Surface Tarnish and Creeping Corrosion on Pb-Free Circuit Board Surface Finishes

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Abstract

The deployment of non-Lead (Pb) surface finishes is well underway throughout the electronics industry. Printed circuit boards, which for many years had relied on Hot Air Solder Level (HASL) finishing, have been using new flatter, Pb-free solderable finishes. Market tracking surveys indicate that the use of HASL has dropped below 50% of all PCB's. HASL alternative finishes include Organic Solderability Preservative (OSP,) Electroless Nickel Immersion Gold (ENIG,) Immersion Silver, and Immersion Tin. While there are significant differences among the HASL alternative coatings, they do have certain characteristics in common. All HASL alternatives are much flatter and thinner coatings than HASL.

PCB surface finishes need to perform several functions. Archived literature provides information on the solderability, contact functionality, solderjoint reliability, and high speed signal integrity effects of the surface finish options. The summary contained herein describes a fundamental criterion of all board finishes: the ability to protect copper for subsequent soldering and field use. The surface finish, and therefore the underlying copper, can be compromised by exposure to harsh environments such as air pollution, condensing moisture, ionic liquid solutions, and contact with corroding materials. Surface finishes are more or less degraded based on the sensitivity of the surface finish to environmental contaminants and the thickness of the protective coating. For example, tin/lead is not especially resistant to corrosion, but it does have the advantage that it is deposited to such a thickness that it withstands corrosion relatively well.

Corrosion of copper circuitry begins as thin tarnish of the surface finish. Circuit functionality will be compromised only if the chemical pollutants, and the means to convey the pollutant, are present long enough to corrode the copper. This paper reviews some specific causes of corrosion, methods used to measure the corrosion, functional aspects of tarnish and corrosion, and methods employed to prevent surface corrosion. Of special interest, this paper reviews the use of ultrathin layer of tarnish protection on new HASL alternatives such as immersion silver. More specifically, the topic of creeping corrosion will be discussed as an example of the extreme results of tarnish and copper migration.

Introduction

HASL alternatives are ultrathin, existing from a few hundred nanometers up to several microns. While HASL may vary in thickness up to 50 micrometers or more, OSP is generally deposited to about 0.2 microns, immersion silver is 0.1 to 0.5 microns, immersion tin is about 1.0 micron, and ENIG is comprised of 0.1 micron of gold on 4-5 microns of nickel. With exposure to various contaminants, all finishes discolor, tarnish, and corrode. OSP is easily removed chemically or mechanically, allowing copper to oxidize directly. ENIG is less vulnerable to common pollutants and contamination, but is more sensitive to high humidity. Tin will form discrete layers of, among other compounds, tin oxide and oxidized copper-tin intermetallic. Silver metal is unique in that its surface films of extremely thin corrosion may be visible to the unaided eye. Sulfide films form as compound with most PCB surface metallizations, but the silver sulfide films are most visible, even at thicknesses below 50 angstroms.

Every reasonable precaution should be taken to prevent the formation of tarnish, since it can lead to visual PCB rejection at QA. Additionally, tarnish which is not prevented can become a functional problem in the most severe environments. The tarnish can eventually expose underlying copper and, when combined with liquid water, can transport corrosive salts on to dielectric areas of the circuitry.

Tarnish Characterization

Tarnish is most easily characterized by visual inspection. Tarnish is usually very irregular and not uniformly distributed across PCB surfaces. Silver tarnish sets up small, densely packed crystalline structures on the microscopic level. The tarnish does not exhibit movement across the surface, unless extreme conditions like those of the "creeping corrosion" phenomenon are exhibited.

Measuring tarnish of extremely thin films is not an easy project. Methods which are normally used to measure tarnish include SEM/EDS, Auger (AES), ESCA, and TOF SIMS. Another method, Sequential Electrochemical Reduction Analysis (SERA) can be used as an expensive screening tool for surface reducible species and is very time-effective. While there is disagreement among the methods when comparing the same surface, the SERA method facilitates a quick and inexpensive way to measure tarnish in a somewhat reproducible manner.

Causes of Surface Finish Tarnish

- Improperly cleaned PCB's as shipped from the PCB manufacturer.
- Improperly stored or handled PCB's as shipped from the PCB manufacturer or received at the component assembler.
- Exposure to sulfur, sulfate, nitrate, oxidizers, chloride and/or chlorine gas
- Contact with materials containing high concentrations of free sulfur and/or pollutant materials.
- Exposure of PCB's to moderate levels of H_2S and/or Cl_2 gas during high temperature reflow.
- Extended exposure to unprotected environments between reflow cycles. (OSP can oxidize in as little as 2 hours; silver's shelf-life can reduce from 10 weeks to as low as 2 days.)

Due to the unique visual detection of very thin layers of silver sulfide, as well as the large interest and growth in the use of silver in PCB manufacturing today, the follow list details silver tarnish in particular. The overall thickness of immersion silver is between 150 and 500 nanometers.

Effects of Silver Tarnish

- Visual detection and potential rejection (40 nm)
- Reduced solderability; solder dewetting (100 nm)
- Increased contact resistance of low-force contacts (once underlying copper is exposed)
- Increased vulnerability for creeping corrosion (once underlying copper is exposed)
- Increased vulnerability for electrochemical migration (once underlying copper is exposed)
- Recognition loss of high frequency signals (in theory; not documented)

The Ag_2S tarnish has some electrical conductivity. This fact, together with the fact that the tarnish is normally extremely thin, results in the observation that tarnish does not cause increases in surface contact resistance.

Harsh Environments

Tarnish will occur most frequently on circuitry manufactured and used in harsh environments. Several conferences are held within the electronics industry each year to discuss the protection of electronics used in harsh environments, such as the environment under the hood of an automobile. Automotive makers have used immersion silver PCB's to a large degree during the past 5-7 years. In some cased, silver is used on nearly every circuit board in the automobile. Of course, some circuitry requires more assembly protection than others.

Recreating Silver Tarnish

For the study of tarnish, it is necessary to employ a consistent method for forming tarnish. This challenge is especially difficult when the amount of tarnish induced is tiny. Additionally, a main intent of the testing is to differentiate among surfaces on their vulnerability to tarnish. When there is even the slightest variation in the surface deposits, it is difficult to calibrate the reproducibility of the tarnish test method. See Table 1 for a comparison of methods used to induce tarnish in the laboratory.

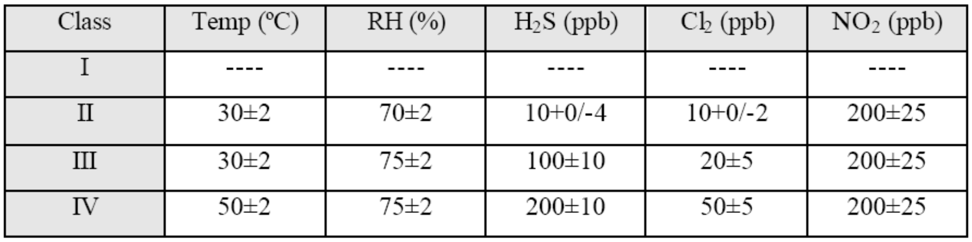
Table 1: Comparison of Tarnish Test Methods

Mixed Flowing Gas Class II	• Well controlled • Usually 1,5, or 9 days • Expensive • Specialized labs • Does not produce Creeping Corrosion
Mixed Flowing Gas Class III	• Well controlled • 2-20 days • Expensive • Specialized labs • May not produce Creeping Corrosion
Sulfur Chamber Test	• Not well controlled • Less than 2 hours • Inexpensive • Specialized labs • Does not produce Creeping Corrosion
Condensing Corrosive Vapor	• Poorly controlled • 12-24 hours • Inexpensive • Should produce Creeping Corrosion • Results not consistent
Saturated Humidity Corrosive Vapor	• Poorly controlled • 12-24 hours • Inexpensive • May produce Creeping Corrosion
Ferric Chloride	• Good control • 1-5 minutes • Inexpensive • Any laboratory • Does not produce Creeping Corrosion

Mixed Flowing Gas

Teams of industry, university and government groups have developed a controlled environment to simulate common pollutants in concentrations intended to accelerate the conditioned age of materials. The range of conditioning environments is documented in ASTM B845-97 (2003.) (See Table 2 and Figure 1.)

Table 2 - Conditions for Mixed Flowing Gas



Class	Temp (ºC)	RH (%)	H_2S (ppb)	Cl_2 (ppb)	NO_2 (ppb)
I	----	----	----	----	----
II	30±2	70±2	10+0/-4	10+0/-2	200±25
III	30±2	75±2	100±10	20±5	200±25
IV	50±2	75±2	200±10	50±5	200±25

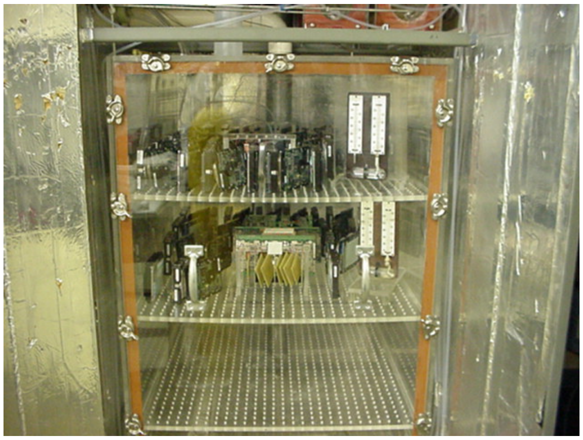


Figure 1 - Mixed Flowing Gas Test Chamber

Sulfur Chamber

As a laboratory mock-up of the Mixed Flowing Gas test, MacDermid's pilot lab constructed a "Sulfur Chamber" for simple and quick comparisons of surfaces without cumbersome complexity. The chamber is plastic box with a sample exposure tray and a tray with chemicals for volatilization. H2S vapor is created when 1% hydrochloric acid is added to a 0.1g/L solution of sodium bisulfide. A fan is used to circulate the contaminated atmosphere within the chamber. Hydrogen sulfide forms quickly when acidified, releasing a spike concentration of over 7000ppm as sulfide within the 1st 15 minutes of exposure. The temperature in the chamber is ambient. Samples are suspended in this atmosphere for 150 minutes. When it was determined that summertime samples corroded more thoroughly than those tested in the colder months, the chamber was controlled to a constant temperature of 38°C. With external heat, the humidity became far more predictable, leading to more consistent results. The time to exposure was lowered to about 0.5 hours, or until sufficient tarnish was exhibited among comparative samples. (see Figure 2.)

Figure 2 - Sulfur Chamber Test Apparatus

Condensing Corrosive Vapors

The Mixed Flowing Gas method is well controlled and does not product condensate on test samples. Industry experts agree that condensation will not form on test equipment as long as the humidity is controlled to 93 +/- 2.5% RH or below. Above that range, condensation is likely. To submit samples to a condensing environment using a simple and quick method, MacDermid's researchers suspended test boards above a boiling solution of acids, salts, and sulfides. When covered with a film of paraffin, the solution refluxed within the 4L beaker, coating the samples in a liquid solution of corrosive salts. This is the most corrosive system used in all our studies. No determination of sulfide vapor concentration has been conducted.

Non-Condensing Corrosive Vapors

A slightly less corrosive system was achieved by the use of two modifications to the sodium bisulfide "NaSH beaker" test. In one case, the beaker was not sealed, so the vapor was allowed to escape. In another case, the beaker was kept in an oven at a constant temperature of 50°C. In this way, condensation by cooling could be avoided. The absence of liquid on the test vehicles was not confirmed. In theory, there should be no condensation since the samples were immediately removed from the beaker at the completion of the test (24 hours) without exposure to temperature variation during the test period. This environment was also referred to as the “100% humidity” environment. (See Figure 3.)

Figure 3 - Corrosive Vapor Test Set-Up

Creeping Corrosion

The condensing and non-condensing corrosive vapor environments produced a type of corrosion named “creeping corrosion.” Creeping corrosion has been documented by Texas Instruments and the University of Maryland (USA) among others. In this extreme corrosion mechanism, the surface finish is corroded, exposing the underlying copper. Then, the corrosive ions form copper salts. Liquid solvents, such as water, will carry the salts across the circuitry in an electrolyte solution. With sufficient liquid and surface tension, the electrolyte can bridge the gap between circuitry and soldermask. With heating, the electrolyte may dry and deposit crystallized corrosion salts. If more liquid comes in contact with the circuitry, the cycle may repeat, with the formation of rings of crystalline deposits.

An interesting observation of the creeping corrosion defines the phenomenon as different from dendritic growth. The corrosion does not follow a linear path between electrodes. Creeping corrosion can not be classified with dendrites or filament growth within the category of electrochemical migration. Creeping corrosion is a phenomenon of the PCB copper circuitry. In all samples measured using SEM/EDS, similar Cu to S ratios are displayed. Silver, Tin, Nickel, and/or Gold will also appear on elemental scans, depending on the surface finish used on the board before corrosion testing.

It proved difficult to recreate creeping corrosion on PCB samples under normal sulfur chamber and mixed flowing gas conditions. Exposure to condensing moisture was the first method to reproduce the phenomenon in the laboratory. Later studies conducted by contract test labs created creeping corrosion with the use of MFG at elevated, condensing humidity. Note that the MFG chamber was calibrated at more than 2,000 nanometers of corrosion in these studies, which is about 5-10 times the thickness of thin surface finish deposits.

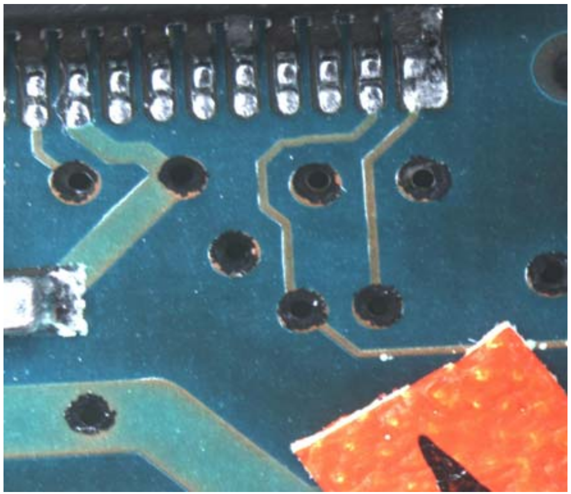


Figure 4 - Test Specimen after 13 Days (>20,000Å) of Class 3 Mixed Flowing Gas under Non-Condensing Humidity (85+/-5% RH) Conditions

Figure 5 - Test Specimen after 15 Days (>20,000Å) of Class 3 Mixed Flowing Gas under Condensing Humidity (93+/-5% RH) Conditions

Tarnish Inhibition

The final finish on a circuit board is generally used to preserve the solderability of copper circuits. Each finish is vulnerable to different corrosive materials. For example, OSP coating are sensitive to solvents, most acids, and many anions; tin is mostly vulnerable to oxidation. All PCB finishes are sensitive to sulfur; the only variable is in the amount of time before the sulfur is able to reach the underlying copper. HASL coatings have a large mass of material which can help protect the copper. Organic coatings use their hydrophobic nature to help delay the transport of corrosive anions by water.

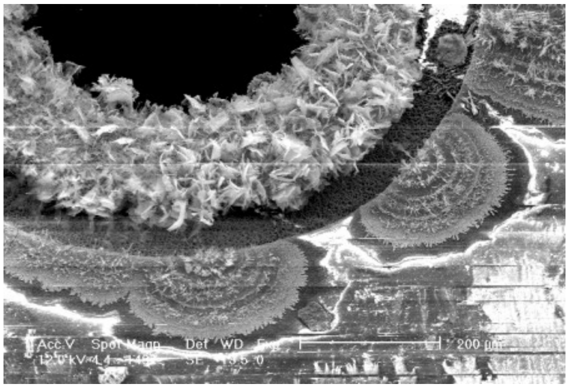


Figure 6 - Creeping Corrosion Observed on a Field Failure

Anti-tarnish coatings act as simple barriers and as hydrophobic agents. It is impossible to render the anti-tarnish thick enough to provide complete protection against corrosion, since the solderability and contact functionality of the surface would be compromised. In practice, an ultrathin coating of long-chain organic material is attached to the silver surface using covalent bonding functional groups. It is predicted that a monolayer coating is formed. (See Figure 7.)

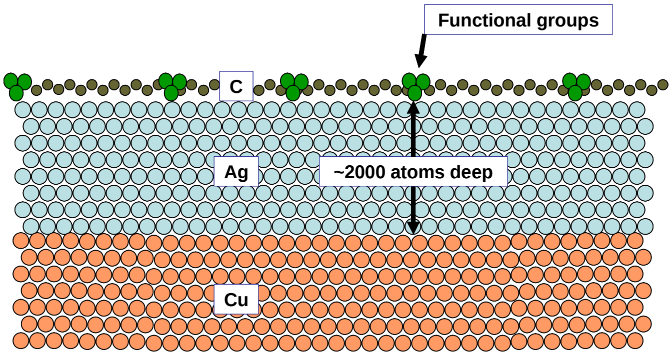


Figure 7 - Schematic Diagram of an Anti-Tarnish Coating for Immersion SilverAnti-Tarnish Characterization

Anti-tarnish composition will vary with the finish to be protected. Copper is most commonly protected with the nitrogen functionality of azole compounds. Immersion silver is more appropriately protected with organic compounds containing sulfur functionality. While not widely deployed in PCB production, thin coatings may be used as a post-dip to immersion silver as a thin barrier to tarnish, providing a hydrophobic surface repelling liquids far better than standard immersion silver. In early deployment, the following properties have been measured on one particular immersion silver anti-tarnish coating.

- No interruption of contact functions, even after natural age, environmental age, heat/humidity, thermal cycling and vibration.
- No affect on solderability, and complete compatibility with normal assembly variables.
- Increased tarnish resistance to a number of environmental and handling conditions.

The material used in the anti-tarnish coating itself was tested using Differential Scanning Calorimetry (DSC) (Figure 8) (where no decomposition peak was witnessed until a slight peak was shown at about 70ºC above the Pb-free assembly temperature. As a follow-up, a test has been proposed to deposit the material on silver powder with a high surface area. Any decomposition of the bonded material should show up on DSC.

In addition, Thermal Gravimetric Analysis (TGA) (Figure 9)was employed to detect any weight loss/gain of the material when exposed to increasing heat. Above 200ºC, the material began to slowly degrade. After about 30 minutes, when the TGA was near Pb-free assembly temperatures, the coating was reduced to less than half of its original sample weight. In studies on actual circuitry, the material showed assembly tolerance in standard assembly conditions, but lost some functionality in Pb-free assembly exposure. The prime benefit of silver anti-tarnishes is pre-assembly tarnish protection, with some degree of functional performance retained following assembly.

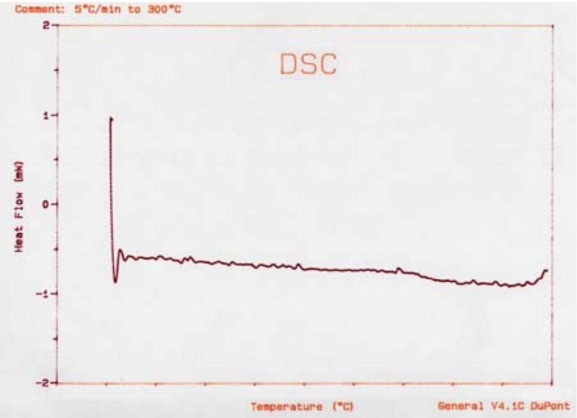


Figure 8 - Anti-Tarnish Material: DSC

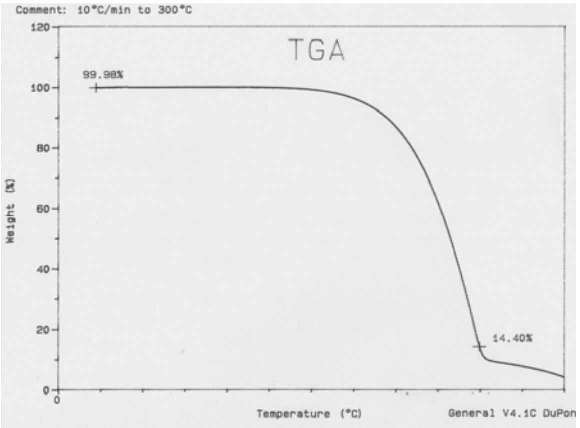


Figure 9: Anti-Tarnish Material: TGA

Anti-Tarnish Limitations

Silver anti-tarnish has repeatedly shown good effectiveness in preventing, or significantly delaying the visible tarnish and functionality of silver coated circuit boards. This functionality is important as a way to minimize complaints and yield loss due to cosmetic tarnish. Also, prevention of tarnish will extend the shelf-life of improperly stored boards, widening the effective operating window at fabrication and assembly. However, the functionality of anti-tarnishes, like that of an OSP coating on copper, is compromised with Pb-Free reflow conditions. Repeated studies conducted during late 2004 and early 2005 show that some amount of functionality is lost when tarnish-protected silver boards are processed through 1X, 2X, 3X and 4X exposures to actual soldering operations.

Recommendations

As always, the most important factor in preventing environment-related problems is the use of proper packaging and enclosure suitable for the intended end-use. If the device is intended for use in an environment of liquid water, suitable barriers need to be in place to prevent short circuits. Any conductor and dielectric system is vulnerable to this functional loss. Systems may be hermetically sealed for use in the most extreme environments. Less harsh environments may rely on the use of conformal coating and other barrier coatings.

For systems which are not intended to operate with liquid water, some precautions should be taken to delay functional loss if the system is exposed to condensing moisture for brief periods of time. For example, a casing or cabinet may be used to shield the device from spills. Also, foam or other gasketing may be used to slow the penetration of corrosive gasses. For immersion silver exposed on assembled circuit boards operating in challenging environments, anti-tarnish may be used to inhibit tarnish and slow the creeping corrosion mechanism. (Figure 10.)

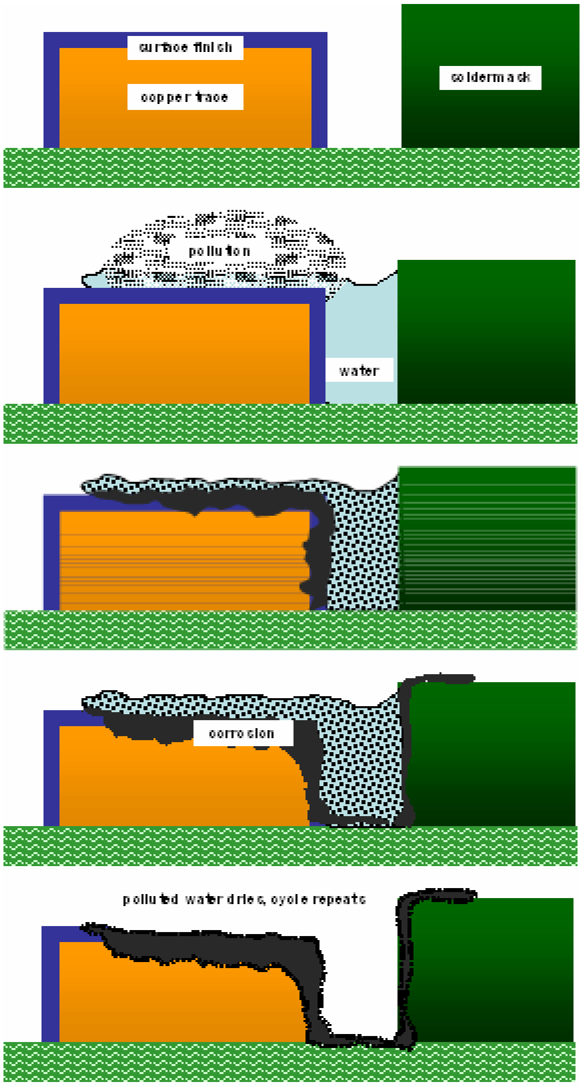


Figure 10 - Mechanism of Creeping Corrosion

Conclusions

- Tarnish of immersion silver is mainly a visual problem and does not pose a functional loss until the depth of tarnish exposes underlying copper.
- Exposed PCB copper, when submitted to environments of liquid water and high sulfur contents, will form soluble salts. The salts may become mobile and creep between conductors resulting in the possibility of electrical failure.
- PCB surface finishes have varying vulnerabilities to corrosive anions. All PCB surface finishes are sensitive to sulfur. For extra protection of immersion silver, a tarnish inhibitor has been introduced.
- Silver anti-tarnish allows for full functional performance of all PCB needs, exactly similar to uncoated immersion silver, but with additional tarnish protection.
- Anti-tarnish can provide a significant improvement in the prevention of visible tarnish on unassembled PCB's. It offers some improvement in the prevention of visible tarnish on assembled PCB's. The durability of the anti-tarnish protection is degraded with multiple exposures to Pb-free reflow environments.
- Anti-tarnish will not prevent the formation of creep corrosion on silver or other surface finishes. Some tarnish experiments show coated parts resisting tarnish and creep corrosion significantly better than unprotected boards. This result is not always reproduced due to the variable nature of corrosive gas testing.
- Creeping corrosion is reproduced using a condensing vapor test. All finishes will exhibit creeping corrosion within 24 hours under this environment.
- Mixed Flowing Gas environments, even at elevated humidity, do not produce creeping corrosion. Only one experiment, with the corrosion of PCB well into the substrate copper, exhibited some indication of creeping corrosion.
- Anti-tarnish may be used to improve shelf life of unassembled boards. It will have solderability and contact functionality advantages for circuit boards exposed to marginal environments.

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