Ultrathin Fluoropolymer Coatings to Mitigate Damage of Printed Circuit Boards Due to Environmental Exposure

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Abstract
As consumers become more reliant on their handheld electronic devices and take them into new environments, devices are increasingly exposed to situations that can cause failure. In response, the electronics industry is making these devices more resistant to environmental exposures. Printed circuit board assemblies, handheld devices and wearables can benefit from a protective conformal coating to minimize device failures by providing a barrier to environmental exposure and contamination.

Traditional conformal coatings can be applied very thick and often require thermal or UV curing steps that add extra cost and processing time compared to alternative technologies. These coatings, due to their thickness, commonly require time and effort to mask connectors in order to permit electrical conductivity. Ultra-thin fluorochemical coatings, however, can provide excellent protection, are thin enough to not necessarily require component masking and do not necessarily require curing. In this work, ultra-thin fluoropolymer coatings were tested by internal and industry approved test methods, such as IEC (ingress protection), IPC (conformal coating qualification), and ASTM (flowers-of-sulfur exposure), to determine whether this level of protection and process ease was possible.

The fluoropolymer coatings chosen for this test were created in a range of coating solids and application thicknesses (100 nm to 30 µm). Being a solution, these coatings were easy to apply by either vertical dip or atomized spray methods. In this study, it was found that both the application method and the thickness of the fluoropolymer coating played a significant role in the level of corrosion resistance and water/vapor repellency results. The data generated demonstrates a general correlation of how thick an ultra-thin fluoropolymer coating must be in order to achieve certain levels of protection.

Background
As electronics become more mobile and are used in more challenging environments, protection from a variety of environmental factors has become increasingly critical to the lifetime performance of electronic devices. This includes protection against sulfur from the air, as well as moisture vapor and water immersion.

Circuitry subjected to harsh environments are susceptible to corroding relatively quickly.[1,2,3] The creep corrosion from exposure to these harsh environments often leads to electrical shorts and failures quickly because the characteristic dendritic growth can cause bridging.[1,2,3] For industries that rely heavily on the use of electronics to function, corrosion needs to be mitigated.

A study was conducted to determine whether ultra-thin fluorinated polymers (carried in segregated hydro-fluoroether fluids) would mitigate corrosion of exposed metal on printed circuit boards and electronic components under harsh environmental conditions. These coatings* do not require thermal curing and dry to a thin, transparent film with hydrophobic properties. Tests were conducted to show the capability of these coatings to protect metals against sulfur, moisture, liquids and corrosion under a variety of sulfur, water and salt water immersion conditions.

Corrosion Protection of Metal Surfaces from Sulfur
During the transition away from printed circuit board finishes that contain lead, many industries have reported corrosion when using circuitry plated with metals such as silver and tin due to sulfur exposure.[1,2,3] Industries that have cited these issues include petrochemical, water treatment, and rubber manufacturing.[3]

*Material Safety Data Sheets should be read and followed as to all applicable precautions and directions. Always practice smart and safe industrial hygiene practices.

Experiment Overview
Coatings were applied to printed circuit boards, which were then placed into a sulfur chamber, aged and inspected for corrosion on the metal traces.

Table 1 – Tested Coatings

Name	Approximate Thickness
F-1	0.1μm
F-4	0.5μm
F-8	1.0μm

Table 1. Three coatings were tested and this table shows the approximate thicknesses used. Coatings F-1, F-4 and F-8 are the same fluoroacrylate coating with 1.0wt%, 4.0wt% and 8.0wt%, respectively, in a segregated hydrofluoroether solution with a boiling point of 76^0C.

F-1

Ingredient	C.A.S. No.	% by Wt
Ethyl nonafluoroisobutyl ether	163702-06-5	50 - 60
Ethyl nonafluorobutyl ether	163702-05-4	30 - 40
Fluorinated polymer	Trade Secret	1
1-Methoxy-2-propyl acetate	108-65-6	< 1

F-4

Ingredient	C.A.S. No.	% by Wt
Ethyl nonafluoroisobutyl ether	163702-06-5	45 - 60
Ethyl nonafluorobutyl ether	163702-05-4	25 - 40
Fluorinated polymer	Trade Secret	3 - 5
1-Methoxy-2-propyl acetate	108-65-6	1 - 3

F-8

Ingredient	C.A.S. No.	% by Wt
Ethyl nonafluoroisobutyl ether	163702-06-5	50 - 65
Ethyl nonafluorobutyl ether	163702-05-4	25 - 40
Fluorinated polymer	Trade Secret*	7 - 9
1-Methoxy-2-propyl acetate	108-65-6	2 - 4

Test Boards
Standard IPC-B-25A test boards are commonly available and were used in the study. These printed circuit boards (PCBs) meet guidelines for the testing of solder masks (IPC-SM-804C) and conformal coatings (IPC-CC-830A).

Immersion silver (ImAg) finish is used in electronics as an alternative to lead-tin finishes.[1] Therefore, IPC-B-25A test boards with ImAg and bare copper (Cu) finishes were both treated with coatings and tested. Additionally, some with ImSnPb finish, vias and solder mask were also tested. Boards of each surface finish that were not treated with the coatings were used as control samples and tested under the same conditions as the boards which were treated.

It has been stated by some groups that flux residues, which result from the board construction process, may be necessary to simulate the dendritic growth involved in creep corrosion in the laboratory.[1] Because of this, in our study some boards were treated with flux and reflowed before being coated and tested. It was found that boards with no flux residues were just as susceptible to creeping corrosion as boards with flux residues. Therefore, the focus remained on the clean IPC-B-25A test vehicles, shown in Figure 1 below.
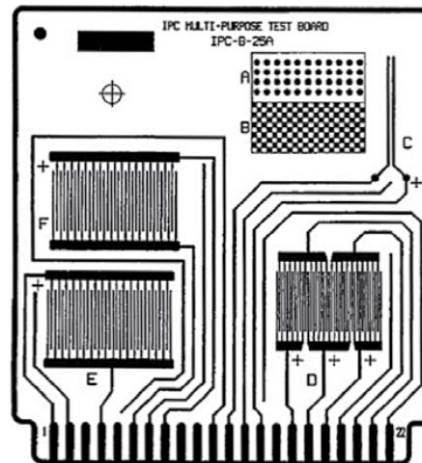
Figure 1. The IPC-B-25A test vehicle.

Coating Process

The IPC-B-25A test boards were cut in half vertically in order to accommodate the ASTM test conditions and the limited space in the test chamber. The cut boards were then cleaned with a segregated-hydrofluoroether fluid in a vapor degreaser. This fluid is effective at removing surface contaminants and particulate that, if left on the board, may have an impact on metal corrosion rates.

Each board was coated by a dip coating process. The process began with a chamber filled with one of the various coatings tested (F-1, F-4, F-8). The chamber sat on a table which moved up and down at a controlled rate. The rate at which the boards were removed controlled the thickness of the coating. In general, the faster the board is removed, the thicker the coating. The boards were dipped, held in solution for 30 seconds and removed from the coating solution at a rate of 12 inches per minute. The boards were allowed to dry and then placed into a flowers-of-sulfur test chamber as described below.

To simulate the type of conditions that might occur in the field, some boards were treated with flux prior to being tested. To do this, the coating process was modified slightly for boards that would be treated with flux. These test vehicles were first cleaned as stated above, the chosen flux was applied and the boards were then reflowed. The boards were allowed to cool to room temperature and then coated by the dip coating process as described above.

High Humidity/High Sulfur Test - "Flowers-of-Sulfur" (FoS)

A variety of methods can be used to test the porosity of coatings and protective finishes. The ASTM B809 method provides a standard method by which to induce corrosion of various metal finishes.[4] The test is designed to recreate the problematic high hydrogen sulfide gas and high humidity environment found in many industries.

The testing setup is shown in Figure 2. A 10L glass desiccator was used as the test vessel. Grease was never used to seal the lid to the chamber and there was a vented stopper which allowed for equilibration of the system without pressure buildup. The test vessel contained a potassium nitrate solution in which there was a Petri dish containing elemental sulfur floats. The samples were suspended at least 75 mm above the sulfur powder. The samples
were held in place above the sulfur source by an apparatus and the clips were not affected by the sulfur.
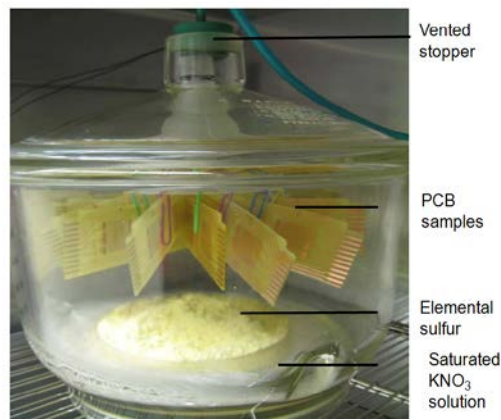
Figure 2. Samples in the flowers of sulfur chamber setup as described in the ASTM B809 test method.

Data

The FoS test method was used to study how the finish of a circuit board behaves in a corrosive, sulfur-containing environment. The method was designed to show whether attempts to mitigate corrosion, specifically creep corrosion, with a protective coating were successful.

Treated and untreated Cu finish test vehicles were exposed to the corrosive high sulfur environment in this study. After 10 days of exposure to the FoS test, untreated Cu finish boards were found to have succumbed to severe tarnish and creeping corrosion.

"Flowers-of-Sulfur" (FoS) Chamber Test Results (60°C, >90% RH)

Cu - Time = 0

Cu/uncoated = 10 days   Cu with F-1 = 10 days   Cu with F-4 = 10 days   Cu with F-8 = 10 days
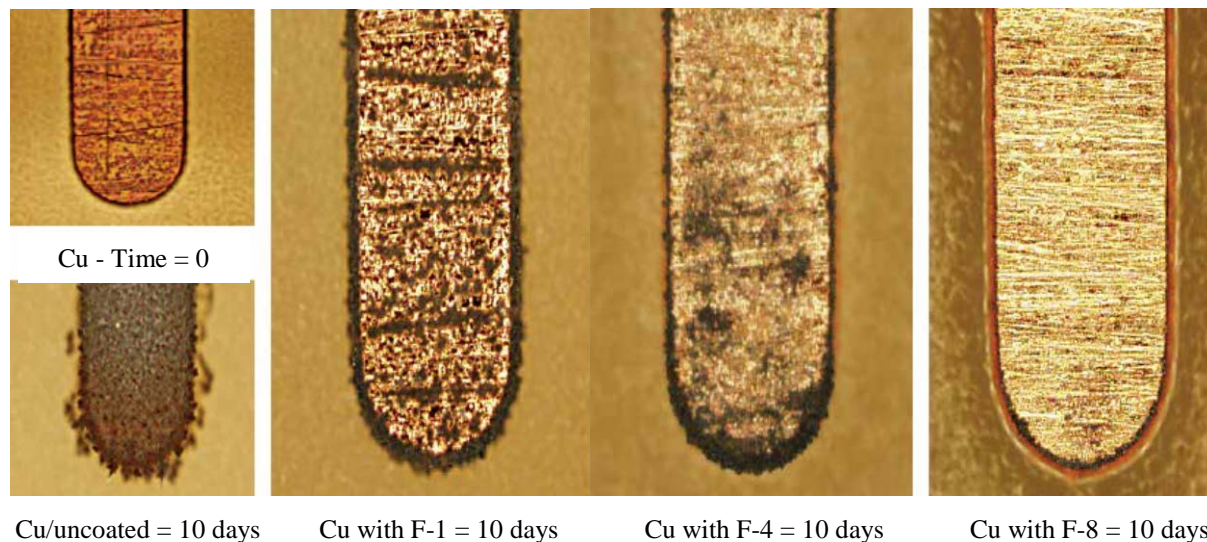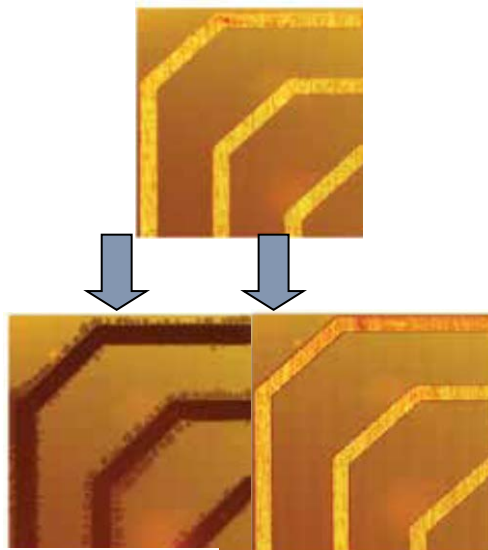
Figure 3. The pictures on the top and bottom left show uncoated Cu finish B-25A test vehicles before and after 10 days exposure in the FoS chamber. The three larger pictures on the right show Cu finish B-25A test vehicles which were coated with F-1, F-4, and F-8 after 10 days exposure in the FoS chamber.

Cu finish boards that were treated with the F-8 coating, however, had minimal tarnish and no creep corrosion after 10 days of exposure. There was also substantially less tarnish and corrosion on Cu finish boards which were treated with F-1 and F-4 coatings after 10 days than on untreated boards. The testing showed that the characteristic dendritic growth of creep corrosion was drastically reduced by the presence of F-1, F-4 and F-8 coatings.

The conclusion was that treatment of circuitry with coatings mitigated damages caused by exposure to the corrosive environment inside the FoS chamber. This difference in corrosion growth is shown in Figures 3 and 4.

Flowers-of-Sulfur (FoS) Chamber Test Results

(60°C, >90% RH) 10 Days

Cu - Uncoated = 10 days   Cu – with F-8 = 10 days

Figure 4. The pictures on the top and bottom left show uncoated Cu finish IPC-B-25A test vehicles before and after 10 days exposure in the FoS chamber, respectively. The bottom right picture shows a Cu finish IPC-B-25A test vehicle which was coated with F-8 after 10 days exposure in the FoS chamber.

Since ImAg and other finishes are often used to protect Cu circuitry, alternate finishes were also included in the study. Figure 5 shows results of coated and uncoated boards with these alternate finishes. The IPC-B-25A design was used for the ImAg finish boards and a custom designed test board was used for the ImSnPb finished boards. The latter was done in addition to the IPC-B-25A boards to determine whether the creep corrosion phenomena could be mitigated on a typical solder mask, which is present on circuit boards in most cases. The coatings did mitigate corrosion on both alternate finishes tested.

Flowers-of-Sulfur (FoS) Chamber Test Results (60°C, >90% RH) Alternate Finishes After 34 days

ImSnPb Finished
No Flux
34 Days

Uncoated   Coated with F-4

ImAg Finished
with Flux
10 Days

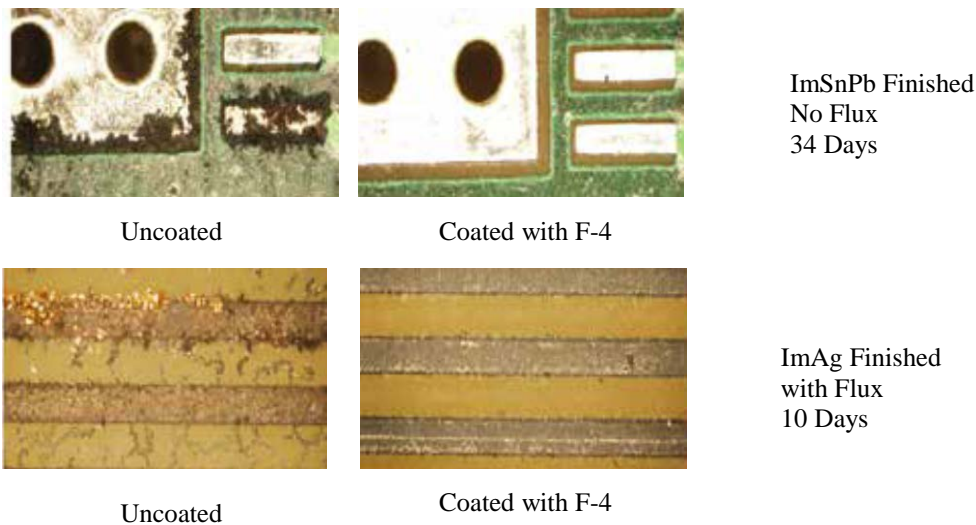Uncoated   Coated with F-4

Figure 5. The pictures on the top show uncoated and coated ImSnPb finish test vehicles after 34 days exposure in the FoS chamber, respectively. The bottom pictures show ImAg finish B-25A test vehicles uncoated and coated after 10 days exposure in the FoS chamber, respectively.

Protection of Printed Circuit Boards and Electronic Components from Water and Salt Water
For protection against moisture vapor and immersion, one method is to coat the internal surfaces of the electronic device components, including its printed circuit boards and connections.

Experiment Overview

Two coatings were tested and this Table 2 shows the approximate thicknesses used. Coatings F-8 and F-10 are different but both use a similar fluoroacrylate polymer in a similar hydrofluoroether solvent.

Table 2 – Tested Coatings

Name	Approximate Thickness
F-8	1.0μm
F-10	1.2μm

Table 2. Coating and typical thicknesses for coating printed circuit boards.

F-8

Ingredient	C.A.S. No.	% by Wt
Ethyl nonafluoroisobutyl ether	163702-06-5	50 - 65
Ethyl nonafluorobutyl ether	163702-05-4	25 - 40
Fluorinated polymer	Trade Secret	7 - 9
1-Methoxy-2-propyl acetate	108-65-6	2 - 4

F-10

Ingredient	C.A.S. No.	% by Wt
Methyl nonafluorobutyl ether	163702-07-6	20 - 80
Methyl nonafluoroisobutyl ether	163702-08-7	20 - 80
Fluoroaliphatic polymer	Trade Secret	9 – 11

Testing began by applying the coating over rigid printed circuit boards with electrical test patterns. The circuit boards were then connected to an external power supply that maintained a constant voltage. Based on a modification of the IPX7[5,6] testing standard, powered test boards were immersed in water or salt water for an extended time period. Current leakage across the circuit was then measured over time and charted to determine the effect of the water on the circuitry.

Test Boards
For this study, the IPC-Association Connecting Electronics Industries approved printed test boards IPC-B-25A[7] were used. The IPC-B-25A test board meets guidelines for testing solder masks (IPC-SM-804C) and conformal coatings (IPC-CC-830B) and is shown in Figure 1 above.

Board Preparation and Coating Application
The boards were cut vertically to isolate the test pattern D from patterns E and F. Test patterns D, E and F were then used separately in the water immersion test. Prior to coating, the boards were cleaned with a segregated-hydrofluoroether fluid in a vapor degreaser. This fluid is effective at removing surface contaminants and particulates that, if left on the circuit board, might impact coating performance.

Either spray coating (in a controlled environment) or dip coating can be used as application methods. For this study, both methods were used to demonstrate the flexibility of application options and to measure any differences resulting from the application methods. For testing, boards with different targeted thicknesses of the coatings were generated by spraying, dipping or a combination of these processes.

For dip coating, the process began with a chamber filled with one of the coatings. The chamber was on a table which moved up and down at a controlled rate. The removal rate of the boards controlled the thickness of the coating. In general, the faster the board is removed, the thicker the coating. To coat the boards, they were dipped, held in solution for 30 seconds and removed from the coating solution at a rate of 12 inches per minute. The boards were allowed to dry and then wire leads were soldered to the board's contacts. These contacts and the lead connected to the open structure comb pattern were insulated by covering with 100% silicone, leaving just the comb structure test pattern exposed. The board was then placed in the immersion test chamber. Spray coating can be done manually or by automated spray.

Spray coating can be done manually or by automated enclosed spray equipment but must be done in a controlled environment. For this study, boards were coated using a hand operated air driven sprayer. The volume of coating applied was varied so a thickness of 2 µm or less was achieved. Wire leads were then soldered to the boards and insulated with silicone as described above.

IPX7 Test Method and Modifications
The water immersion test was based on a modification of the IPX7 test standard that has been established by the International Electrotechnical Commission (IEC).[8,9] The IP Code, sometimes referred to as the Ingress Protection Rating,[10,11] classifies the degree of protection against intrusion into the interior of a device. The IPX standard and tests have been used by the electronics industry for evaluating the ability of water, dirt, dust and other contaminants to ingress into an enclosure. Protection from these contaminants is critical as they have the potential to create conditions that could shorten the service life of an electronic device.

Although there are multiple levels of IPX protection classifications, IPX7 is often referenced for water immersion testing. It provides an indication as to how well an electronic device would survive if immersed in water. This test calls for an unpowered electronic device to be immersed in 1 meter of water for 30 minutes. After the 30 minutes, the device is removed and the power turned on. If it operates as it was designed, the device is considered to meet the IPX7 classification. While the IPX7 test method uses actual commercial devices, device enclosures can vary in their design and ingress capability. For this reason, this study eliminated the enclosure and evaluated the performance of coatings applied directly on exposed test boards.

To test at a rigorous level (beyond the IPX7 test protocol), testing in salt water was also carried out. To ensure that a device's electronics would survive these conditions, plus add another level of performance requirements, the sample boards were tested under power. A comparison of these test methods are described in Table 3.

Table 3: IPX7 and test conditions A and B

Test Method	Immersion Depth	Liquid Media	Time (Min)	Powered
IPX7	1 Meter	Water	30	No
A	1 Meter	Water	60	3 Volts
B	1 Meter	5% aqueous NaCl	60	3 Volts

Using a potentiostat[12] in conjunction with an impedance analyzer, a constant current of 3 volts was applied to the test pattern. Current leakage across the open comb structure test pattern (D, E or F from Figure 1) during the 60 minute immersion test was then measured. After 60 minutes, the board was removed, rinsed with water and evaluated. The system for Test Methods A and B is depicted in Figure 6.
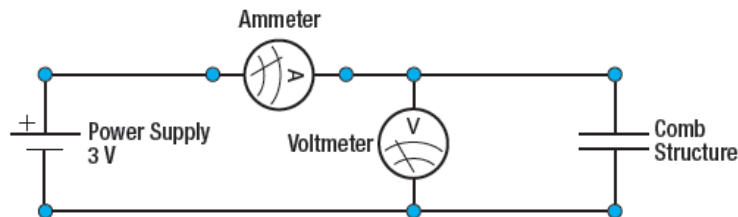

Figure 6. Electrical wiring for Test Methods A and B

Test Results
While the IPX7 is a test to show water ingress, our testing eliminated the enclosure, ensuring that test boards were completely exposed to the aqueous solutions. To make the testing more aggressive, modifications were made beyond the IPX7 protocol: 1) immersing in both water and salt water, 2) powering the electronics during testing and 3) extending the immersion time to 60 minutes. In all of these cases, the coated sample boards did not demonstrate the corrosion and degradation of the metal traces to the extent that the uncoated samples boards showed.

Test Method A was used to test IPC-B-25A printed test board patterns D, E and F coated with F-10 or F-8. There was no corrosion, dendritic growth, copper loss or line thinning observed (Figure 7). When Test Method A was used on uncoated test patterns, there was significant corrosion and line thinning (Figure 8).
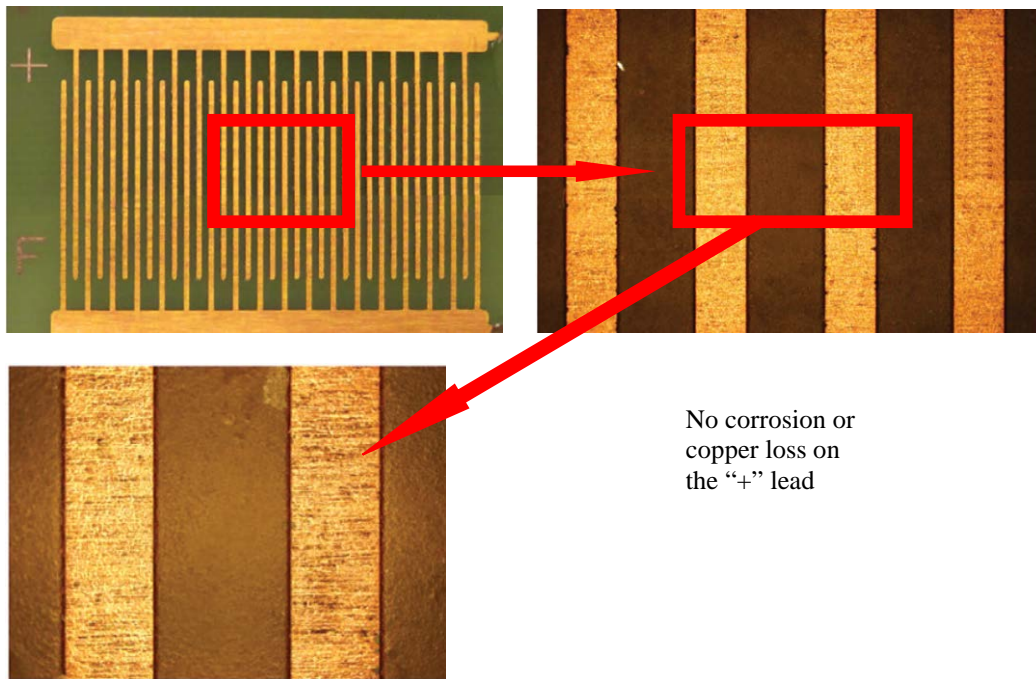
No corrosion or copper loss on the "+" lead

Figure 7. Example: F-10 and F-8 coated test patterns performed similarly after Test Method A.

Test Method B replaced the water with a 5% aqueous sodium chloride solution. This method made for an extremely aggressive test, as exemplified by the striping of the copper trace lines from the test boards during the immersion time. Even within this environment, the coatings protected the surfaces. When Test Method B was used to test boards coated with F-10 or F-8, there was minimal corrosion in spots along the edge of copper traces. Uncoated test patterns when tested with Test Method B were completely corroded and much of the copper tracings were removed from the board, thus creating electrical connection opens (Figure 8).

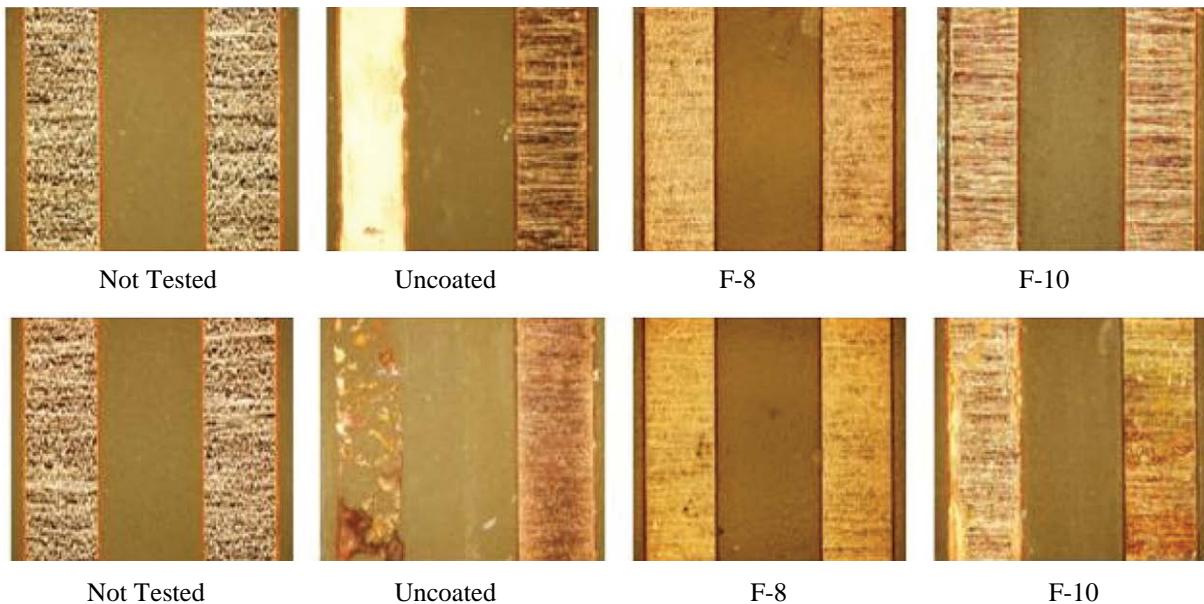| Not Tested | Uncoated | F-8 | F-10 |

| Not Tested | Uncoated | F-8 | F-10 |

Figure 8: Summary of F-8 and F-10 coated test patterns after Test Method A and Test Method B. Note that the uncoated lines show signs of loss of the copper traces.

For the coated boards, current leakage (as measured by the potentiostat) across the test circuit was negligible at less than 0.01 amps. In contrast, for the uncoated boards, current leakage across the test circuit was immediate and significant (exceeding 2 amps) when using either Test Method A and B. The uncoated test pattern under these conditions typically failed within 60

minutes as shown by complete copper loss on the positively charged side of the pattern. Boards coated with F-8 and F-10 did not fail (Figure 9).
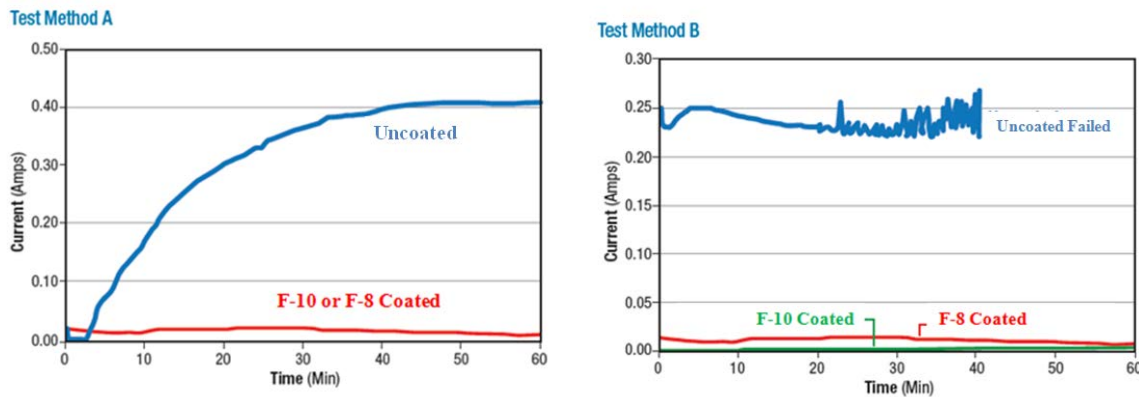

Figure 9: Potentiostat data showing current flow

Uncoated test boards had extensive corrosion when immersed in both water and salt water. This was evident by observing current flow immediately across the test pattern when exposed to the test fluid. In contrast, test boards coated with F-8 or F-10 showed no current flow even after 60 minutes.

Summary and Conclusions
Protection of printed circuit boards and their components is an increasing concern as electronics are used in more environmental conditions. Sulfur, water vapor and water immersion can significantly shorten the working capabilities of an electronic device.

The testing above highlights how ultra-thin fluorochemical coatings and their thicknesses needed, can provide an effective barrier for metals, surfaces and electronic circuit boards for protection from sulfur, moisture, liquids, and corrosion. This barrier adds to the performance, longevity and reliability of the surfaces, metal connections and an electronic device's service life.

References

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[2] Kenny, Jim, Karl Wengenroth, Ted Antonellis, ShenLian Sun, Cai Wang, PhD, Edward Kudrak, and Joseph Abys, PhD. "PWB Creeping Corrosion Mechanism and Mitigation Strategy." Enthone Inc., Crookstone Electronics, n.d. Web.

[3] Schueller, Randy, PhD. "Creep Corrosion on Lead-Free Printed Circuit Boards in High." Dfrsolutions.com. SMTA International Proceedings, Oct. 2007. Web. 19 Aug. 2013.

[4] "ASTM B809 - 95(2008)." Standard Test Method for Porosity in Metallic Coatings by Humid Sulfur Vapor ("Flowers of Sulfur"). N.p., n.d. Web. 15 Aug. 2013.

[5] The IP Code is a test standard published by International Electrotechnical Commission (IEC) and describes the level of protection provided by an enclosure. For an explanation of the IP code see: http://www.ce-mag.com/archive/06/ARG/bisenius.htm

[6] IP Code Defined: http://www.osram.com/media/resource/hires/342330/technical-applicationguide---ip-codes-in-accordance-with-iec-60529-gb.pdf

[7] IPC-Association Connecting Electronics Industries is an organization that sets standards used by the electronics manufacturing industry: https://www.ipc.org/default.aspx

[8] IEC 60529: Degrees of protection provided by enclosures (IP Code). International Electrotechnical Commission, Geneva: http://www.iec.ch/

[9] IP Ratings vs. NEMA Ratings: http://www.bisonprofab.com/ip-ratings-explained.htm

[10] Understanding the IP (Ingress Protection) Ratings: http://www.maximintegrated.com/app-notes/index.mvp/id/4126

[11] Interpreting the acronym officially in the standard text: http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=39578

[12] Solartron is a trademark of Solartron Analytical and is a manufacturer of electronic instruments: http://solartronanalytical.com/