SILVER AND SULFUR: CASE STUDIES, PHYSICS, AND POSSIBLE SOLUTIONS

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ABSTRACT

The reaction of silver platings to atmospheric sulfur has been documented for several decades, but the fundamentals as to its initiation are still poorly understood. This is aggravated by the general inconsistency observed when exposing silver platings to accelerated test conditions and the relatively long incubation period before issues are observed (12 to 48 months). Speculation has also been presented as to the influence of various potting materials and their ability to 'absorb' sulfur-containing gases. This talk will provide an overview of known silver sulfide corrosion failures, with examples for component (resistor), substrate, and printed board. The fundamentals of these case studies will provide a path for a discussion on the physics of this phenomenon, including how sulfur reacts with silver, how this reaction is influenced by humidity, temperature and other reactive gases, how classic corrosion behavior may accelerate this reaction, and how sulfur-containing gases may migrate through and be retained by polymeric materials. Only after an understanding of the observed field failure behavior and a comparison to the known science can possible corrective actions be reasonably identified and implemented.

Key words: Silver, sulfur, immersion silver, corrosion, sulfidation, Ag_2S, silver sulfide, mixed flowing gas, flowers of sulfur, hydrogen sulfide, H_2S, printed circuit boards, solderability platings

INTRODUCTION

The placement of silver on electronic components and products has always been a source of concern due to its tendency to migrate between isolated conductors and cause an unintended electrical short [1]. The migration of silver is driven by its propensity to undergo an oxidation reaction in the presence of moisture and an electric field [2]. This behavior has led to restrictions on the use of silver in some applications, additional test requirements [3,4], and alloying of silver electronic materials with more noble metals [5,6]. A more recent phenomenon of concern in regards to silver and electronics is the mechanism of sulfidation.

Sulfidation (aka sulfuration) is the corrosion of elemental metal (e.g., silver, copper, etc.) in the presence of sulfur compounds in a liquid or gaseous phase. It generally requires the presence of elevated levels of moisture. Sulfidation of silver has been around since antiquity and has been well-known in museum and conservation studies for decades [7,8,9].

The initiation of sulfidation is through the reduction of H_2S or COS to HS^-. In an aqueous solution, HS^- can then either react directly with silver ions that have oxidized or can they can absorb to the surface, subsequently reacting to form the sulfide salt. The presence of an oxidizing species, such as Cl, has been shown to increase the corrosion rate.

The principal product of the reaction of HS^- and silver is silver sulfide (Ag_2S), also known as acanthite. Acanthite is monoclinic and is one of three polymorphs of Ag_2S. The other two structures, body-centered cubic argentite and a face-centered cubic polymorph have not been observed in corrosion of silver by reduced sulfides.

CASE STUDIES: SULFUR CORROSION OF SILVER

The review and understanding of case studies is a classic problem solving approach in business education. In this section, four case studies of sulfidation of silver are presented as an introduction to this particular failure mechanism. By reviewing the particulars of each case study, including packaging configuration, material composition and morphology, environmental exposure, time to failure, and failure mode, insight into the drivers for sulfur attack and the valuation of potential corrective actions can be better understood.

Corrosion Behavior and Mixed Flowing Gas (MFG)

The first case study provides a baseline to the behavior of immersion silver when exposed to a standard mixed flowing gas (MFG) testing environment. In this case study, corrosion coupons plated with immersion silver were exposed to a Class II, mixed flowing gas environment. An image of the corrosion coupon is shown in Figure 1. The corrosion test coupon had no solder mask and consisted of two arrays. The first array, labeled A, consisted of 44 circular pads, 1.5 mm in diameter, spaced approximately 1 mm apart. The second array, labeled B, consisted of a cross-hatch pattern.
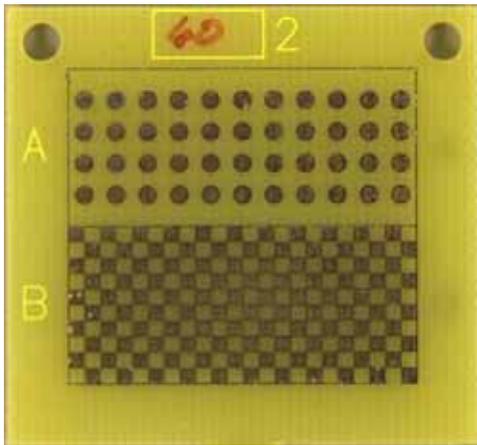
Figure 1: Photographic image of corrosion coupon plated with immersion silver

The purpose of a mixed flowing gas test is to simulate corrosion phenomenon due to atmospheric exposure. Development of the industry standard MFG test was initiated in the 1980's by researchers at Battelle Labs (Columbus, OH), who carried out tests on the use of MFG to accelerate atmospheric corrosion and its effect on electronic applications [10-14]. In the 1990's, professional organizations, including American Society for Testing and Material (ASTM), Electronic Industries Association (EIA), International Electrotechnical Commission (IEC), and Telcordia, began to standardize these test methods and published corresponding documents as guidelines. The EIA specification, EIA-364-TP65A, as seen in Table 1, was used in this experiment.

The operational environments for electronic equipments in atmosphere are divided into four classes, from least corrosive (Class I) to most corrosive (Class IV). Class I means well-controlled office environment with continuous adjustment. Class II means light industrial environment, such as business offices without effective or continuous environment control. Class III means moderate industrial environment, such as storage areas with poor environment control. Class IV means heavy industrial environment, such as locations adjacent to primary sources of atmospheric pollutant gases.

Since available data for Class I indicate no precedent for environmental effects on reliability, there is no accelerated testing for Class I. The other three classes use some combination of the four most common corrosive gases in the environment, NO_2, H_2S, Cl_2, and SO_2, to accelerate corrosion. The absence or presence of SO_2 under some of the conditions is due to the uncertainty of its effect above and beyond H_2S. Some researchers believe that H_2S and SO_2 have a synergistic effect on metal corrosion and SO_2 is necessary to stress nickel in corrosive environments.

Class	RH (%)	Temp (ºC)	H_2S (ppb)	Cl_2 (ppb)	NO_2 (ppb)	SO_2 (ppb)
I	----	----	----	----	----	----
II	70±2	30±2	10±5	10±3	200±50	----
IIA	70±2	30±1	10±5	10±3	200±50	100±20
III	75±2	30±2	100±20	20±5	200±50	----
IIIA	70±2	30±1	100±20	20±5	200±50	200±50
IV	75±2	40±2	200±20	30±5	200±50	----

Table 1: Gas concentrations for EIA MFG standards. IIA was the class used for the solderability testing

The corrosion coupons were subjected to a preconditioning consisting of two passes through a reflow oven and one pass through a wave solder machine. The parameters of the reflow profile were not provided. A total of 30 coupons were then exposed to 1, 2, 4, 6, 8, and 10 days of Class II conditions. Five coupons were exposed after each pre-defined period. The coupons were characterized for weight gain, surface insulation resistance (SIR), and visual appearance. The results for weight gain and SIR are displayed in Figure 2 and Figure 3, respectively.
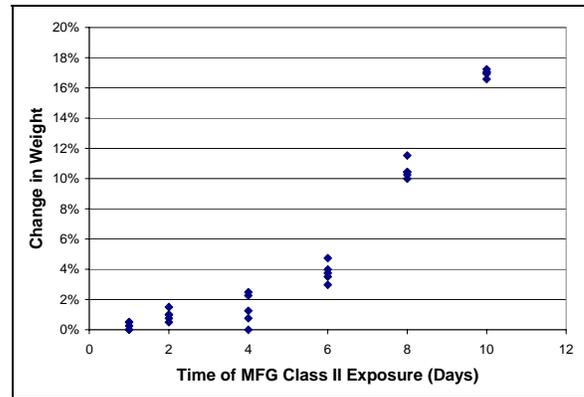
Figure 2: Weight gain of immersion silver coupons after exposure to Class II MFG environment
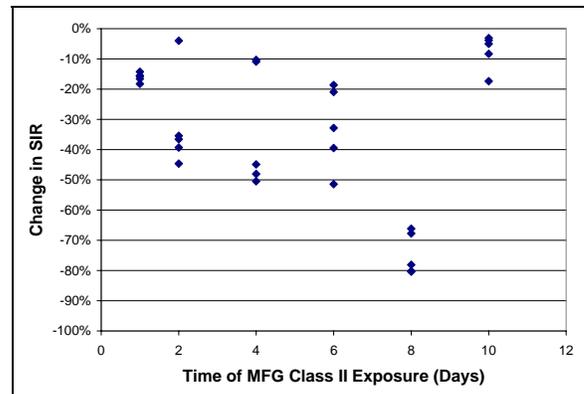
Figure 3: Change in surface insulation resistance (SIR) of immersion silver coupons after exposure to Class II MFG environment

The weight gain behavior shows strong evidence of chemical reaction, especially in comparison to baseline HASL coupons which gained less than a third as much. Weight gain behavior also seems to show a potential shift in the corrosion mechanism after 6 days of exposure. The change in SIR is much less definitive. Even though the magnitude of change is greater in comparison to weight, the absolute SIR value was still greater than 1×10^{12} ohms.

The results of post-exposure examination using optical and electron microscopy are shown in Figure 4 and Figure 5, respectively. The immersion silver turned a strong black after exposure to the mixed gas conditions. Elemental analysis using energy dispersive spectroscopy (EDS) identified both chlorine and sulfur, as well as silver and copper[1]. The presence of chlorine and sulfur would seem to suggest the formation of silver chloride (AgCl) and silver sulfide (Ag_2S) compounds. While silver chloride is initially white, when exposed to light it experiences a photoreduction process and disassociates into chlorine molecules and silver atoms. [15] The resulting metallic silver can have a gray-black appearance. Silver sulfide will also have a black appearance. Note that no corrosion products appear beyond the plating area.

Figure 4: Immersion silver coupons before (left) and after (right) eight days of exposure to Class II MFG conditions
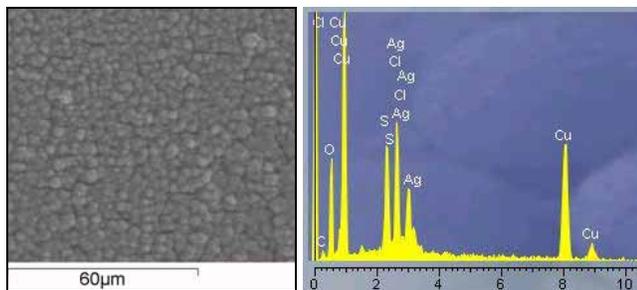
Figure 5: Electron micrograph (left) and elemental spectrum (right) of immersion silver coupon after eight days of exposure to Class II MFG conditions

Sulfur Attack of Silicone Encapsulated Hybrid Circuit
A silicone encapsulated ceramic hybrid (see Figure 6) used in an industrial control application was experiencing

elevated failure rates after approximately two to three years of operation in the field. Parametric characterization of inputs-outputs in failed devices identified elevated electrical resistance on several pins.

Figure 6: Photodocumentation of ceramic hybrid

X-ray of the encapsulated hybrid identified several disturbances or separations in the silver thick film traces (see Figure 7).
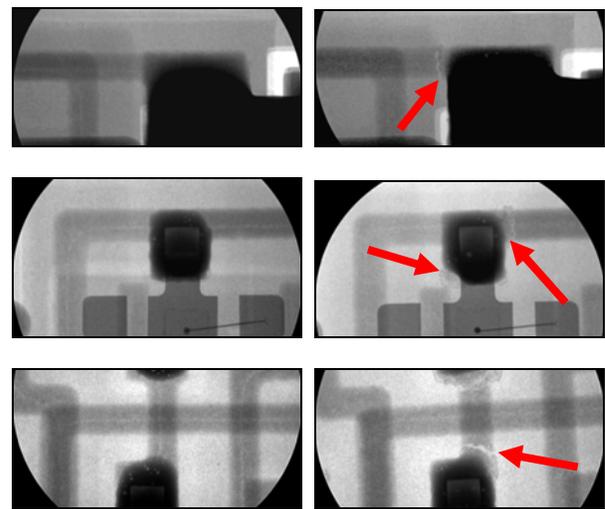
Figure 7: X-ray images of as-received (left) and failed (right) hybrids. Red arrows reveal separations/disruptions in the silver thick film circuit of the failed hybrid.

To better identify the root-cause of separation, the silicone encapsulant was removed using Dynasol. Visual inspection of the decapsulated hybrid revealed a black corrosion product throughout the ceramic substrate. The most severe reactions were areas where neither solder nor solder mask covered the silver thick film traces, though there was some indication of attack through the solder mask in some locations.

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[1] The presence of copper is not surprising as standard depth penetration of EDS is approximately 1 micron and the thickness of immersion silver can range from 0.05 to 1.25 microns.
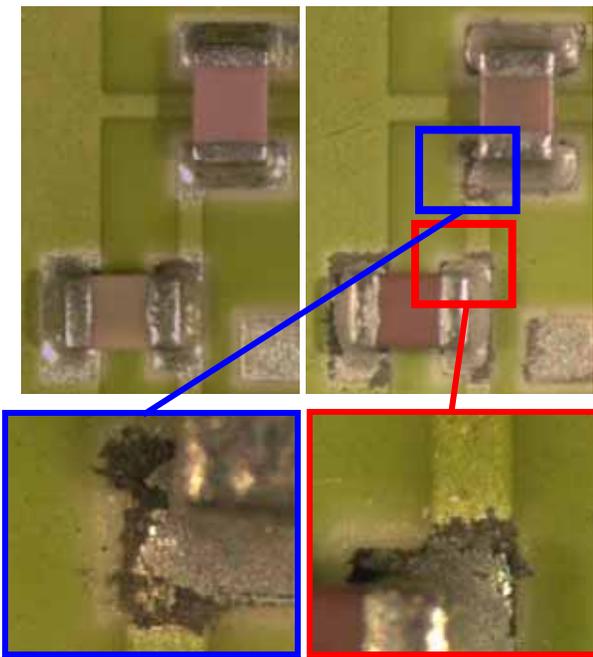
Figure 8: Optical micrographs of decapsulated as-received (left) and failed (right) hybrids.
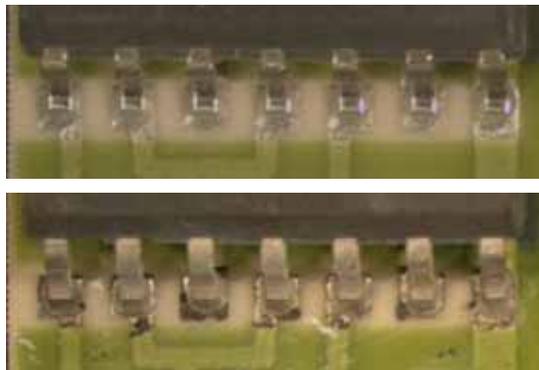
Figure 9: Optical micrographs of decapsulated as-received (top) and failed (bottom) hybrids.
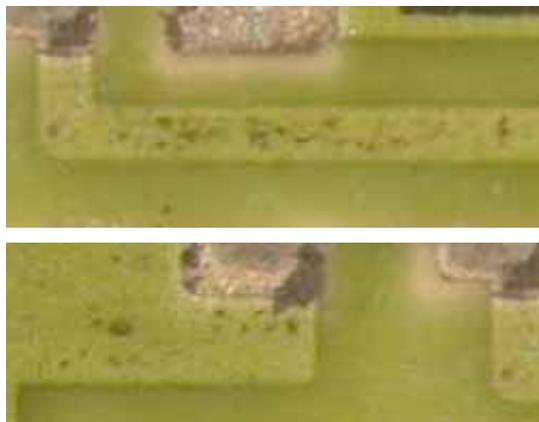
Figure 10: Optical micrographs showing potential corrosion product emanating through the solder mask.

Elemental analysis of the corrosion products identified strong sulfur and silver peaks (see Figure 11).
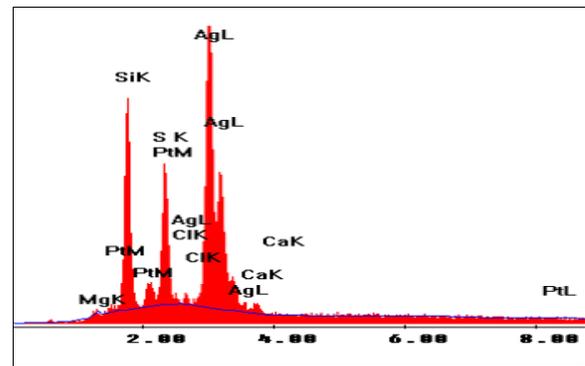
Figure 11: Elemental spectrum of corrosion products identified in ceramic hybrid

When the manufacturer of the hybrid was presented with evidence of sulfur-based corrosion, their corrective action was to a silicone coating under the silicone potting. The ability of this second coating to retard or prevent sulfur corrosion is uncertain. Silicone is a polymer that has an open structure (porous). Even with this open structure, silicone does not hold water due to its silicon chains. There for it is hydrophobic and making it an excellent choice for conformal coating. This basic open structure however allows other contaminates to penetrate it, such as sulfur-based gases.

Elevated Resistance of Surface Mount Resistors
The remaining two case studies provide more of an anecdotal review of the failure modes demonstrated by silver exposure to sulfurous environments as the authors were not directly involved in the experimentation or investigation of the corrosion behaviors.

Over the past several years, field issues have been reported in thick film chip resistors. These resistors use silver as the base conductor due to its relatively low cost, stable conductance, oxide resistance, and its compatibility with the resistor material, which is usually ruthenium oxide. In environments with high levels of sulfur-based gases, such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and carbonyl sulfide (COS), some users of thick film chip resistors have noted an increase in resistance over time and an eventual electrical open.

As seen in Figure 12, the sulfur-based compounds seem to attack the silver base conductor at the abutment of the glass passivation layer and the resistor termination. Cracks or openings in this location allow the ingress of corrosive gases, which react with the silver to form silver sulfide (Ag_2S).
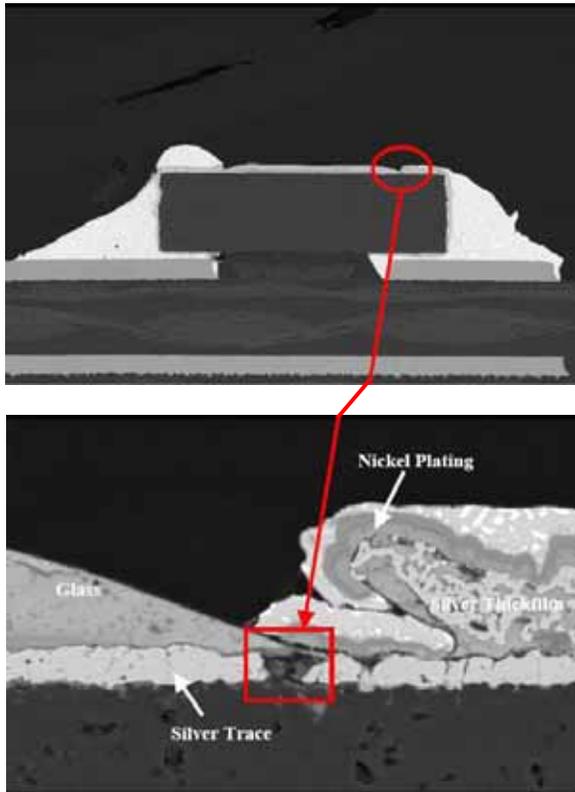
Figure 12: Electron micrographs of a cross-section of a thick film resistor that experienced sulfidation.

The nominal resistivity of silver sulfide is 0.1 to 10 ohm-m [16]. By comparison, the electrical resistivity of silver is 1.6 x 10^{-8} ohm-m [17]. Therefore, for the same geometric configuration, the resistance could theoretically increase by 7 to 10 orders of magnitude (for a very low resistance resistor). With a thickness and span of 10 microns and a width of 500 microns, the resistance across the silver sulfide reaction product would be approximately 20K ohms. If cracks initiate in the silver sulfide, the resistance could potentially be much higher.

Thick film resistor manufacturers are aware of this behavior and as a result do not recommend the use of commercial resistors in high sulfur environments. Instead, two options are offered. The first involves a sulfur "tolerant" design, which uses silver alloyed with precious metals. The second is the use of military qualified resistors, which are sulfur "resistant". The sulfur resistance is imparted through the use of a silver alternative, such as palladium or platinum.

This particular mode of sulfur corrosion of silver displayed two interesting behaviors. The first was the extended time period, one to four years, over which the failures initiated.

The second was the observation that a majority of failures seem to have occurred in assemblies that were encapsulated in silicone. Silicone potting compounds are typically used to insulate electronics from the harmful effects of the ambient environment, but in this situation there may be some

indication that the silicone structure acts as a 'sponge' for the sulfur-based gases. This behavior is not uncommon for gases and polymeric compounds and has been observed with water molecules and epoxy resins. In that situation, the water molecules can exist in the epoxy resin in two forms, bound and unbound. The bound molecules are attracted to the polymer chains through hydrogen bonding and become immobilized [18].

If this mechanism exists with H_2S or SO_2 and silicone, it may provide the gases time to react with the silver conductor. The sulfur-based gases may also undergo phase changes through reactions with moisture present in the silicone potting material and at the silicone-resistor interface.

Creepage Corrosion on Immersion Silver Plated PCBs
The final case study reviews recent field issues experienced on printed circuit boards (PCBs) plated with immersion silver. Users of these products reported faults within months of installation at field sites. Visual inspection of the failed units identified gray concentric circles emanating from plated through holes.
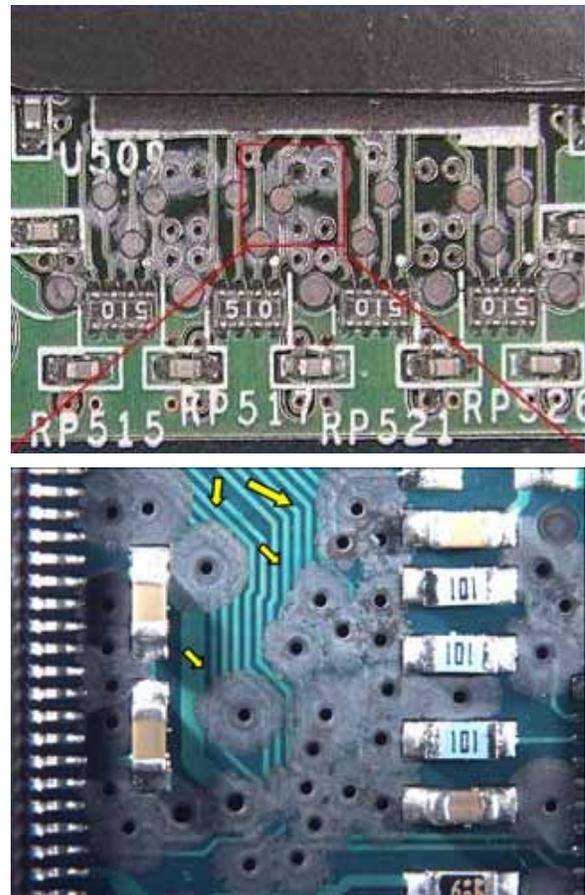
Figure 13: Photo-documentation of sulfur-based corrosion products on PCBs (source of top image: confidential; source of bottom image: ref. 19)

Corroded PCBs were identified in several locations with elevated levels of reducing sulfur-based gases, including

- Rubber manufacturing
- Sewage/waste-water treatment plants
- Vehicle exhaust fumes (exit / entrance ramps)
- Petroleum refineries
- Coal-generation power plants
- Paper mills
- Landfills
- Large-scale farms
- Automotive modeling studios
- Swamps

It is primarily this field behavior, along with resistor failures, that has recently drawn the interest of the electronics industry to silver-sulfur corrosion mechanisms and a desire to understand the fundamental drivers and relevant test strategies.

Creepage corrosion is a material transport mechanism that can occur in connectors, printed boards, and electronic components. The requirements for creepage corrosion to occur is a base metal (typically copper or silver), the presence of chlorine and sulfur-containing gases, elevated humidity levels, and a porous corrosion product (non-self limiting). The migration seems to occur when the force driven by the concentration gradient overcomes the 'attraction' forces on the surface. The force required has a lower threshold when migration occurs over a noble metal surface, such as palladium. The migration over dielectric/organic material is much more infrequent and seems to require exposure to severe environments, such as those with near-condensing humidity.

DISCUSSION OF CASE STUDIES
As mentioned at the beginning of this paper, a review of case studies can provide a foundation for understanding of silver-sulfur corrosion mechanisms. There are several contradictory and comparative behaviors among the four case studies that should be discussed.

Testing for Creepage Corrosion
The fourth case study identifies creepage corrosion of silver sulfide corrosion products as the root-cause of field issues. However, creepage behavior was not observed after exposing immersion silver corrosion coupons to Class II MFG tests for up to 10 days (see the first case study). The lack of creepage corrosion in the first case study is in direct conflict with results reported by Veale [20]. In his studies, immersion silver plated surface insulation resistance (SIR) coupons were subjected to a modified Class IIIA MFG and biased with 10VDC. The results are displayed in Figure 14.
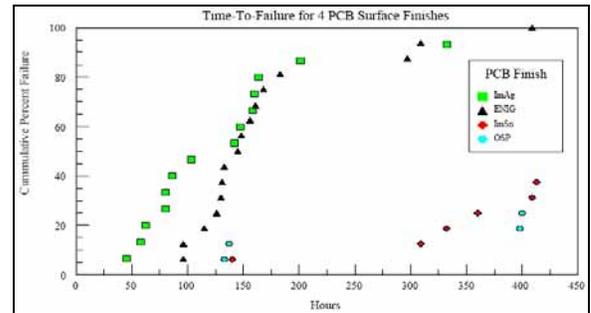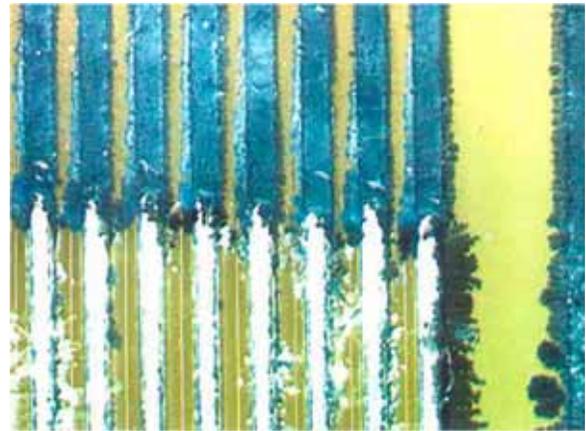
Figure 14: Visual (top) and insulation resistance (bottom) results from exposing immersion silver plated SIR coupons to MFG test conditions [20]

The corrosion behavior observed by Veale shows a strong correlation to the morphology seen in the fourth case study. This would seem to suggest that the Class II test condition in the first case study is insufficient for some use environments and Class IIIA may be more appropriate as a general qualification procedure. However, additional work in this area seems to indicate that none of the classifications in standard MFG testing may be insufficient to replicate the field behavior observed in the fourth case study.

Follow up work on the behaviors observed in Ref. 20 was unable to duplicate the extensive creepage corrosion originally reported [21]. This may suggest that one or more of the environmental parameters (gas concentrations, temperature, humidity, air flow) may have varied sufficiently to exceed the range specified by the industry body (i.e., EIA, ASTM, IEC, Telcordia). This type of test deviation has been observed in other studies. Cullen [22] recently demonstrated that elevated levels of relative humidity, exceeding 93%RH, were required to induce creepage corrosion.

A similar mechanism of creepage corrosion has also been investigated with components with palladium plated leadframes [23]. In this particular study, creepage corrosion behavior was found to be relatively independent of a wide variety of factors, including packaging material, lead spacing, lead material, mounted vs. unmounted, pitch, surface roughness, and various preconditioning steps. The

creepage of corrosion products over the epoxy packaging material primarily occurred when specified environmental parameters for Class III conditions were exceeded (>20 ppb Cl_2, >75%RH, >100 ppb H_2S). This limitation of creepage corrosion has also been observed by Texas Instruments in previous round robin studies [24].

These results would seem to suggest that the specified conditions in standard MFG tests, originally developed to accelerate <u>copper</u> corrosion, may not be sufficient to identify the field failures detailed in the second, third, and fourth case studies. In developing a more appropriate test for silver sulfide corrosion, a review of environmental parameters in regards to expected levels in field applications and their influence on silver-sulfide reactions and creepage corrosion may be appropriate.

Influence of Test Structures

Initial observations of field returns due to creepage of silver-sulfide corrosion products identified a unique design influence. Those annular rings that were solder mask defined (SMD) experienced creepage corrosion, while those annular rings not defined by solder mask were relatively corrosion-free (see Figure 15). Additional testing under accelerated conditions demonstrated that this phenomenon seems to simply delay the mechanism and non-solder mask defined (NSMD) silver-plated structures eventually experience corrosion behavior.
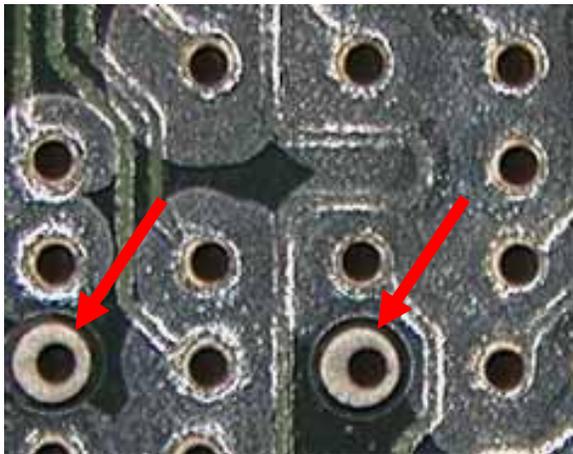
Figure 15: Optical micrograph of immersion silver plated PCBs returned from the field due to sulfur-based corrosion. The red arrows identify NSMD pads that have not experienced sulfidation

This solder mask specific dependence has been observed in similar corrosion mechanisms that initiated on the surface of a printed circuit board (PCB). As seen in Figure 16, corrosion products were observed emanating from the copper structures at the boundary of the solder mask. In this situation, the solderability plating is electroless nickel / immersion gold and the driver for the corrosion is the presence of plating residues on the surface of the PCB.

However, the morphology and coloration of the growths are very similar to the sulfidation of immersion silver.

Figure 16: Optical micrographs of corrosive growths observed on ENIG-plated PCBs

Additional characterization of the corrosion sites through cross-sectioning suggested crevice corrosion due to the loss of copper under the solder mask directly adjacent to the solder mask boundary (see Figure 17).

Figure 17: Optical micrograph of cross-section of ENIG-plated bond pad experiencing crevice corrosion

The preponderance of corrosion sites at the edge of the solder mask may suggest at least three potential mechanisms. As discussed in the case study on resistor failure, polymeric compounds can have a tendency act as a 'sponge' by binding gaseous constituents and accelerating corrosive behavior due to the presence of elevated levels of reducing sulfur-gases.

The second accelerating factor, as discussed above, may be crevice corrosion. Crevice corrosion is a highly aggressive form of corrosion that occurs in a corner or narrow gap between a metal and another material (metal, ceramic, polymer). While the exact mechanism in regards to immersion silver or copper foil is unknown, classic crevice corrosion is believed to be driven by the depletion of oxygen. This differential aeration can shift the micro-system within the crevice from cathodic to anodic and eventually induce a highly acidic solution.

The final accelerating factor is the entrapment of flux residues. These residues are acidic by nature. As with crevice corrosion, these residues may create a highly acidic solution that would accelerate most corrosion processes (its influence on the specific reaction of silver and sulfur is not well characterized).

Understanding the exact influence of solder mask can proscribe effective corrective actions. For example, binding of gaseous constituents is likely driven by cross-link density and free volume. Therefore, changes in epoxy formulation

could potentially reduce the concentration of reducing sulfur gases at surface sites. If crevice corrosion is identified as the primary driver, attempts to eliminate solder mask defined structures or the tenting or plugging of vias structures may be more effective.

MFG TEST CONDITIONS
For the purposes of this discussion, the primary environmental parameters within a MFG test are concentration of sulfur-based gases, relative humidity, and temperature. Understanding the relevancy of the current specifications and the potential need for modification requires a review of conditions in the field and an understanding of how the physics of the corrosion process changes with variation in these parameters.

Sulfur-Based Gases: Sulfur Dioxide (SO₂)
Information from the EPA on annual average concentrations of SO_2 are provided in Figure 18. The national standard is 30 ppb for SO_2. It can be seen that historically, the actual SO_2 concentration has been far less, with ranges from 2 to 19 ppb. This has decreased over time to the point that the 90 percentile value for SO_2 is less than 10 ppb. This is not the case for recently industrialized countries in East and Southeast Asia. Average outdoor levels in Asian 'Megacities' have been found to vary between 25 to 100 ppb, with short-term maximum values increasing those levels by a factor of 4 to 16 [25].
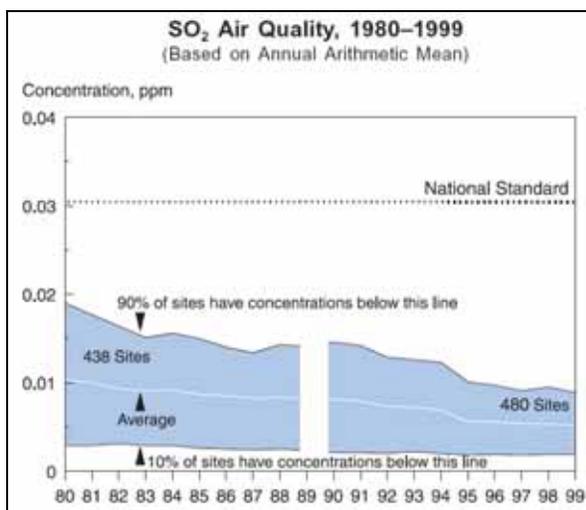
Figure 18: Latest Findings on National Air Quality: 1999 Status and Trends, Environmental Protection Agency (Office of Air Quality Planning and Standards) August 2000, Research Triangle Park NC 27711 EPA-454/F-00-002

While the average annual levels are approximately an order of magnitude below the test specifications, it is not uncommon in industrial environments for short term levels to be equivalent or higher than MFG concentrations. Purafil, a company that manufactures gas-phase air filtration equipment, used environmental reactivity coupons (ERCs), specially designed copper and silver sensors, to assess the concentrations of airborne contaminants in outdoor air used for ventilation in a hard drive manufacturing facility. The monitoring showed concentrations in the ranges of 10-100 ppb for sulfur oxides.

The 24-hour health-based National Ambient Air Quality Standard (NAAQS) for SO_2 is 140 ppb, but poor atmospheric mixing and air inversions can increase concentrations to higher levels. For example, continuous monitoring at a steam generation power plant found 24-hour SO_2 concentrations exceeding NAAQS levels several times over the calendar year, with maximum concentrations on the order of 600 ppb.

Since the MFG test is relatively short term in duration, ranging from 5 to 20 days, the 24 hour exposure limits and measurement maybe most applicable. This can be seen in Telcordia GR-63-CORE, which identifies outdoor levels of SO_2 for telecom equipment as 150 ppb [26], or roughly inline with the NAAQS specification.

While it is important to detail the correlation between field and test concentrations, the value of SO2 in regards to sulfidation of silver is limited. As demonstrated by Rice [39] and Graedel [27], the corrosion behavior of silver in mixed environments tends to be independent of SO2 concentration and exposure to single gas SO_2 tends to create a different corrosion product (H_2SO_4 as opposed to H_2S).

Sulfur-Based Gases: Hydrogen Sulfide (H₂S)
The standards for hydrogen sulfide tend to be based on its nuisance odor and its ability to cause nasal histological changes. The primary source of H_2S is farms and hydrocarbon processing plants. At the federal level, U.S. EPA does not currently classify hydrogen sulfide as either a criteria air pollutant or a Hazardous Air Pollutant (HAP). This prevents direct comparison with the numbers provided for SO_2. However, the U.S. EPA has developed a (chronic) Reference Concentration (RfC) of 0.8 ppb (1 $\mu g/m^3$) for hydrogen sulfide (USEPA, 1999). This is roughly inline with the nominal indoor level of 0.3 ppb proscribed by Graedel [28] and 0.05 – 0.6 ppb measured by Ankersmit [29], but a factor of five below the IEC environmental guidelines [30] for controlled environments (see Figure 19), and a factor of 50 below the levels identified in Telcordia GR-63-CORE [26].

	Clean room	Controlled environment	Rural	Urban with heavy traffic or industrial	Adjacent to industrial	Inside industrial
SO2	100	100	100	1000	10000	40000
	38	38	38	380	3800	15300
H2S	1.5	10	10	500	10000	70000
	0.6	4	4	200	4075	28500

Figure 19: IEC classifications for chemically active substances (top value is ug/m³; bottom value is ppb)

As with SO_2, the long term background level is approximately an order of magnitude below the

concentrations provided in the EIA MFG IIA test. This deviation is not always the case near industrial sites. A study by the Massachusetts Department of Environmental Protection [31] identified several residential sites adjacent to a city landfill that would experience H_2S concentrations exceeding 30 ppb for 80 to 100 hours per year. These levels are more along the lines of MFG Class III test conditions.

Most standards on exposure to H_2S are set by the states. The current California Ambient Air Quality Standard (CAAQS) from the California Office of Environmental Health Hazard Assessment (OEHHA) for hydrogen sulfide is 30 ppb, (42 $\mu g/m^3$) for one hour. OEHHA (2000) also adopted a lower level of 8 ppb (10 $\mu g/m^3$) as the chronic Reference Exposure Level (cREL). North Dakota has implemented a slightly less strict standard of 200 ppb for 1 hour of exposure, 100 ppb for 24 hours of exposure, and 20 ppb for 3 months of exposure. The Pennsylvania ambient air quality standards set by the Department of Environmental Protection (DEP) for hydrogen sulfide are 100 parts per billion (ppb) for a one-hour period and 5 ppb averaged over 24 hours.

These standards are maximum values that should not be exceeded and are primarily designed for sites *outside* the manufacturing facility. Within the facility, the Occupational Safety and Health Administration (OSHA), which regulates hydrogen sulfide in the workplace, established an acceptable ceiling concentration of 20,000 ppb for hydrogen sulfide [32]. The Agency for Toxic Substances and Disease Registry (ATSDR) also provides guidance on estimated hydrogen sulfide exposure levels which pose minimal risk to human health (Minimal Risk Levels or MRLs). ATSDR's acute MRL is currently set at 500 ppb, which means 24-hour daily human exposure at a level of 500 ppb over a period of 14 days or less.

H2S concentrations are critical in the sulfidation reaction of exposed silver. As seen in Figure 20, material changes in silver during exposure to H2S displays a linear behavior and a strong dependence on H2S concentration.
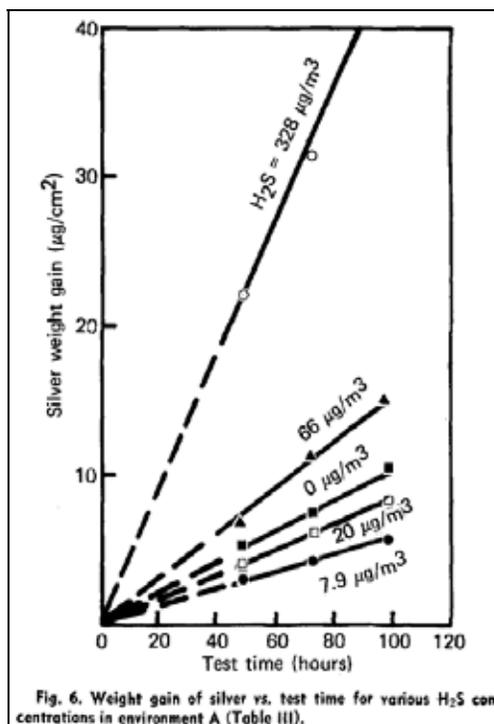
Fig. 6. Weight gain of silver vs. test time for various H_2S concentrations in environment A (Table III).

Figure 20: Weight gain of silver as a function of H2S concentration [41]

Sulfur-Based Gases: Carbonyl Sulfide (COS)
One of the reducing sulfur-based gases not proscribed in the MFG test environment is carbonyl sulfide (COS). COS is considered a major sulfur compound because it is naturally present in the atmosphere at levels similar or exceeding [**Error! Bookmark not defined.**] H2S concentrations (0.5 to 0.8 ppb). Levels as high as 80 ppb have been reported near natural sources [33].

COS can also be as corrosive as H_2S in regards to its reaction with silver. As shown in Figure 21, COS induces approximately the same rate of corrosion product generation as H_2S as a function of total exposure.
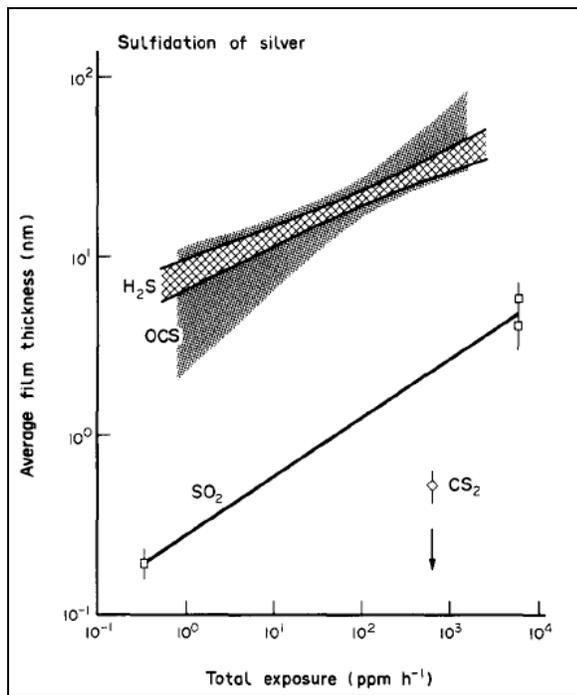
Figure 21: The thickness of Ag2S corrosion film as a function of total exposure to H2S, OCS, SO2 and CS2, All exposures were made with RH = 92 ± 4%, t = 21 °C [34].

Sulfur-Based Gases: Summary
Concentrations prescribed by EIA's class II MFG test are consistently an order of magnitude higher than background concentrations measured by a variety of governmental organizations. However, areas in and around industrial locations, including light and heavy industry, can experience gas concentrations inline or higher than any of the MFG Class specifications, with some levels in the ppm range [19,32].

Indoor levels of sulfur-based gases, where electronics are expected to operate, require more comprehensive and thorough measurements, especially considering that some studies have identified elevated levels of corrosive gases [25,32] and an accelerated silver-sulfur corrosion process compared to outdoor environments [34,35].

Relative Humidity
The influence of relative humidity on the corrosion of silver when exposed to reducing sulfurous gases is and somewhat contradictory. Vernon [36] demonstrated a critical relative humidity, above which the corrosion rate is rapid because of substantial acquisition of moisture by the metal surface. For most metals, Vernon identified the critical relative humidity as in the range of 70 to 80%.

Vernon's viewpoint is slightly modified by comments by Graedel [28], who stated that silver corrosion increases with increasing relative humidity, based on the work by Sharma [37], Volpe [38], Franey [39], and Lorenzen [40]. Graedel seems to imply that this relationship is driven by the amount

of adsorbed moisture on the silver surface, which is given in monolayers as

$$\ln (ml) = 2.73 \ p/p_0 - 0.366$$

where ml is the number of monolayers of water adsorbed on the silver surface and p/p_0 is the relative humidity.

Rice reported no influence of relative humidity on the corrosion rate of silver in two different mixed flowing gas environments [41]. This observation is supported by work performed by Reagor [42] (see Figure 23) and Leygraf and Graedel [41], who state that the higher corrosion rate of silver indoors is due to its independence to relative humidity levels.

Sinclair [43] provides some nuance to this argument by demonstrating similar reaction rates in environments with high and low relative humidity until the silver sulfide film reaches approximately 60 nm thickness.
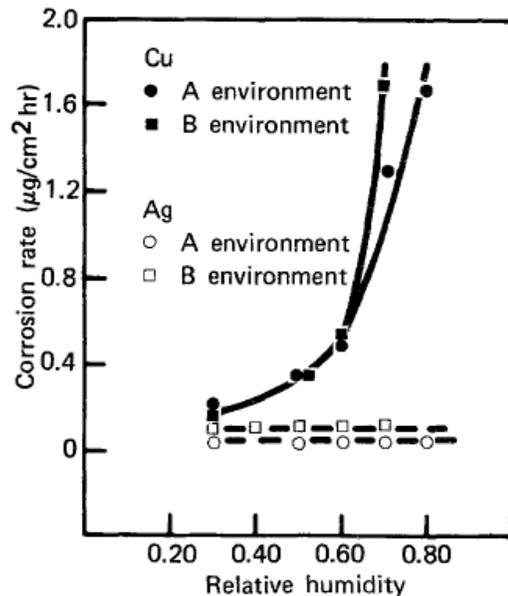
Figure 22: Corrosion rates of copper and silver as function of relative humidity during exposure to A (810 ug/m3 SO2, 940 ug/m3 NO2, 334 ug/m3 O3, 8.5 ug/m3 Cl2, 21 ug/m3 H2S) and B (860 ug/m3 SO2, 990 ug/m3 NO2, 8.5 ug/m3 Cl2, 17 ug/m3 HCl, 54 ug/m3 H2S) environments [41].
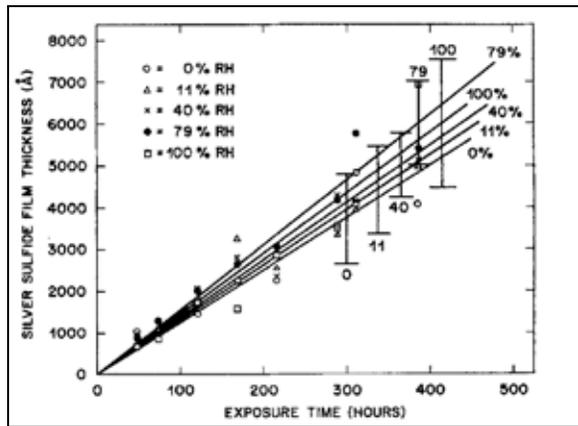
Figure 23: Thickness of silver sulfide film as a function of relative humidity [42]

The correct prediction of humidity's influence is somewhat dependent upon the exact corrosion mechanism that is being described. Based on a review of the case studies detailed in this paper, the reaction of reducing sulfur gases with silver is likely independent of relative humidity. The humidity levels inside the ceramic hybrid and thick film resistor encapsulated with silicone potting compound is likely to be low due to the hydrophobic nature of silicone. This did not prevent sulfidation from occurring, though the extensive time required for failure to occur (1 to 4 years) may be an indication of some influence of moisture.

However, relative humidity will play a critical role in the occurrence of creepage corrosion. As seen in the work by Cullen [22] and prior work on creepage corrosion over epoxy encapsulants, very high humidity (>80%RH) is required to induce creepage corrosion. It is conjectured that the rough surface of the polymeric material becomes conducive to material transport once micro-condensation within occurs. This 'filling-in' of surface pores may greatly reduce the adhesion of the polymer surface and allow the forces created by volumetric expansion of corrosion product to 'push' the growth out to an adjacent conductor.

Conclusion: MFG Test Conditions for Sulfidation of Silver

Based on the body of evidence to date, there is strong need to review existing MFG test specifications to determine their relevancy for silver-based corrosion mechanisms, specifically in a reducing sulfur environment. Future versions of silver-oriented MFG testing may wish to eliminate SO2 gases, increase H2S gas concentrations to potential maximum levels encountered in indoor and outdoor environments (> 200 ppb), and consider the introduction of organic sulfur compounds, such as carbonyl sulfide.

In addition, the reduction or elimination of chlorine gas should also be considered. As far back as 25 years ago, Rice [41] theorized that the presence of an AgCl surface product may inhibit sulfidation of silver. More recent work by

Dubus [44] demonstrated that in environments with elevated levels of chlorine gas, relative to sulfur-based gases, the corrosion behavior is dominated by the formation of AgCl, which follows a parabolic corrosion law. This time-dependent behavior, indicates that the corrosion rate is limited by the diffusion of chlorine through the film, resulting in the formation of a fully protective corrosion layer.

By comparison, silver in environments with elevated levels of reducing sulfur-gases shows a linear behavior, suggesting unlimited growth potential (the type of behavior required for creepage corrosion).
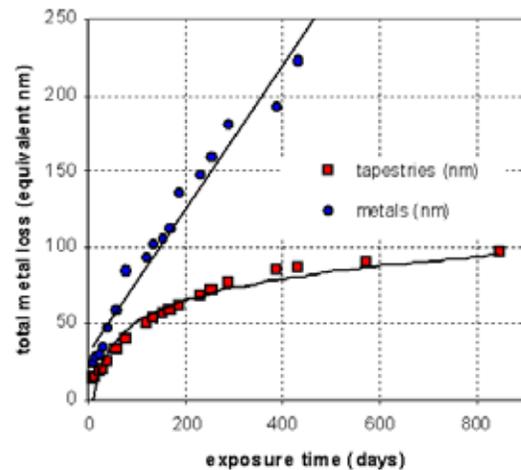
Figure 24: Corrosion rate of silver as a function of exposure time and ambient environment (tapestries had elevated levels of Cl2; metals had elevated levels of H2S)[44]

Finally, the humidity levels can be maintained or even lowered for investigations into sulfur attack on encapsulated components, but will likely have to be increased to levels equivalent to standard industry temperature / humidity / bias (THB) testing (>90%RH) to replicate the creepage corrosion observed in fielded immersion silver plated PCBs.

CONCLUSION

The industry has a strong need to gather additional information on the phenomenon of sulfur-based corrosion of silver in electronic components and assemblies and identify tools and techniques to prevent these mechanisms from inducing failure at the customer site.

Questions that remain to be answered include

- What is the interdependence of %RH, and sulfur gas concentration in regards to the preponderance for creepage corrosion? E.g., does a higher %RH allow for a lower critical H2S concentration?
- What are the influence of surface contaminants (hygroscopic, sources of chlorine, various acids) in terms of concentration and activity?

- Why were the organic inhibitors added to immersion silver to resist tarnishing unable to prevent creepage corrosion?
- Is there a critical sulfur-based gas concentration limit, below which these reactions will not occur?
- Would this critical gas concentration vary as a function of other gases, temperature, or relative humidity?
- What is the role of silicone potting compounds and epoxy solder mask on sulfidation and creepage corrosion?
- What is the potential role of board design and manufacturing processes?
- Is there a test to identify if this is a problem for my products?
- How can this mechanism be prevented in future products with exposed silver metal?

The last two questions provide an opening to investigate potential solutions to this problem. Anti-tarnishing agents for silver have been around for some time [45], but their compatibility with solderability requirements may require some improvement [22]. An alternate approach is to alloy the silver with palladium. Prior work has demonstrated that approximately 15% is sufficient to greatly retard silver migration. However, cost and chemistry considerations would still need to be resolved.

Potential modifications to the existing MFG test specification for better correlation to sulfidation of silver have been proposed. While modification of the MFG test should be feasible, use of single gas tests, such as the Humid Sulfur Test (Flowers of Sulfur; 3ppm H2S, 40-50C, 90-95%RH), should be taken cautiously. Prior work in these environments tended to induce sulfur whiskers, which is not the morphology observed on any of the field case studies. This may indicate that this test condition is not representative of field environments. In addition, the Humid Sulfur Test may have very low acceleration factors.

A resistor manufacturer introduced Humid Sulfur testing to demonstrate the resistance to sulfidation of its reformulated chip resistors. Failures in the 'non-improved' discrete components occurred after 4500 hours (approximately 6 months). Given a time to failure in the field of 1 to 4 years, this produces an approximate acceleration factor of 2 to 8. This is likely insufficient for a viable accelerated life test.

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