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Silver and Sulfur: Case Studies, Physics, and Possible Solutions

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Introduction

- Silver is a common metal in electronics
  - Along with gold, copper, and solder
- Tendency to migrate
  - Driven by oxidation behavior in presence of moisture + bias

- Industry response
  - Additional test requirements
  - Alloying with noble metals (Ag + Pd)
- Concerns with sulfidation a more recent phenomenon

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Silver Sulfidation

- Also known as sulfuration
  - Well known in museum and conservation studies
- Initiates through the reduction of hydrogen sulfide (H_2S) or carbonyl sulfide (COS) to HS-
- Two potential subsequent reactions in an aqueous solution
  - HS- can react directly with silver ions that have oxidized
  - HS- can absorb to the surface, reacting to form a sulfide salt
- Presence of oxidizing species (i.e., Cl) can increase corrosion rate
- Principal product of HS- and silver is silver sulfide (Ag2S)
  - Also known as acanthite (monoclinic)

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Case Studies

- Classic problem-solving approach in business education
- Four case studies of sulfidation of silver
  - Corrosion Behavior and Mixed Flowing Gas (MFG)
  - Sulfur Attack of Silicone Encapsulated Hybrid Circuit
  - Elevated Resistance of Surface Mount Resistors
  - Creepage Corrosion on Immersion Silver Plated PCBs
- Provides a path for discussion of physics of this mechanism
  - Initial reaction, influence of environment, etc.

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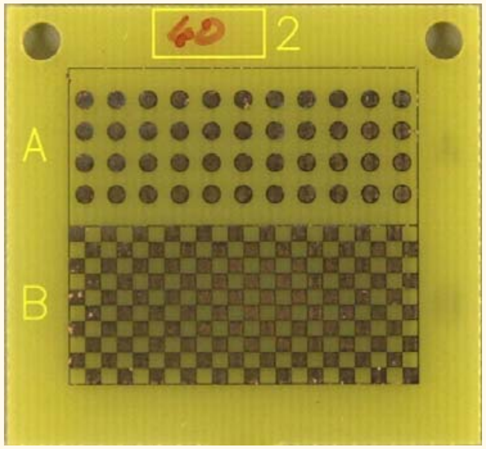
Corrosion Behavior and MFG

- Corrosion coupon plated with immersion silver
  - No solder mask
  - Two arrays
- Preconditioning
  - 2X Reflow
  - 1X Wave
- 30 coupons
  - Up to 10 days exposure



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	----

Gas concentrations for EIA MFG standards. IIA was used for the solderability testing

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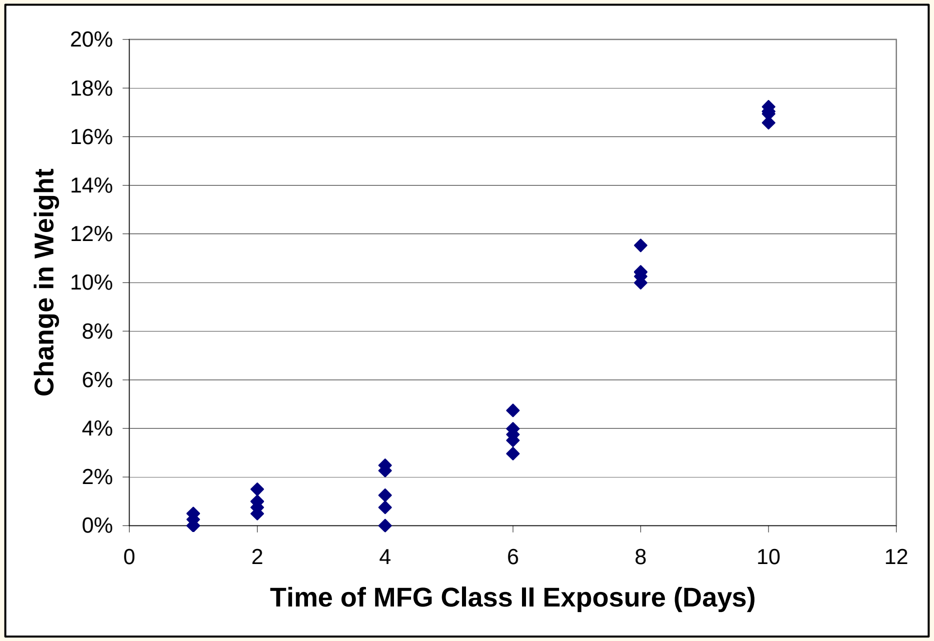
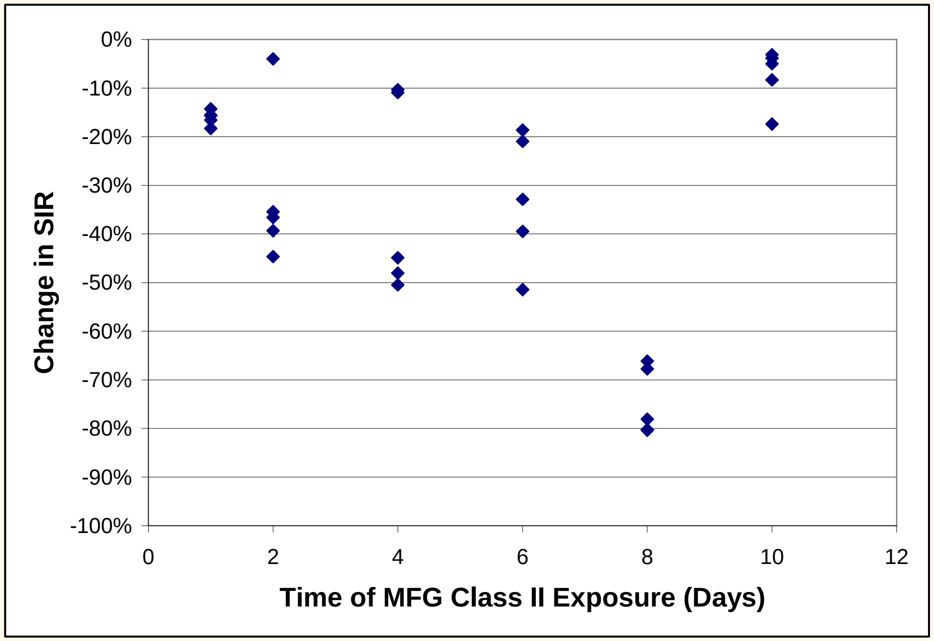
Results

Weight Gain



Change in Surface Insulation Resistance (SIR)



- Weight gain provides strong evidence of chemical reaction
  - 3X weight gain compared to SnPb HASL coupons
- Change in SIR likely due to moisture absorption
  - Absolute SIR still above 1 x 10^{12} ohms

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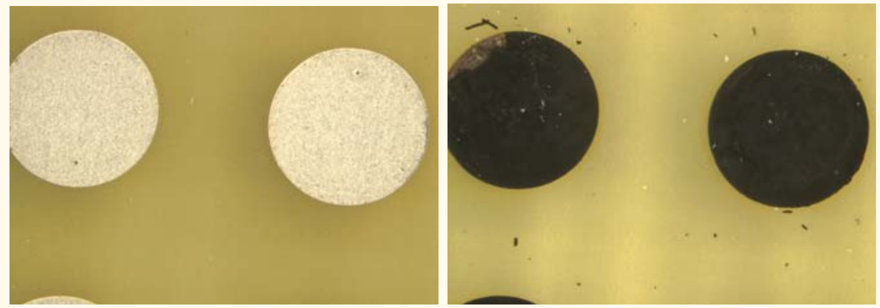
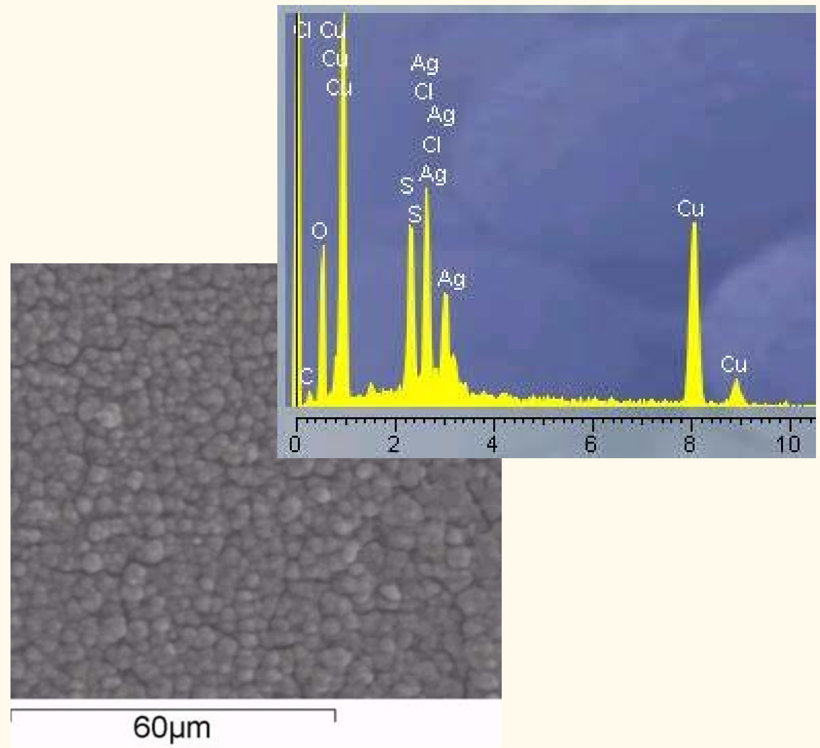
Results (cont.)

- Strong black color change after exposure
  - Consistent with sulfidation
  - Ag2S is black
- Detection of chloride and sulfide
  - Could suggest presence of AgCl
- AgCl is white, but exposure to light can cause disassociation into chlorine and silver
  - Metallic silver is gray-black
- Note: No migration products





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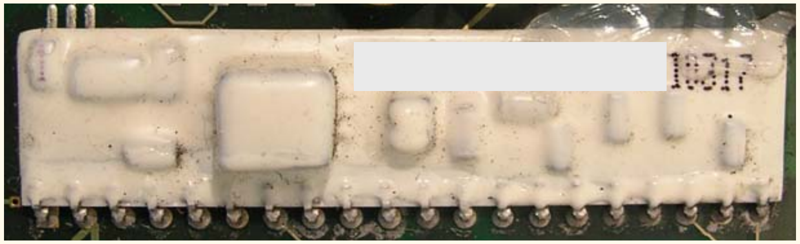
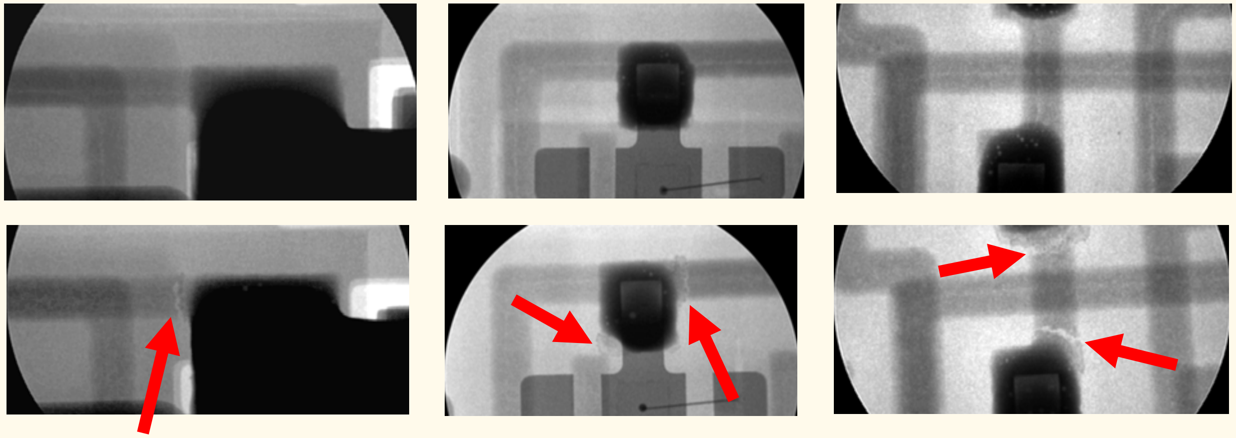
Sulfur Attack of Encapsulated Hybrid

- Silicone encapsulant, ceramic hybrid
- Used in industrial controls
- Customer reported failures after 12 to 36 months in the field
- X-ray identified several separations



'Good' hybrid

'Bad' hybrid



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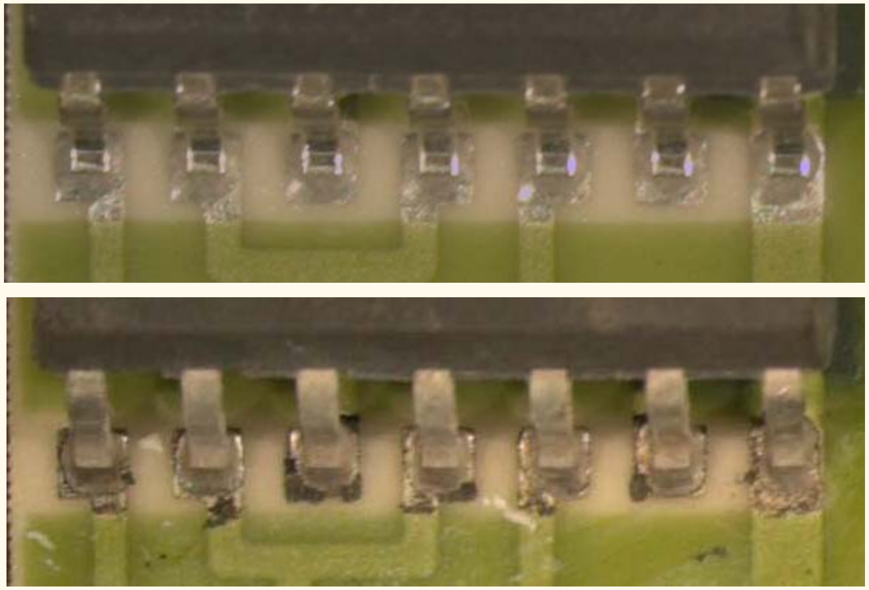
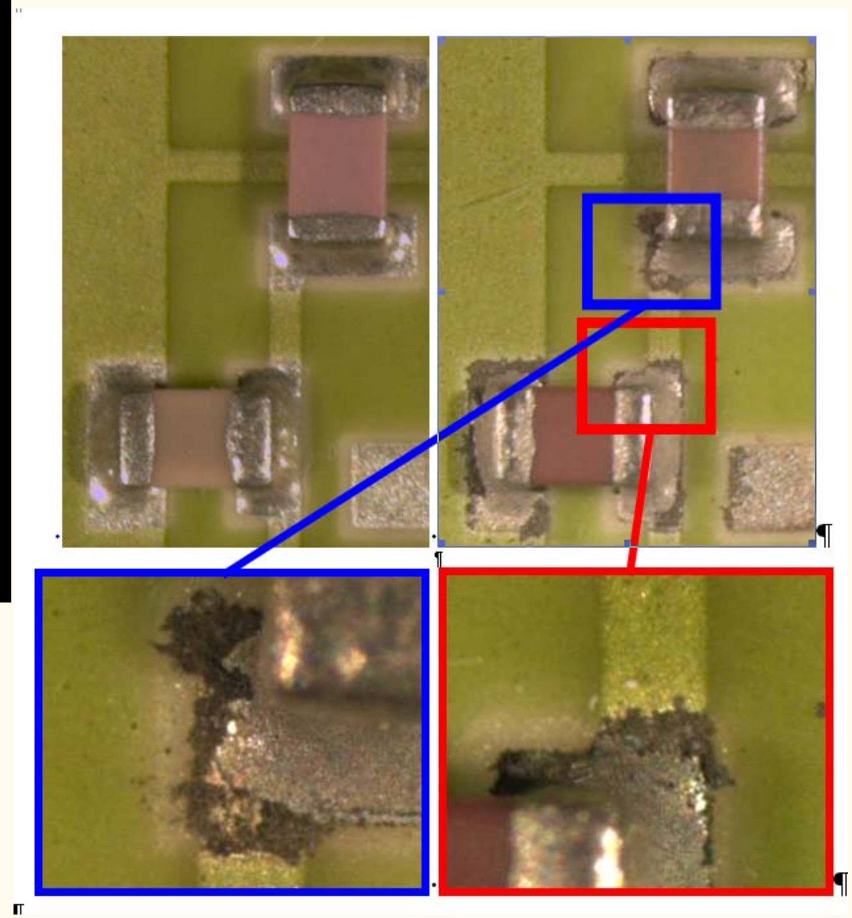
Encapsulated Hybrid (cont.)

- Silicone encapsulant was removed using Dynasol
- Visual inspection revealed black corrosion product throughout the hybrid
  - Most severe in areas with no solder or solder mask covering silver thick film traces
  - Attack through the solder mask in some locations

Sulfur Corrosion Sites





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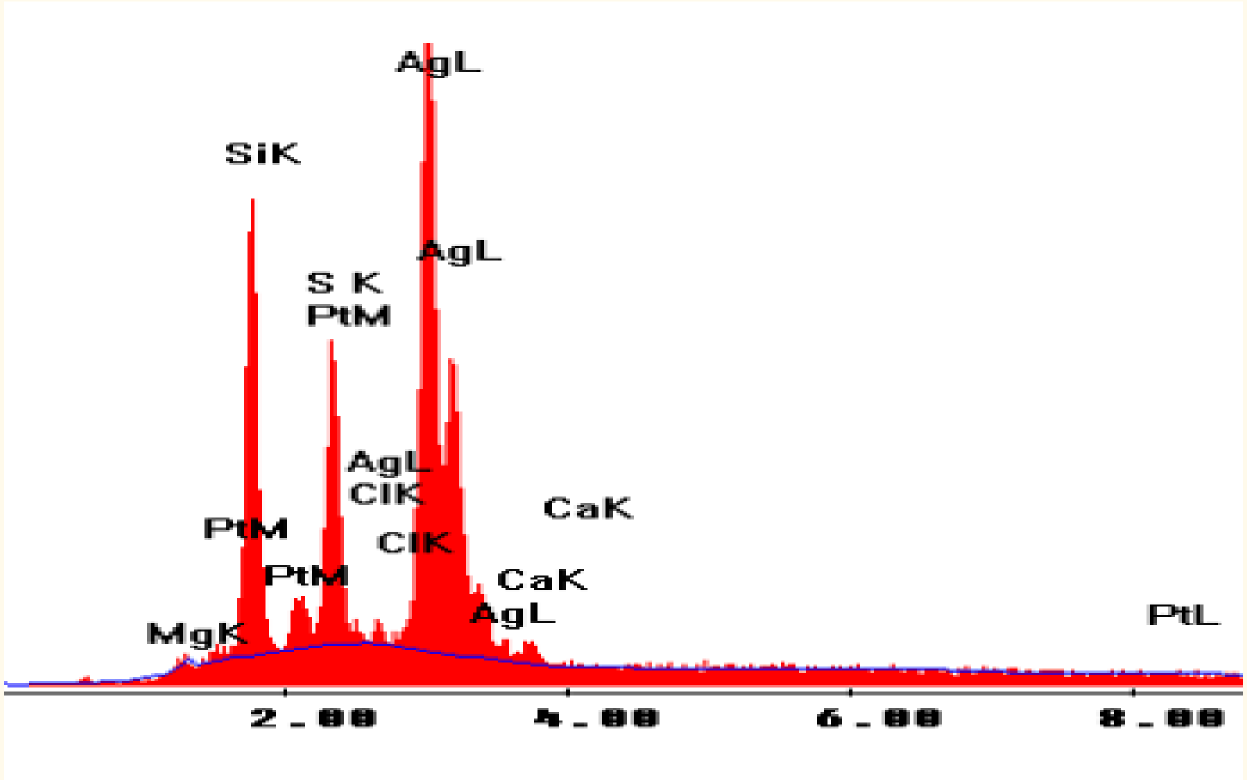
Elemental Analysis



- Sulfur and silver peaks detected
- Note: No migration products were observed

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Corrective Actions

- Manufacturer added a silicone coating under the silicone potting
  - Will this help?
- Possibly
  - Corrosion primarily occurred in areas where silver thick film traces were exposed
  - Additional coating should slow the reaction sufficiently to provide desired lifetime
- Silicone potting was not successful in preventing sulfidation
  - Silicone coating will have the same open structure (porous)
  - Could allow penetration of corrosive gases (e.g., H_2S)

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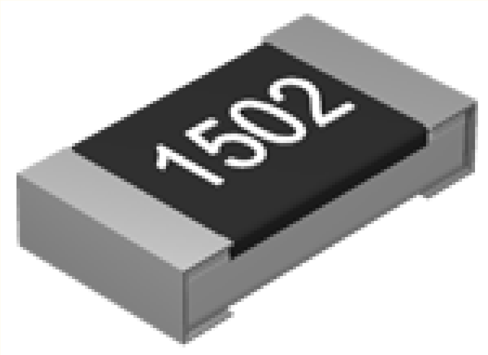
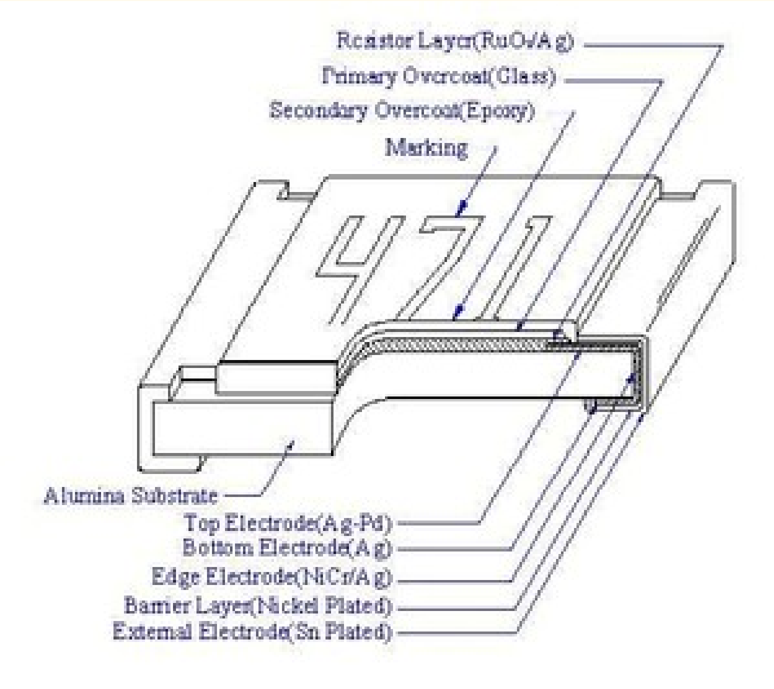
Elevated Resistance of SMT Resistors

- Several field issues reported in thick film resistors
  - Use silver as the base conductor (cost, stability, oxide resistance, compatibility with ruthenium oxide)
- Failures reported in environments with high levels of sulfur-based gases
  - E.g., hydrogen sulfide (H2S), sulfur dioxide (SO2), and carbonyl sulfide (COS),
  - Failure mode is increasing resistance (electrical open)





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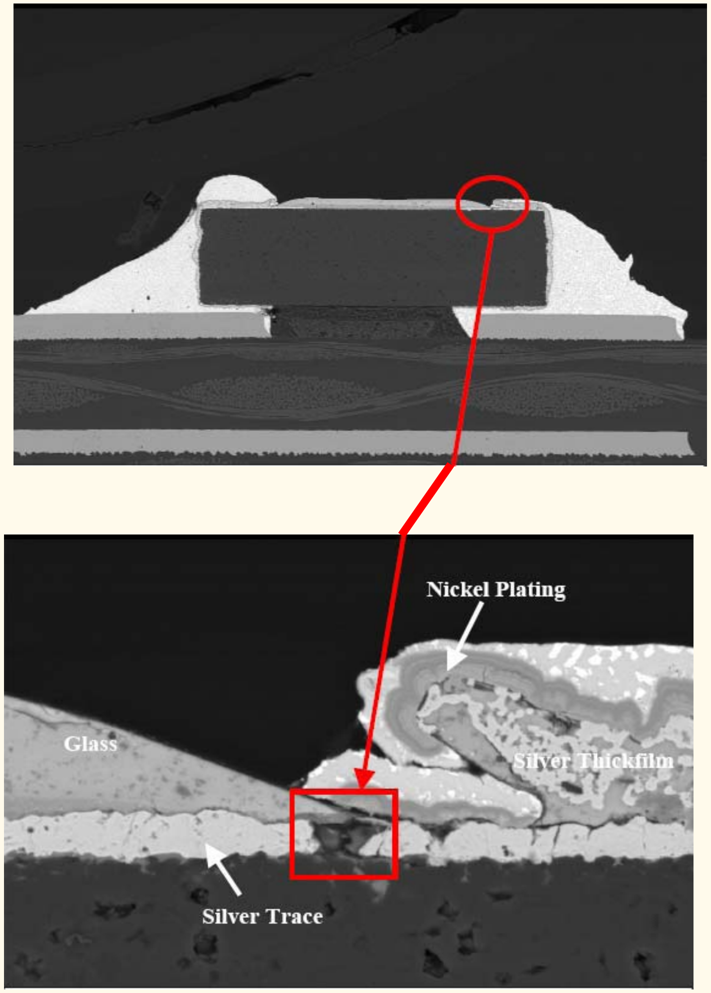
SMT Resistors (cont.)

- Sulfur attack of silver occurs at the abutment of the glass passivation layer and the resistor termination
  - Cracks or openings can allow the ingress of corrosive gases,
  - Reaction with the silver to form silver sulfide (Ag2S)
- Large change in resistance
  - ρ_{Ag} = 10^{-8} ohm-m;
ρ_{Ag2S} = 10 ohm-m
  - Up 20K ohms (0.01 x 0.01 x 0.5mm)
- Manufacturers' solutions
  - Sulfur tolerant – silver alloys
  - Sulfur resistant – silver replacement



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SMT Resistors (Observations)

- This mode of sulfur corrosion displayed two interesting behaviors.
- First: Extended time to failure (1 - 4 years)
- Second: Observation that a majority of failures occurred in assemblies that were encapsulated in silicone
  - Silicone structure could act as a ‘sponge’ for sulfur-based gases.
  - Behavior is not uncommon for gases and polymeric compounds; observed with water molecules and epoxy resins
- In epoxies, water can exist in two forms (bound and unbound)
  - Bound molecules are attracted to the polymer chains through hydrogen bonding and become immobilized.
- If ‘bounding’ exists with H2S or SO2 and silicone, it may provide the gases time to react with the silver conductor
  - Alternate theory: Presence of moisture and H2S / SO2 in silicone create aggressive chemistry

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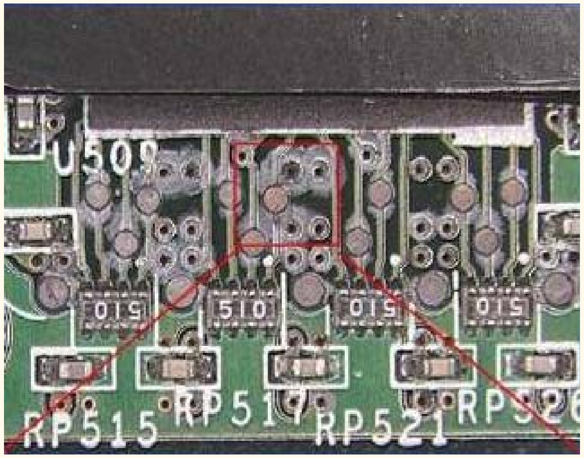
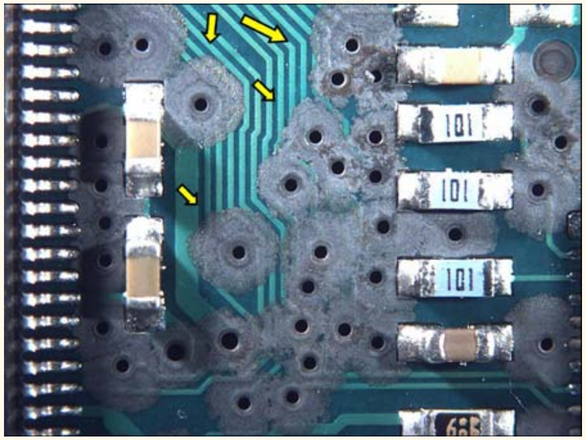
Corrosion of Immersion Silver

- Recent field issues with printed circuit boards (PCBs) plated with immersion silver
  - Sulfur-based creepage corrosion
- Failures in customer locations with elevated levels of sulfur-based gases
  - 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





P. Mazurkiewicz , ISTFA 2006

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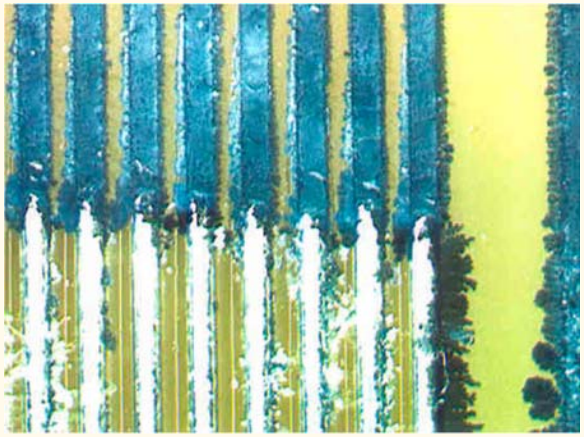
Case Study Discussion (Creepage Corrosion)

- Creepage in field
- No creepage under Class II MFG
- Creepage under Class III?
  - Sometimes (Veale; Hillman)
- Strong indication that creepage mechanism requires that one or more MFG test parameters are exceeded
  - Especially %RH
  - Hillman: >75%RH
  - Cullen: 93%RH
- How must MFG be modified to replicate field issues?



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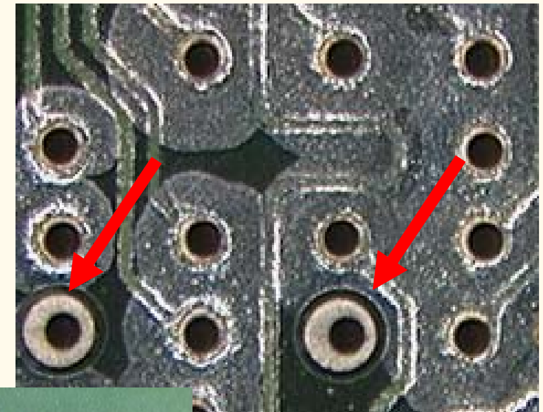
MFG Test Structures

- Influence of solder mask
  - Field: Creepage primarily on solder mask defined (SMD) pads
  - Test: Delay in creepage on non-solder mask defined pads (NSMD)
- Similar mechanism observed with electroless nickel / immersion gold (ENIG) plating
  - Corrosion of copper trace at solder mask edge
- Potential mechanisms
  - Solder mask absorption of sulfur-based gases
  - Crevice corrosion (depletion of oxygen)
  - Entrapment of flux residues



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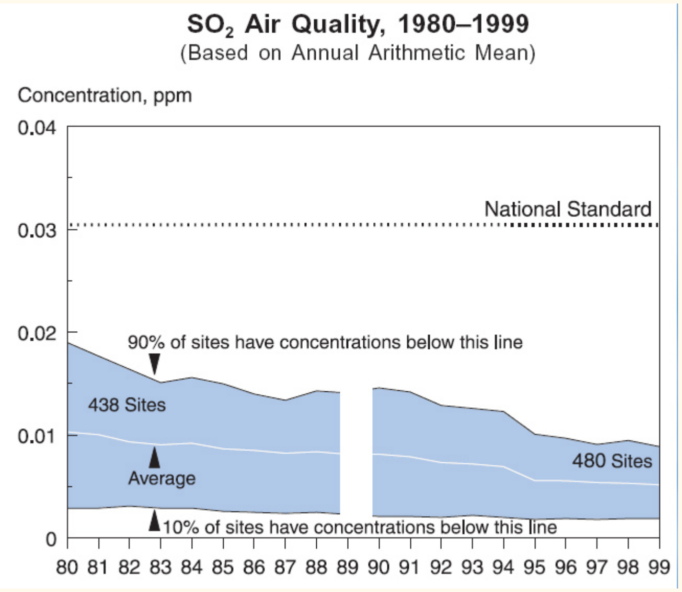
MFG Test Conditions

- Are existing MFG test conditions still relevant?
  - Different material system (silver, not copper)
  - Changing environment (is there more / less pollution?)



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MFG Test Conditions (Sulfur-Based Gases)

SO2

- MFG Test
  - 100ppb, 200ppb
- Average annual outdoor
  - 2-20ppb (USA)
  - 25-100ppb (Asia)
- 24 hour
  - ~150ppb (NAAQS / Telcordia)
  - 150-600ppb (Industrial-USA)
  - 100-1500ppb (Asia)
- May not be critical for sulfidation of silver
  - Rate independent of SO2 concentration

H2S

- MFG Test
  - 10ppb, 100ppb, 200ppb
- Average annual outdoor/indoor
  - 0.05 to 0.8ppb
- 24 hour (outdoors)
  - 8 to 100ppb (State Regs)
- 24 hour (indoors)
  - 500 to 20,000 ppb
- May be more critical

	Clean room	Controlled environment	Rural	Urban with heavy traffic or industrial	Adjacent to industrial	Inside industrial
SO2	100 ug/m^3 38 ppb	100 38	100 38	1000 380	10000 3800	40000 15300
H2S	1.5 0.6	10 4	10 4	500 200	10000 4075	70000 28500

IEC 60721-3-3

Test Conditions (cont.)

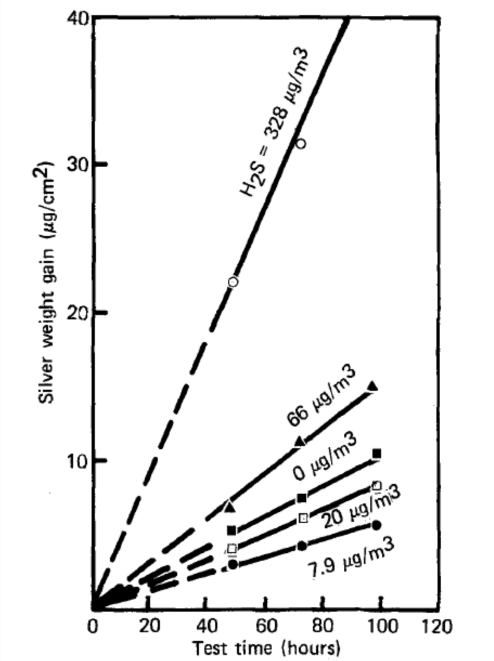
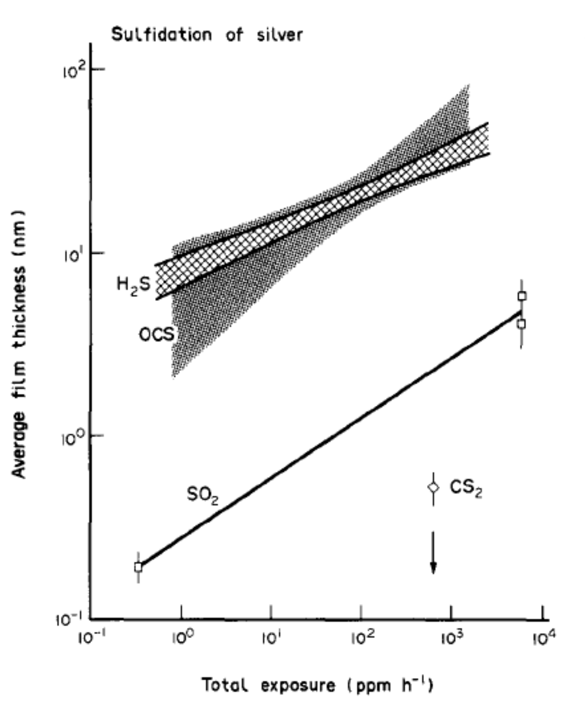


Fig. 6. Weight gain of silver vs. test time for various H_2S concentrations in environment A (Table III).

Carbonyl Sulfide (COS)

- Ignored by MFG
- Outdoor levels can be higher than H2S
  - Nominal: 0.5 – 0.8ppb
  - Elevated: 80 ppb
- Can be as corrosive as H2S



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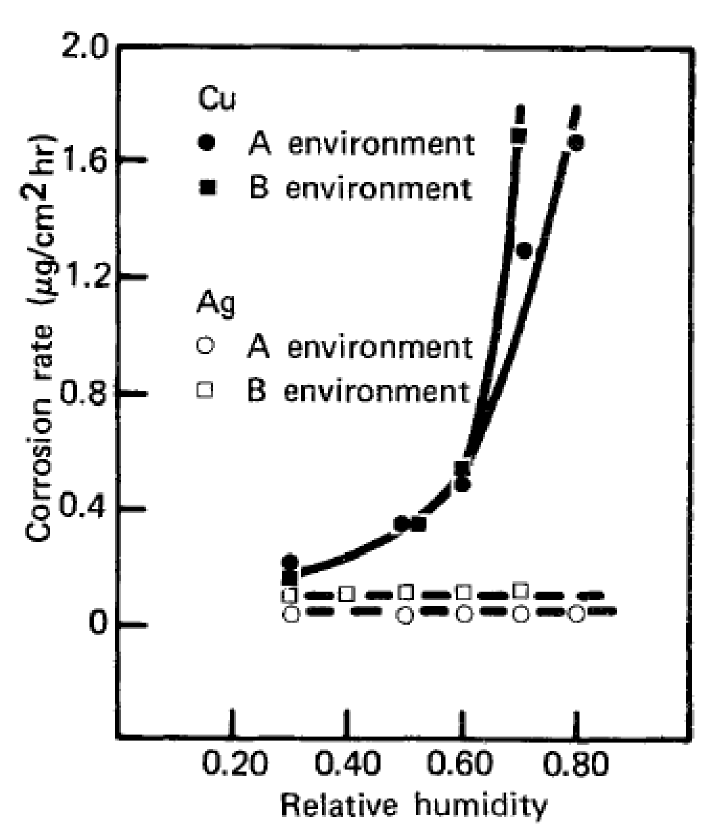
Test Conditions (Relative Humidity)

- Influence of %RH somewhat contradictory
- Vernon reported a critical %RH (70-80%)
- Graedel reported an increasing corrosion rate with increasing %RH
  - Driven by monolayers (ml) of moisture
  - ln (ml) = 2.73 p/p0 - 0.366
    - (p/p0 is %RH)
- Rice reported no influence of %RH



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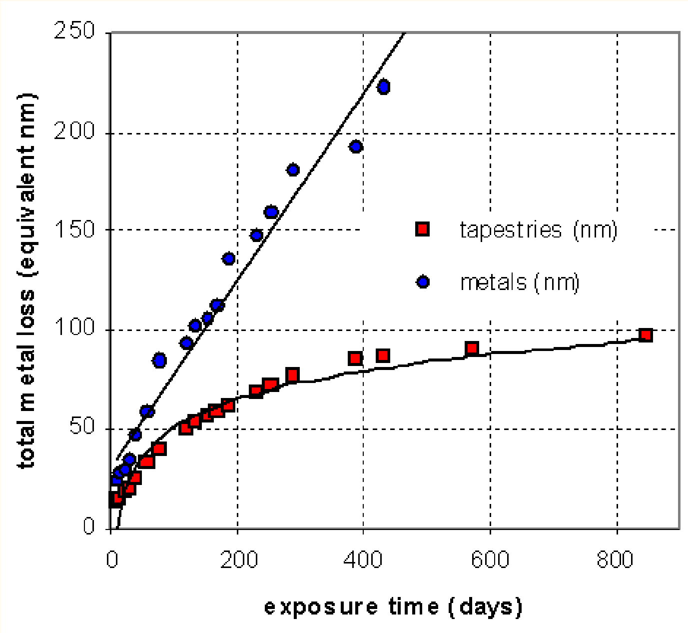
Relative Humidity

- Validation of Rice's observation
  - %RH levels in ceramic hybrid and thick film resistors coated with hydrophobic silicone likely low
- Important differentiation by mechanism
  - Most references investigate the tarnish aspect of sulfidation
  - Creepage behavior is likely very sensitive to %RH
- The rough surface of a polymeric material becomes conducive to material transport once micro-condensation within occurs.
  - 'Filling-in' of surface pores may greatly reduce the adhesion of the polymer surface
  - Allows forces created by volumetric expansion of corrosion product to 'push' the growth out to an adjacent conductor

Discussion

- Modification of MFG test specs may be appropriate
  - Elimination of SO2 gases
  - Increase in H2S concentrations (>200 ppb)
  - Possible intro of COS
  - Elimination or reduction of Cl2
- Speculation that formation of AgCl inhibits sulfidation of silver
  - Elevated Cl2 displays parabolic behavior
  - Elevated H2S displays unlimited growth



Conclusion (Questions to Ask)

- 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 H_2S 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?

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Dr. Craig Hillman, CEO

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