

The Path to Robust Electronics - Preventing Corrosion of PCB Assemblies

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Abstract

All things corrode, and the rate of corrosion among electronics devices is accelerating. Electronic devices are being used in more places than ever before. They are finding more uses, they're more portable, and they're increasingly used in polluted areas. Worldwide industrialization has produced more sulfur, chlorine and nitrogen compounds that aggressively attack electronics. The initiatives to eliminate lead (Pb) in electronics reduced the ability for circuitry to resist corrosion. To replace thick tin-lead deposits more circuits employ thin, easily corroded surface finishes on the PCB, connectors, and component leads. There is a need for better prediction of service-life corrosion, yet there is a lack of adequate test methods. Environmental testing rarely progresses beyond thermal cycling or heat/humidity. Mixed flowing gas testing uses standardized pollutants as a stress to electronics, but has limited success in reproducing all corrosion failures. An elevated rate in the observation of one type of failure, termed creeping corrosion, motivated the electronics industry to review corrosion test methods. As part of the IPC 3-11g committee, a number of OEM's, EMS providers, PCB fabricators, material suppliers, universities, and testing laboratories joined forces to address the need for better corrosion prediction.

The project conducted experiments using environmental pollutants and various levels of exposure to moisture to form corrosion salts from copper circuitry. A main objective of the testing was to create a standardized method for inducing corrosion. Test results will show the ability to recreate creep corrosion at the participating laboratories. As a project summary, this paper will review the many attributes of a PCB surface finish, the ways that each finish can fail under environmental contamination, the mechanism of creeping corrosion, and new ways to interrupt the corrosion mechanism while preserving other surface finish attributes. The summary contained herein had been intended to include the latest corrosion results from the IPC 3-11g team; however, the testing was not complete by the time of publication. This review will detail the status of the team's findings to date, provide references to newly collated data, and chart the team's forward direction.

Introduction

The electronics equipment manufacturing industry encounters many challenges, including: fast time-to-market, diminishing product cycle, piracy of circuitry layout, and the need for uninterrupted reliability for as long as 25 years in sectors such as telecom. Reliability is one factor which remains largely in their control, but new market dynamics are challenging the reliability factor as well. Corrosion-induced service failures are increasing at a troubling rate. Corrosion of printed circuit boards can have the effect of causing electrical opens in very fine line circuitry, as well as the creation of electrical shorts when the corrosion products creep among conductors. This latter failure mode, creep corrosion, is seen more and more as sensitive electronic products are deployed in the more polluted regions of the developing world. Increasingly, telecom products are used in uncontrolled environments, e.g.: switches and routers in internet-savvy Bangalore. Lastly, we have seen the rise in use of thin coatings to replace thick hot air solder level, a victim of Europe's RoHS legislation. These coatings provide an easier access to copper, the material identified as the creep corrosion product.

As a reaction to the troubling creep corrosion failure mode, an international organization concerned with electronics specification, IPC, has commissioned a sub-committee IPC 3-11g Metal Finishes Data Acquisition to collect data on the interactions of circuit board surface finishes and various corrosive environments. The committee is expected to determine the rate of corrosion of circuit materials, allowing equipment makers to better plan for reliability, service, and environmental requirements. Already, we have seen changes in the way circuit boards are protected. A goal of the committee is to produce a statement increasing awareness of the issue, providing data for planning purposes, and issuing recommendations for increased circuit protection. As the IPC membership acts as a group of volunteers, chemical suppliers contribute test vehicles and plated coatings, circuit vendors provide time on their equipment, assembly contractors solder components, and OEM's provide access to analytical test equipment.

Corrosion failure rates rise when three key factors intersect: increased pollution, reduced circuit protection, and wider use of electronics. Figure 1 graphically represents this intersection. "Approximately 75 percent of all industrial sites have some form of electronic corrosion which leads to premature equipment failure. Premature equipment failure occurs in less than a year in about 5 to 10 percent of current industrial process control applications."¹

This study focuses on the corrosion of exposed metal in the field use of assembled printed circuit boards. An anecdotal increase in field failures was observed during the time immediately following implementation of the RoHS initiative. An explanation for the somewhat sudden increase in field failures follows three converging and conspiring trends, increased overall pollution, portability of electronic devices, and the use of less robust materials for protecting corrosion. Similar to the FMEA methodology, the severity of corrosion is due to less robust materials, the occurrence is due to more interaction opportunities, and unless the amount of pollution is drastically reduced, an effective solution is not readily available.

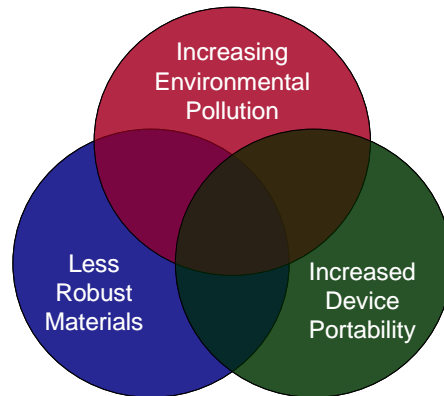


Figure 1: The Intersection of Key Factors Resulting in Increased Corrosion of Electronic Circuitry

Factors influencing corrosion rate

- Exposure of surface materials with corrosive pollutants (porosity, weak protectant films)
- Thermodynamic spontaneity and favorable energy of formation values
- Galvanic difference between metal layers
- Transport and residence time of pollutant (humidity, condensation)
- Replenishment of reacting pollutants (air flow)
- Time and temperature at corrosive conditions
- Solvent environment (air, water, oils, partial vacuum...)
- Movement of metals with a system (diffusion, recrystallization, density change with growth of corrosion)

Creeping corrosion has been documented by Battelle labs, Texas Instruments, Rockwell Automation, Alcatel-Lucent, Hewlett Packard, Dell Computer, and the University of Maryland among others.^{2,3,4,5} 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. When heated, the electrolyte may dry and deposit crystallized corrosion salts. If more liquid comes in contact with the circuitry, the cycle repeats, with the formation of rings of crystalline deposits. When analyzed, the material found to creep is copper with its corrosion product anion, usually sulfide.

Causes of Surface Finish Tarnish

- Improperly cleaned PCB's as shipped from the PCB manufacturer,
- Improperly applied PCB surface finish,
- Improperly stored or handled PCB's as shipped from the PCB manufacturer or received at the component assembler,
- Exposure to the reactive compounds of sulfur, nitrogen, oxygen, and chlorine,
- Contact with materials containing high concentrations of elemental sulfur and/or pollutant particulates,
- Exposure of PCB's to moderate levels of corrosive gas during high temperature solder 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.)

Corrosion can manifest itself in several ways. Simple surface corrosion can be as benign as the creation of invisible oxides, sulfides and chlorides in sub-micron layers on circuit metals. Usually invisible and self-limiting as the availability of surface metal is consumed, these films are normally invisible to the unaided eye. Copper, and especially silver, tarnish is more visible even at very thin angstrom-level films. With more corrosion, replenishment of reactive materials, and movement of the materials by (typically) water, a new class of corrosion is manifested. Thick corrosion can impact electrical surface contact functionality. Under electrical bias, dissolved materials can conduct current and form dendrites. Even without dependency on electrical bias, corrosion can move across insulating surfaces. Creep corrosion relies on high humidity to exhibit such movement. It is hypothesized that condensing moisture is required for the creep corrosion phenomenon.

Corrosion is not limited to these examples. Conductive anodic filament growth, whiskers, and fretting are other examples of metal movement linked to corrosive mechanisms. See Figure 2 for examples of corrosion types.

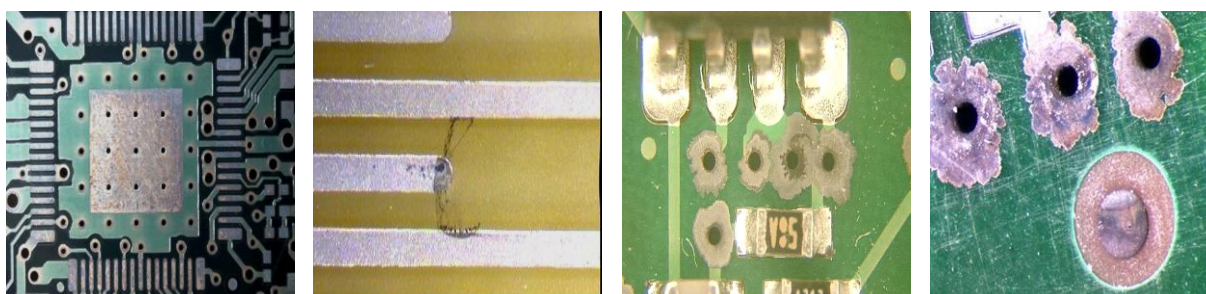


Figure 2: Examples of Tarnish, Dendrite Formation, and Creeping Corrosion of Silver and Copper

Techniques for Measurement

Environmental measurement can be conducted by “sniffers” for individual chemicals such as H_2S , SO_2 , Cl_2 and solid particulates. These levels can be compared with the levels recorded at field observation stations set up worldwide. In many cases, H_2S is not actively measured, but SO_2 is the more common sulfur species tracked by government agencies. Another measurement method uses sacrificial metal strips to record corrosion. Metal strips are placed in an industrial environment. The strips are carefully prepared to a controlled texture and cleanliness. Corrosion is measured by weight loss and weight gain. The surface can be analyzed to determine the corrosion products. This method is limited by corrosion mechanism – loosely adherent corrosion materials can peel and flake off the sample showing a weight loss, while adherent corrosion products result in a weight gain.

Analysis of corrosion products is conducted by several methods including acid digestion, desputtering elemental analysis, energy dispersive spectroscopy, depth profiling and analysis by binding energy, and sequential electrochemical reduction (e.g. SERA.) For the specific measurement of creeping corrosion, the distance of creep can be measured linearly. The corrosion products will creep on soldermask more quickly than across epoxy substrate. This may be due to smoothness, extent of water repulsion, and other material factors.

Methods for Reproducing Corrosion & Acceleration Factors

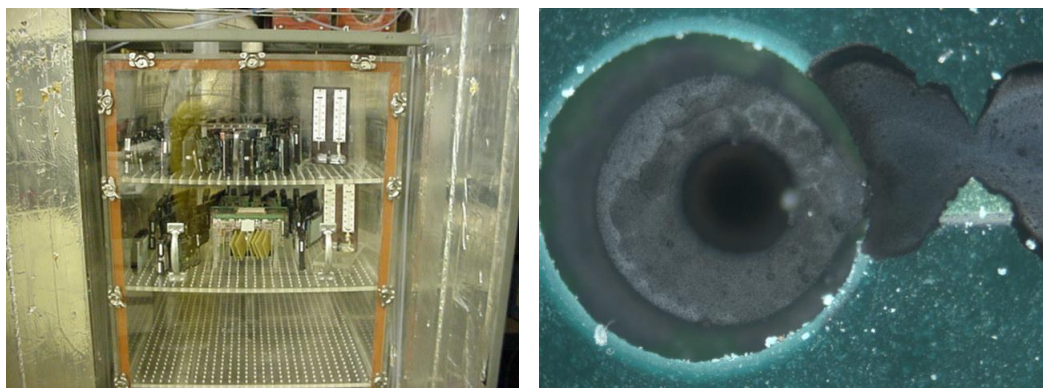
For general use, industry, university and government groups have developed controlled environments to simulate corrosion by common pollutants. The pollutants are delivered in concentrations intended to accelerate the corrosion reactions. The contamination can be liquid, gaseous, static, flowing (replenished), homogenous, and heterogeneous. Electronic circuitry is most often exposed to replenishing, heterogeneous, gaseous environments. For this reason, the mixed flowing gas technique (MFG) is well suited for predicting material compatibility in field use. The range of conditioning environments is documented in ASTM B845-97 (2003) and summarized in Table 1. Mixed flowing gas methodology is very useful in creating representative corrosion of electronic circuit materials. The original literature published during the invention of the test method does indicate success in creating creep corrosion on electroplated metals.⁶ However, the use of Class IV MFG methods in well controlled application did not result in creep corrosion of contemporary PCB surface finish coatings in repeated work conducted in 2003-2005.⁷

Table 1: Conditions for Mixed Flowing Gas

Class	Temp (°C)	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

Toscano⁸ details the work conducted to reproduce the creeping corrosion mechanism on bare copper, immersion silver organic solderability preservative (OSP), and immersion silver coated with thin, protective films. By trapping corrosive gasses in static, non-flowing environments with condensing moisture, creep corrosion was produced within 24 hours. The chemicals used were those found in the specialized environment of several industries: tire factory, fertilizer manufacturing, paper mill, and clay modeling studio. Methods were developed based on the use of actual, known contaminants, such as high-sulfur modeling clay and rubber vulcanization chemicals. When analyzed, the environments simulate the industrial settings, but are intended to allow for accelerated conditioning through concentration, air flow, and humidity adjustments.

Humidity was essential in this testing. Condensing moisture and 100% humidity produced creep corrosion. When reproduced, creep corrosion was demonstrated about equally on all surface finishes tested. Lower humidity, as achieved in MFG testing, normally did not produce creep corrosion. At Class IV conditions, with elevated humidity, a few surface finish samples did show creep, as shown in Figure 3b. The laboratory technicians hypothesized the likelihood of localized condensation, as is a known challenge with high humidity in flowing gas testing.



Figures 3 a&b: Mixed Flowing Gas Equipment and an Example of Creep Corrosion on Immersion Tin Formed Using MFG

Surface Finish Effects

Modern PCB surface finishes can be categorized into four technologies, thin metal immersion coatings (Ag and Sn), thick physical deposits (HASL), metal layers (ENIG, NiPdAu), and organic copper protectants (OSP). All of the metal finishes have susceptibility to sulfide-induced corrosion. HASL offers good protection from corrosion due to its high thickness of sacrificial metal. About 50 microns of relatively passive tin separates copper circuitry from any polluted environment. HASL becomes vulnerable when residues prevent full HASL coatings and inadequate thickness allows copper intermetallics to reach the surface. Intuitively, one expects the extra metal layer of ENIG to best resist corrosion, but observations report otherwise. In part, porosity can explain ENIG's poor performance in mixed flowing gas. The rest of the explanation is given by the galvanic potentials of the layered metal. A more noble metal on a less noble substrate can actually accelerate corrosion.² The galvanic corrosion mechanism works to the advantage of thin organic coatings such as OSP. Organics do not set up the electron transfer needed for galvanic corrosion. Corrosion of OSP coated PCB's occurs only when the coating is compromised, exposing copper. In general, organic coatings are hydrophobic, shedding water. This minimizes the contact time of pollutants, when soluble contaminants are shed from OSP surfaces.

Given the ability for organic coatings to resist corrosion (when intact), should the industry concentrate on instituting OSP? In some cases, yes. In other cases, OSP cannot deliver the performance of metal finishes needed for high volume assembly of complication circuit designs. OSP suffers from challenges in surface contact functionality, and from insufficient wetting of wavesolder in PTH's. Other organic coatings have been deployed to offer the contact and soldering advantages of metal finishes, while shedding moisture like an OSP. A tarnish inhibitor on silver was deployed as early as 2005.¹⁰ While initially successful; the effectiveness of the first anti-tarnish formulations was reduced by the transition to higher Pb-free soldering temperatures. A new set of higher functional anti-tarnish coatings is now in deployment.

Committee Work Summary

Complex problems such as corrosion of electronics are best studied by a coalition of numerous resources. For the study of dendrite formation on surface finishes, several stakeholders in the electronics supply chain formed the Metal Finishes Data Acquisition committee under the IPC (Association Connecting Electronics Industries) umbrella. The dendrite behavior of immersion silver was characterized. Members of the committee began to report observation of the creep corrosion phenomenon. In 2005, the group decided to study creep corrosion in depth. Several members of the committee shared their company's internal corrosion testing results.¹¹ Others shared results of field failure analysis. When it was determined that there were data gaps in the environmental testing, a new round of tests was proposed. The proposed testing would expose the set of commonly used PCB surface finishes to a range of accelerated corrosive environments. The testing would build on the 3-11g team's previous corrosion results gathered in the dendrite phase of the project.¹² The test plan quickly grew very large. It was decided to tackle the testing in phases; the first phase would examine mixed flowing gases on PCB surface finishes. Extensive background work had been completed by Abbott at Battelle during 1980-1986.¹³ When this work was consulted, the group found an exhaustive set of studies. To avoid duplication, and to make the best use of resources, the IPC 3-11g team embarked on a literature review of the Battelle work. The work was divided into five sections with committee members

assigned to summarizing the work for the larger team. At the time of this writing, the group had conducted four of the five reviews.

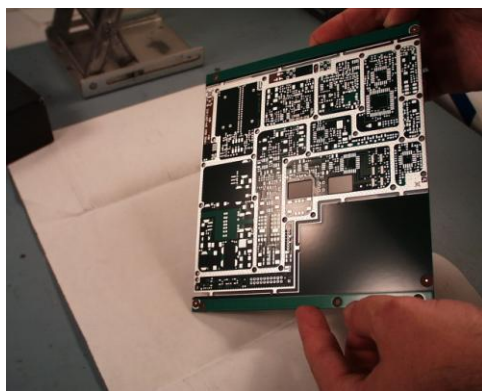
The Battelle data was specific to electronics, but was more general in studying all metals associated with electronics corrosion: copper, silver, tin/lead, palladium, nickel, and gold. The metals were in bulk or electroplated thick coatings. In contrast, the creep corrosion testing of interest with our present day committee involves the use of thin coatings on copper. The 3-11g team wished to study the thin coatings, with the expected increase in porosity, as well as the galvanic couple created when metal pairs were layered, e.g. Cu/Ag and Cu/Ni/Au. Also, the Battelle tests focused on levels of pollutants measured in environments housing electronics during the 1970's. Abbott dismissed more aggressive pollutant levels; levels now regularly exceeded in real consumer and industrial environments.

Good records of pollution over time are difficult to obtain, especially in the most challenging (emerging economy) regions. We do know that electronics are used in environments much more difficult than those envisioned by the Battelle team. The Battelle SO₂ level of 200µg/m³ was described as excessive, but World Health Organization records show SO₂ in indoor environments reaching above 655µg/m³ due to indoor cooking with solid fuels.¹⁴ During our generation, electronic devices are being introduced in these environments. The WHO limit on SO₂ is 20µg/m³. Records for H₂S, considered to be far more important in electronics corrosion, are much more difficult to obtain.

More data gathering is needed to help predict useful service life of electronics. With more data, engineers can plan the effective use of materials, develop new coatings, and determine acceleration factors for corrosion at varying levels of pollution. For the next round of IPC 3-11g testing, several gaps have been identified. Corrosion of actual PCB surface finish layers is needed. Testing of mixed flowing gas at elevated gas levels is needed; Class IV and beyond. Testing of elevated humidity is essential, as most creeping corrosion observations have been linked to cases of condensing humidity. The use of particulate elemental sulfur as a corrosive medium should be tested, as well as the inclusion of organic sulfides. With the final review of the Battelle literature, the 3-11g team will continue testing intended to fill the gaps. If new results fit the statistics created by Abbott, a powerful predictive model will be available.

Corrosion Prevention

Corrosion prevention can be improved by taking action in several areas. The surface texture of the conductor will need to have a predictable, even, low roughness texture in order to minimize surface area. Non-uniform surface texture can set up localized galvanic effects which affect corrosion.¹⁵ The surface finish coating needs to be deposited according to chemical supplier guidelines. The guidelines mimic the parameters used when testing the coating according to EMS, OEM, and industry specification requirements. Operating outside these parameters results in a coating of unknown functional performance. The final PCB needs to be clean. Ionic materials can corrode the conductor directly, or the ions may combine with humidity, flux, or other materials to begin corrosion. Ionic materials can be analyzed individually using ion chromatography; the identity of the contaminant will give clues to the contaminating material. Proper handling, shipping and storage techniques are very important, see Figure 4. Fingerprints transmit a variety of contaminants, including chlorides. Packaging materials should be certified as "sulfur-free," as sulfur can easily corrode copper, tin, nickel, and silver. It is no surprise that packages of PCB's stored under leaking roofs can fail in the field. Once opened at assembly, unused PCB's need to be returned to original packaging and vacuum sealed if they are to be stored for extended time. Other standardization efforts at IPC intend to provide more handling and storage guidance.



Figures 4 a&b: Use of Packaging Material and Proper Handling Can Help Prevent Tarnish and Corrosion.

Reinforcement, Remediation, Relocation

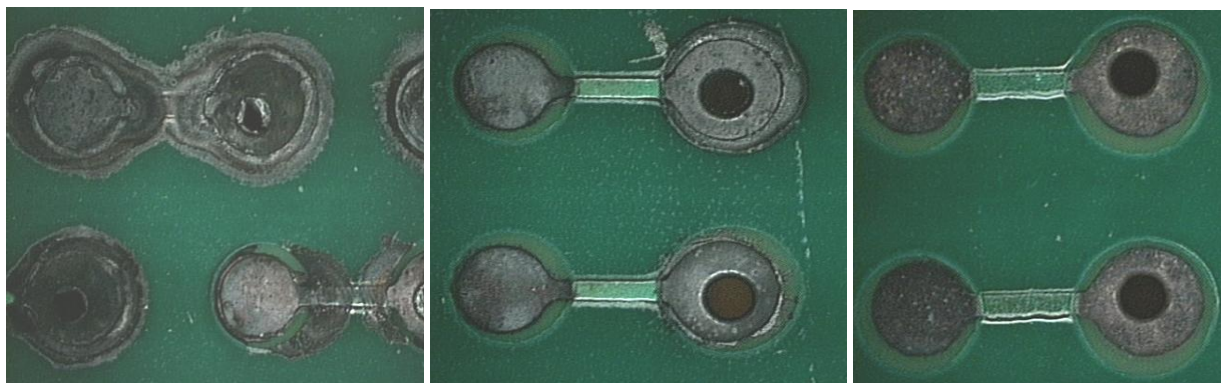
The best coating, handling, shipping and storage methods will not prevent corrosion of electronics used in heavily polluted environments. Consider a tire manufacturing facility as a hypothetical example. By the time computers were deployed to industrial locations such as a tire manufacturing site in the USA, some environmental restrictions were in place. Even then, the computer would have been located in an office environment, removed from the production line. As electronics became more widely used, computer workstations were placed directly on the production line. With worldwide industrialization, these factories were replicated in countries without strong environmental policy. Then, with the transition to lead-free, the computers became more vulnerable, as thick HASL coatings were replaced with thin organic and metallic finishes. Lastly, PCB design changes resulted in non-soldered surface features. Previously, all surface areas were soldered. Now, many features are left unsoldered to allow test point, surface contact connection, and ground shielding functionality.

For very difficult environments, a corrosion prevention strategy can be viewed in three steps: reinforcement, remediation, relocation. The corrosion resistance of the PCB assembly can be reinforced with more robust protection. Protection can be at the PCB level, such as improved finishes. At component assembly, conformal coating or full soldering of all features is effective. Protection at box-build includes the use of filtering and hermetic sealing of devices. Some industry sectors are expert in environmental protection. On the outdoor decks of cruise ships, plasma display TV's are regularly used, but all materials and connections are thoroughly protected.

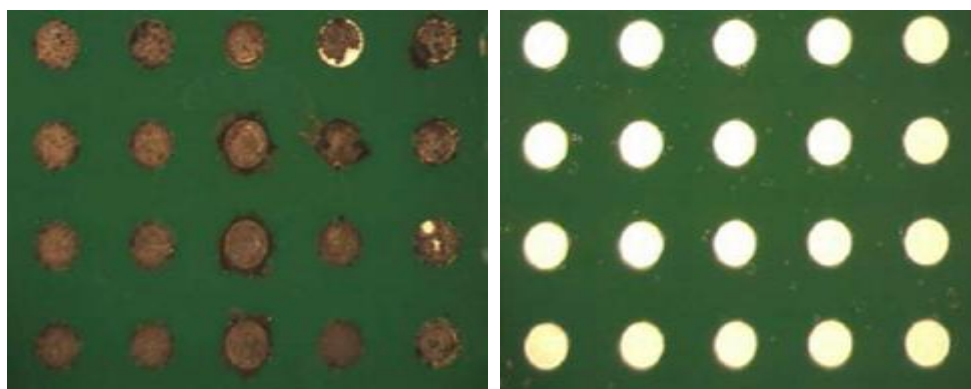
Very difficult environments can be improved with filtering, air conditioning, humidity control and general housekeeping. Sensitive devices can be installed even in difficult industrial environments, with use of positive airflow, double doors, and interlocks. Battelle describes corrosion measurements taken 1) without any controls, 2) with humidity control, 3) with air circulation through chemical purification, and 4) with seals installed on equipment cabinet.¹³ It should be noted that humans have a way of defeating protective interlocks, as described by Mazurkiewicz.⁵ Relocation is the last resort. If there is repeated failure of a device when introduced into an industrial environment, even when other preventative measures have been taken, the computer workstation may have to be relocated to a less corrosive environment within the factory. For some devices, such as programmable controls on robotic manufacturing equipment, this may not be an option.

Anti-Tarnish Films

To protect PCB surface finishes, antitarnish films have been used for many years. To protect bare copper in early circuitry, thin azoles and resins were used; these are still employed for simple single-sided consumer electronics. These nitrogen based coatings evolved into the OSP's used for multiple soldering operations. There has been some use of organic topcoats to protect tin, silver and gold. Immersion silver antitarnish films are very effective at preventing sulfur or chloride tarnish during packaging, shipment and storage, but the simple coatings can lose effectiveness when exposed to soldering temperatures. MacDermid's STI coating, was determined to be effective for 1-2 standard soldering operations, but was less able to survive Pb-free soldering temperatures. A newer coating described as STI Plus incorporates the organic protectant of STI and additional metal passivation functionality; Figure 5. The prevention of tarnish showed some benefit in protecting silver surfaces from sulfur and chloride. The mean time to observation of creeping corrosion could be extended when using the clay and tire-factory simulation environments. In most environments, STI films provided better protection than ENIG and OSP, but the search for a better prevention for creeping corrosion continued. At the time of this writing, a new set of topcoat films had been formulated. The new film XD-7526 showed a dramatic increase in corrosion prevention; Figure 6. Organic topcoats should protect the metal surfaces, but they must allow for good solderability and contact functionality. Several sets of data do indicate acceptable soldering and contact results with XD-7526 coatings; these data will be published at a later date.



Figures 5 a,b,c: Silver, STI, and STI Plus Coatings Exposed to MFG Class IV+ Gas Levels; 38°C, 90% RH



Figures 6 a&b: Silver and XD-7526 Corrosion Prevention Film Exposed to Tire Factory Simulation Environment

Summary

Corrosion is an inevitable fact in our increasingly polluted environment. Corrosion can be mitigated in several ways. The materials used in the manufacture of electronic devices need to be chosen wisely, based on available corrosion data. The materials should be protected from pollution by the use of protective coatings, device enclosures, or relocation of equipment to more protected environments. Humidity is a chief contributor to corrosion, as water allows intimate access of concentrated contaminating species and transportation of corrosion products. The choice of protective films needs to be weighed against other functional aspects of the film choices. Materials used in electronics manufacture will interact with different pollutants at differing rates based on pollutant levels and other environmental effects. In some cases, galvanic pairs can be created when using dissimilar materials, which can accelerate corrosion. To predict corrosion, and useful service life of electronic devices, historical data set can be consulted, but gaps exist in the rate of corrosion on surface finishing materials used in today's electronics. To fill in data gaps, industry groups can share resources in studying corrosion. New findings will allow for better predictability on service life, selection of appropriate coatings to fit specific needs, and development of more robust materials to protect circuitry.

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Prior to this position, Don served as Technology Manager for the circuit board surface finish business at MacDermid. Starting in MacDermid's Central R&D group 18 years ago, Don holds three patents and has been published in over 50 magazines, journals, and industry technical conferences. His chapter on PCB surface finishes is featured in Coombs' recently published "Printed Circuits Handbook." Don is a chemist; an alum of Rensselaer Polytechnic Institute in New York.