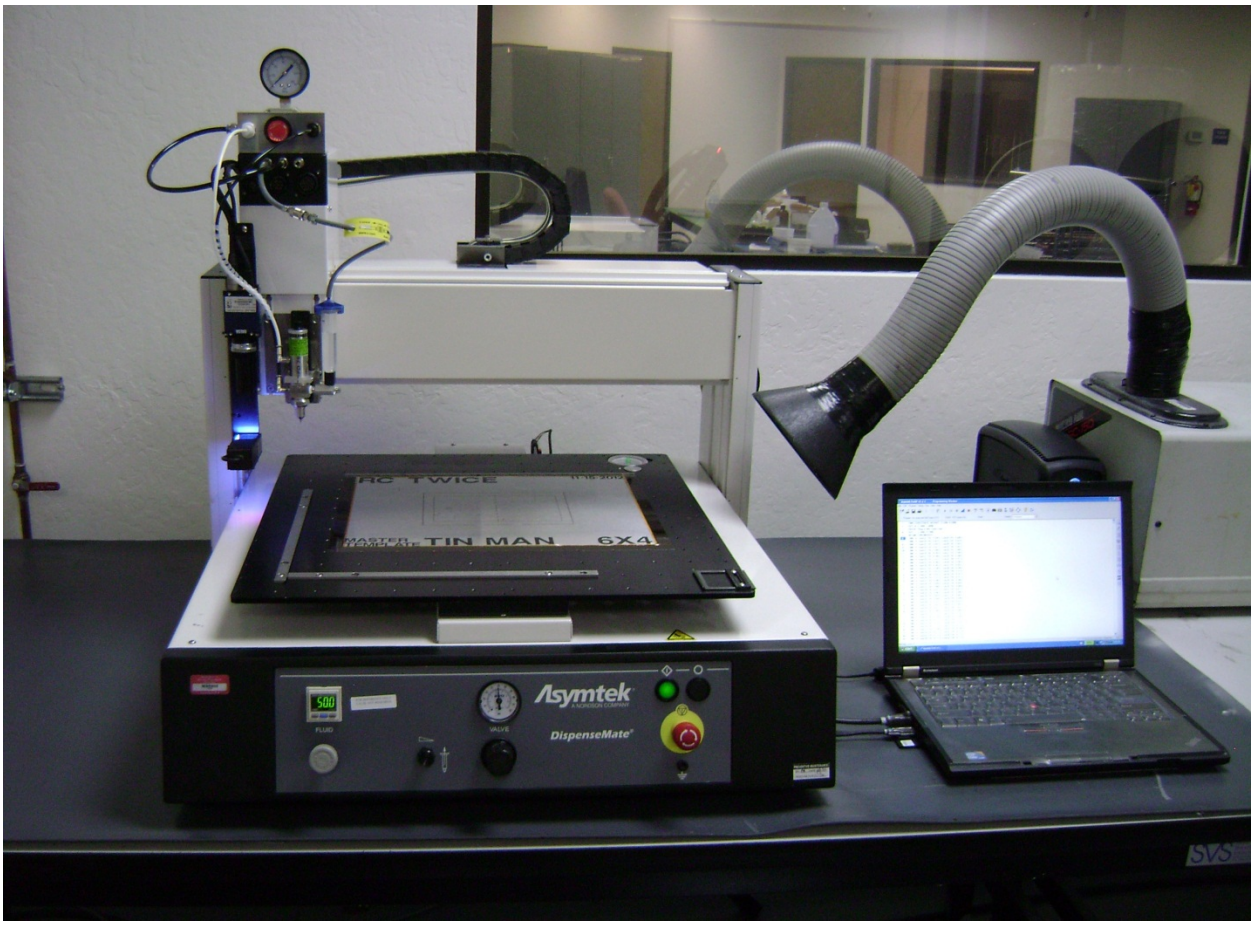
Image 3 Glass Slide (as masked)

Figure 1

The slides were coated on one side only; the coating encompassed the lower 2/3 of the glass slide (approximately a 50 mm x 25 mm area) with the remaining 1/3 masked to create the step height to be measured. The coated side was marked with a dot and/or indelible markings identifying the specifics details for each slide. The glass slides allowed for measurements to be taken which provided the nominal thickness of coating (excluding the random peaks associated with debris and/or large particles.

Automated ASG Application

The automated application of the ASG materials was adapted from the recommended Rockwell Collins processes which were provided to Plasma Ruggedized Solutions Inc. (PRS). An automated Asymtek DispenseMate® 585 dispense system was selected from PRS inventory and modified to spray the ASG materials using the original programs developed at Rockwell Collins **- HTC Spray PWB 6X4 5 Pass 10-15-12.fmw** - with an equivalent hardware configuration. The system format of the Asymtek DispenseMate® D-585 coating system is very similar to the Asymtek Spectrum S-820 utilized with the major difference in the D-585 system being a table top version without an enclosure.



Asymtek DispenseMate® D-585 with ASG Spray Configuration

Automated Dispensing Equipment

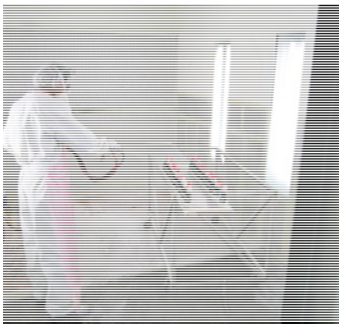
- Asymtek DispenseMate® D-585; S/N 31260 DOM 11/08
  - Running PC based Windows XP with Fluidmove® software.
  - Using an EFD 787MS-SS Micro Spray LVLP Precision Valve.
    - Utilizing an EFD 32 Gauge, 0.5 inch long Precision Dispense Tip, P/N 7024648.
    - Fed by an EFD 10 CC Barrel and adaptor.
    - Filtered by a CAMEO 0.22 micron x 1 inch diameter luer lock Nylon particulate filter.
  - Operating under Program Recipe HTC Spray PWB 6X4 5 Pass 10-15-12.fmw
    - 10 mil steps
    - 0.75 inch needle height
    - 5 inches per second travel speed
    - 0.5 psig nominal fluid (barrel) pressure. Note constant air pressure delivered by a remote dual stage filtered regulator system.
    - 15 psig nominal atomizing spray air (coax) pressure

        - 50 psig nominal valve pressure
        - 15 passes in total (program repeated 3 continuous cycles)
    - Residual vapor extraction provided by a Micro Air SC-150 HEPA fume extractor
- Test Vehicle Pre-treatment.
    - IPA cleaning followed by a 2 hour dehumidification bake at 77°C.
    - Plasma treatment; 3 minute etch cycle followed by a 5 minute oxygen clean cycle.
- ASG materials.
    - ASG 4A Combo mix A, September 05, 2013 and October 29, 2013 date of manufacture.
    - ASG 4A Combo mix A-Z, October 29, 2013 date of manufacture
- Final coating thickness: 2 microns.
- Cure: Air cure for one hour, followed by a 125°C bake for one hour.

Manual Acrylic Application

Humiseal 1B31 acrylic was applied to two of the five sets of test vehicles. The ASG material was applied first as a primer to one of the sets. Then the acrylic was applied using a manual spray application with a target thickness of 0.003” +/- 0.002”. Measured thickness of the acrylic averaged 1.8-2.0 mils.

DeVilbiss Model JGHV 531



Plasma Spray Booth

Semi-Automated Parylene Application/Deposition

Type C parylene coating was applied to 1 of the 5 sets of Test Vehicles during Phase 2 of the project utilizing a Model 494 vertical parylene vacuum deposition tool. Galentis GALXYL C parylene dimer was utilized to conformal coat the test vehicles at a nominal thickness of 0.001” (1 mil/25 microns). Measured thickness of the film was 0.00105” (1 mil/25.4 microns) +/- 0.00005” (0.05 mils/1.27 microns).

Parylene Machine

<u>Analysis</u>

Validation of thickness as measured from glass slide coupons.

Table 2

Run Description	Target Thickness	Thicknesses	Average Measured Thickness
Parylene C	0.001”nominal	Batch process; 0.00105”	0.00105”
Acrylic Humiseal 1B31	0.003”+/- 0.002”	0.002, 0.0015”	0.0018”
ASG 4A Combo Mix A + Humiseal 1B31 (Acrylic) Board #103-106	2 microns 0.003”+/- 0.002”	0.002, 0.002”	0.002”
ASG 4A Combo Mix A Board #87-94	2 microns (0.0000787”)	0.1, 0.2, 0.1, 0.1, 0.1, 0.1, 0.2, 0.1 mils	0.000125”
ASG 4A, Combo Mix A-Z Board #95-102	2 microns (0.0000787”)	0.1, 0.3, 0.2, 0.1, 0.15, 0.1, 0.1, 0.15	0.00015”

Observations

The automated process was typical of such coating process with respect to process methods and consistency. However, it took approximately 2 hours to coat a single side of one board.

In the initial setup, it was intended to filter the ASG inline while dispensing. This proved to be problematic as the filter clogged frequently. After several attempts to filter inline, the material was pre-filtered before loading it onto the dispensing machine.

The ASG 4A Combo Mix A-Z was preferred to the Combo Mix A because it remained fluid longer preventing spray head clogging and could be seen with the naked eye more easily, both during application and as a finished product. We believe that this is primarily a function of the length of time that it remained wet verses the Combo Mix A. It was an aid in processing to be able to see the coating as it was applied.

The cure schedule used on Phase 2 was a big improvement over the schedule in Phase 1. It was shorter and much more simplified.

Recommendations

1. Improve cycle time to apply material. For this process we were applying extreme thin layers in very controlled fashion. It would be advantageous to try other methods of application to see if it could be applied faster.
2. Address filter clogging. Is it possible to pre-filter all material in bulk or must the material be filtered just prior to application. Or is it possible to find another application method that does not require filtration at all?
3. To make the process more standard, modify the material to have a more conventional thickness (1/2 mil and up).
4. Inspection is difficult; a UV indicator would be helpful.

Acknowledgements and References

DoD SERDP

RC Rockwell Collins

AEP

Appendix 10: List of Scientific/Technical Publications

Conference and Symposium Proceedings:

1. D. D. Hillman, "Tin Whiskers Inorganic Coatings Evaluation (TWICE)", IPC Tin Whisker Conference, April 17-19, 2012, Fort Worth TX.
2. D.D. Hillman and R.K. Wilcoxon, "Tin Whiskers Inorganic Coatings Evaluation (TWICE)", Pb-Free Electronics Risk Management (PERM) Consortia Meeting #13, October 1-4, 2012, Melbourne, FL
3. D.D. Hillman, R.K. Wilcoxon, N.P Lower, D.E. Grossman, "Tin Whiskers Inorganic Coatings Evaluation (TWICE) Phase 1 Interim Report", WP SERDP Spring Interim Project Review (IPR), April 22-26, 2013, Arlington, VA
4. D.D. Hillman, R.K. Wilcoxon, N.P Lower, D.E. Grossman, "Tin Whiskers Inorganic Coatings Evaluation (TWICE)", IPC/CALCE 7th Tin Whisker Symposium, November 12-13, 2013, Costa Mesa, California 92627
5. D.D. Hillman, , "Tin Whiskers Inorganic Coatings Evaluation (TWICE) Phase I Results", Pb-Free Electronics Risk Management (PERM) Consortia Meeting #13, February 2014, hosted by NASA, Cape Canaveral, FL
6. D.D. Hillman, R.K. Wilcoxon, N.P Lower, D.E. Grossman, "Tin Whiskers Inorganic Coatings Evaluation (TWICE)", SMTA Upper Midwest Chapter Meeting, May 8, 2014 Brooklyn Park, MN 55445
7. D.D. Hillman, R.K. Wilcoxon, N.P Lower, D.E. Grossman, "Tin Whiskers Inorganic Coatings Evaluation (TWICE)", SMTA International 2014, September 28-October 2, 2014, Rosemont, IL 60018