Relative Humidity Dependence of Creep Corrosion on Organic-Acid Flux Soldered Printed Circuit Boards

Haley Fu
iNEMI, Shanghai, China

Prabjit Singh
IBM Corporation, Poughkeepsie, NY, USA

Dem Lee and Jeffrey Lee
iST-Integrated Service Technology, Inc., Taiwan

KarlosGuo and Julie Liu
Lenovo (Beijing) Limited Corporation, Beijing, China

Simon Lee and Geoffrey Tong
The Dow Chemical Company, Taipei and Hong Kong

Chen Xu
Nokia, Murray Hill, NJ, USA

Abstract
Creep corrosion on printed circuit boards (PCBs) is the corrosion of copper metallization and the spreading of the copper corrosion products across the PCB surfaces to the extent that they may electrically short circuit neighboring features on the PCB. The iNEMI technical subcommittee on creep corrosion has developed a flowers-of-sulfur (FOS) based test that is sufficiently well developed for consideration as an industry standard qualification test for creep corrosion. This paper will address the important question of how relative humidity affects creep corrosion. A creep corrosion tendency that is inversely proportional to relative humidity may allow data center administrators to eliminate creep corrosion simply by controlling the relative humidity in the data center,thus, avoiding the high cost of gas-phase filtration of gaseous contamination. The creep corrosion relative humidity dependence will be studied using a modified version of the iNEMI FOS test chamber. The design modification allows the achievement of relative humidity as low as 15% in the presence of the chlorine-releasing bleach aqueous solution. The paper will report on the dependence of creep corrosion on humidity in the 15 to 80% relative humidity range by testing ENIG (gold on electroless nickel), ImAg (immersion silver) and OSP (organic surface preservative) finished PCBs, soldered with organic acid flux.

1. Introduction

Creep corrosion on printed circuit boards (PCBs) is the corrosion of copper metallization and the spreading of the copper corrosion products across the PCB surfaces to the extent that they may electrically short circuit neighboring features on the PCB**[1-9]**. Creep corrosion occurs in computers located in geographies high in sulfur-bearing gaseous contamination. The question often raised by data center administrators is the role of humidity on creep corrosion: Can the lowering of relative humidity alone lower creep corrosion propensity? If creep corrosion happens to be a strong function of relative humidity, such that it becomes negligible or nonexistent at low relative humidity of, say, 50% or less, then creep corrosion can be eliminated simply by lowering the relative humidity in data centers, saving the data center administrators from having to take the costly step of gas-phase filtration of gaseous contamination. Even though hundreds of creep corrosion incidents have occurred worldwide, there is no reliable recorded or published information on the data center temperature and humidity range in which these failures occurred. ASHRAE is the only organization known to have surveyed data centers for corrosion. The survey published in a white paper concluded that the two common modes of corrosion related hardware failures, the creep corrosion of copper on PCBs and the corrosion of silver termination in surface mount resistors, occur when the copper and silver corrosion rates are more than 300 and 200 Å/month, respectively **[10]**. The survey did not include the temperature and humidity conditions under which corrosion occurs. This paper attempts to address the role of relative humidity on creep corrosion through laboratory tests in an iNEMI designed flowers-of-sulfur (FOS) chamber **[11-15]**. The mixed-flowing gas chamber approach was not considered as a viable approach given its expense and limited availability to the taskforce member companies. The chamber used in the study was the same as that described earlier for creep corrosion qualification testing by iNEMI**[11-15]**with a major change in the way the chloride and water vapor are allowed to escape in to the chamber. In the

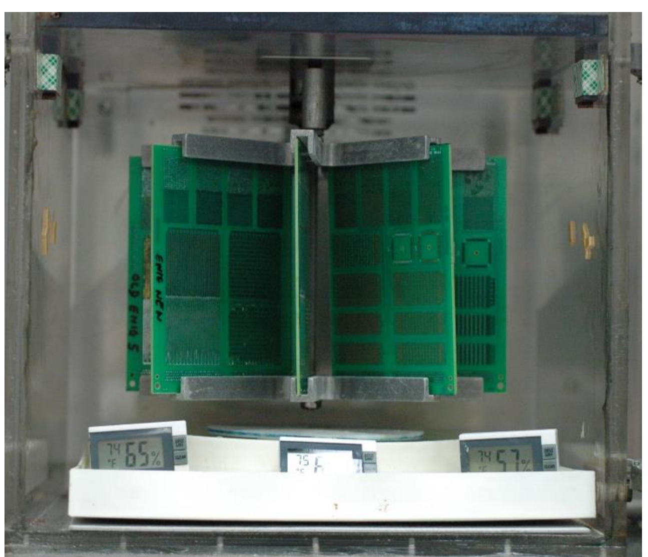


Figure 1: FOS test setup loaded with test PCBs. The tray-like setup below the test PCBs provides the sulfur and chlorine gases and maintains the relative humidity in the chamber at the deliquescence relative humidity of the saturated salt solution in the setup.

creep corrosion qualification test, the sulfur vapor with controlled concentration is provided by two 100-mm diameter petri dishes and by maintaining the chamber temperature at 50°C. The relative humidity is maintained at 81% using two 80-mm diameter petri dishes containing KCl saturated solution. The source of chlorine, while repeatable though time varying in concentration, is provided by 40-ml of household bleach in a 100-ml beaker. While this setupworks well for creep corrosion studies where the 81%RH is desirable, it does not lend itself to a study of creep corrosion as a function of relative humidity because the water vapor evaporating off the bleach in an uncovered beaker overwhelms the capability of the saturated salt solution to control the humidity in the chamber. This paper describes in detail an innovative way of controlling the relative humidity in a FOS chamber from about 15 to 80% in the presence of a bleach containing 8.25% sodium hypochlorite. The innovate setup allows the escape of enough chlorine from the bleach while having the saturated salt capture the water vapor, coming off the bleach, at a fast enough rate to allow the saturated salt solution to dominate the relative humidity in the chamber. The paper describes the creep corrosion on PCBs in FOS chambers as a function of relative humidity in the 15-80% range at 50°C.

2. Experimental procedure and results

The FOS chamber, shown in **Figure 1**, isa 300-mm cube acrylic box with 8-paddle wheels rotating at 20 RPM that can accommodate 8 printed circuit boards under test. The setup to control the sulfur and chlorine gas concentrations and the relative humidity in the chamber is described in **Figure 2**. The sulfur is provide by a 275-mm square tray, 20-mm deep, with a 195-mm circular opening in the center. The sulfur concentration is controlled by placing the chamber in an oven maintained at a constant 50°C. The household bleach, containing 8.25% sodium hypochlorite, is contained in a 145-mm diameter petri dish that sits inside the sulfur tray on the same platform as the sulfur tray. The saturated salt solution is in a 190-mm diameter tray with a circular opening of 65-mm diameter in the center, which is covered by a circular plate with 1-mm setup gap to allow controlled escape of the chlorine gas from the bleach. The cover plate also throttles the escape of water vapor from the bleach such that the saturated salt solution can dominate the relative humidity in the chamber at its deliquescence relative humidity. The ability of the setup to control the temperature and relative humidity and maintain them at the desired values is demonstrated in **Figure 3**. The chamber reaches steady state in two hours. With zinc chloride saturated solution in the chamber at 50°C, the humidity stabilized at about 15%, which is the deliquescence relative humidity of $ZnCl_2$.

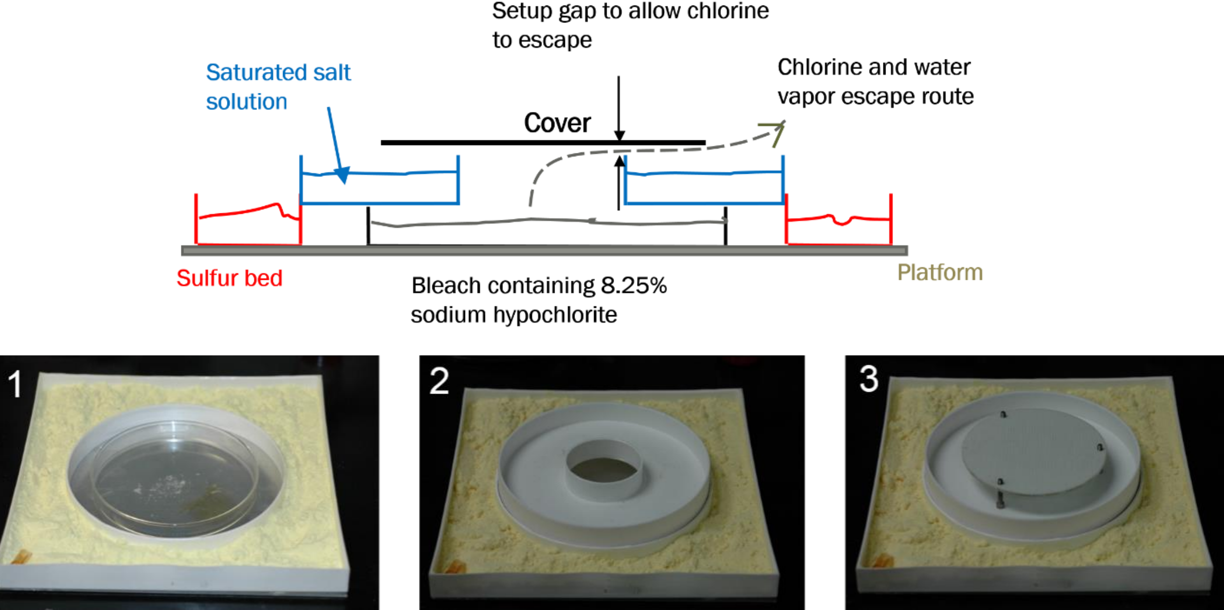


Figure 2: Bleach setup in cross section and in pictorial format.

The copper and silver corrosion rates in an empty chamber, containing no PCB test boards, as a function of humidity and setup gap are shown in **Figure 4**. The corrosion rates, based on one-day exposure of 25x50 mm copper and silver foils, were measured using the coulometric reduction technique **[16]**. The copper corrosion rate was about 600 Å/day at 15% RH and rose three fold to about 1600 Å/day at 80%RH. The silver corrosion was also about 600 Å/day at 15%RH but rose to a lesser extent as the humidity was raised. Interestingly, the AgCl growth rate decreased from about 100 Å/day at 15%RH to about 25 Å/day at 80%RH. The effect of setup gap on copper and silver corrosion rates was not significant: the corrosion rates increased only slightly with setup gap increased from 1 to 3 mm. However, the AgCl formation rate did see a dramatic increase from almost zero for a 1-mm gap to about 100 Å/day for a 3-mm gap. The iNEMI test boards used in the study were of the same design as described earlier by the taskforce on creep corrosion testing **[11-15]**. **Figure 5** shows the top and the bottom views of the test boards. PCBs of 5 finishes were tested: two types of organic surface preservation (OSP) finishes, one immersion silver (ImAg) finish and two types of gold on electroless nickel (ENIG) finishes. The flux used for the wave soldering was ORL0 organic acid no-clean flux. The top side locations L12 and L14 had reflowed solder paste. The bottom side was wave soldered with the middle half shielded from the solder wave. As per the standardized iNEMI creep corrosion qualification test **[14-15**], the test PCBs were prebaked at 105°C in flowing nitrogen gas for 24 hours. Creep corrosion test runs were conducted in 5 humidity levels. At each humidity level, a 5-day test run was followed by another 5 day test run on the same PCBs. The copper and silver corrosion rates and the rate of formation of AgCl measured during each 5-day period using the coulometric reduction -technique are plotted in **Figure 6**. The extent of creep corrosion was documented after each 5-day run. **Table 1** lists the creep corrosion results at the 5 humidity levels after 5 and 10 day test runs.

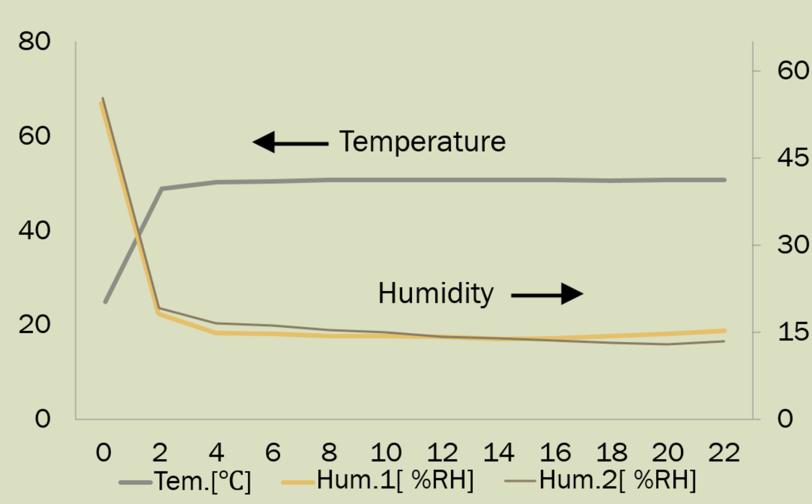


Figure 3: Ability of the setup to control and stabilize the temperature and humidity.

All tests were run All tests were run with 1-mm setup gap, except for the 78-81% relative humidity run which was conducted with a 3-mm setup gap to ensure enough chlorine gas entered the FOS chamber.

3. Discussions

The major challenge in this research project was the attainment and the control of relative humidity in the FOS chamber in the 15-80% range in the presence of the aqueous household bleach, containing 8.25% sodium hypochlorite, which is the source of chlorine gas necessary for acting synergistically with sulfur vapors to cause creep corrosion on susceptible PCBs. Many approaches were tried to throttle the water vapor evaporating off the bleach to allow the saturated salt solution to dominate and control the relative humidity in the chamber. The successful setup is shown in **Figure 2** in cross section and in a pictorial format. The main feature of the setup is the 1-mm setup gap, described in **Figure 2a**,which throttles the water vapor evaporating off the bleach and forcing the water vapor to flow horizontally over the saturated salt solution so that the saturated salt solution can dominate and control the humidity in the chamber. The challenge of humidity control is especially acute at low humidity. **Figure 3** shows that this challenge was met: Zinc chloride saturated salt solution successfully controlled the relative humidity at about 15% in the presence of household bleach. The chamber reached equilibrium in about 2 hours.

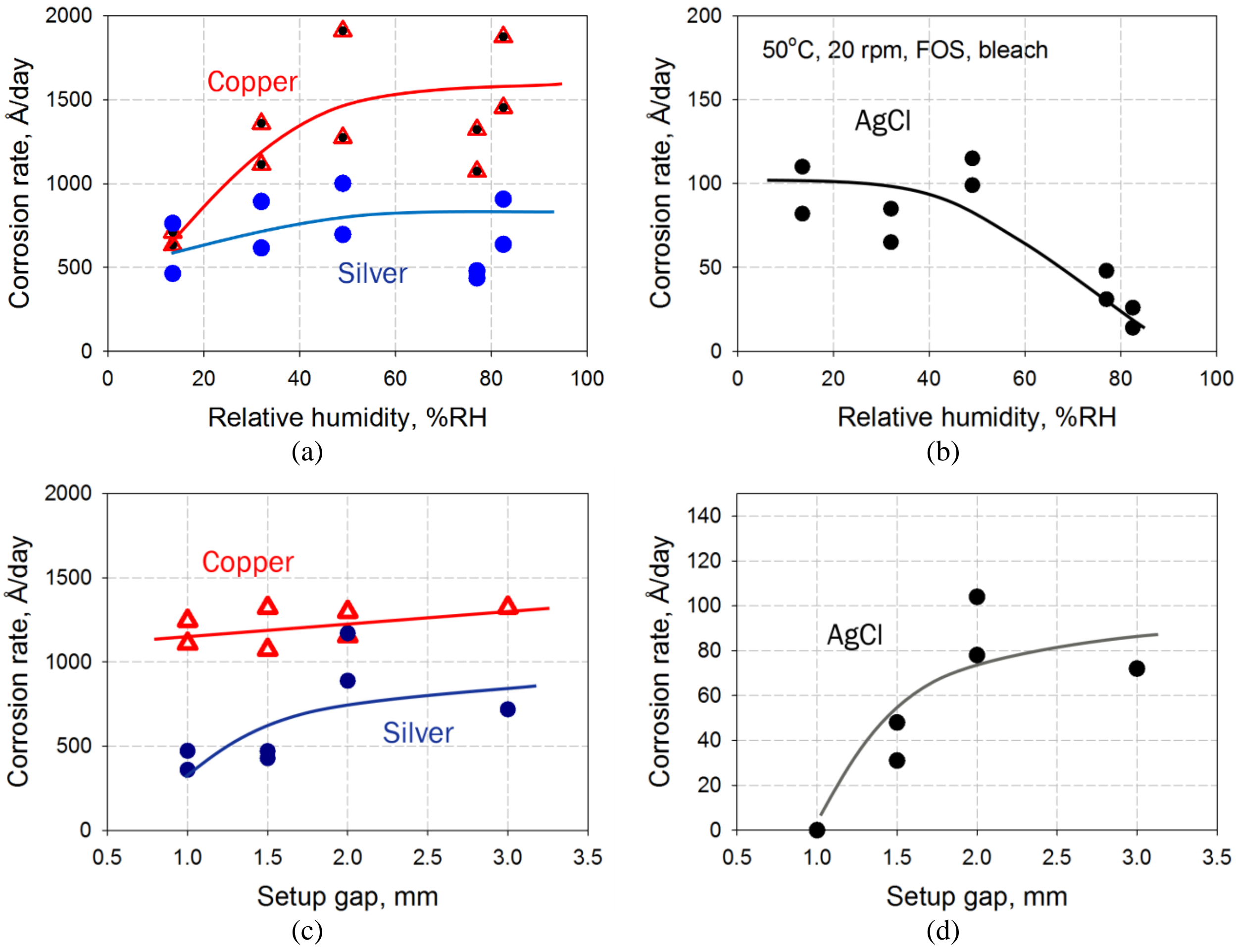
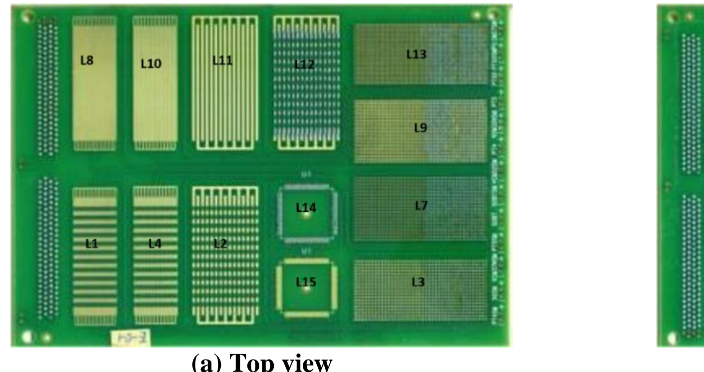
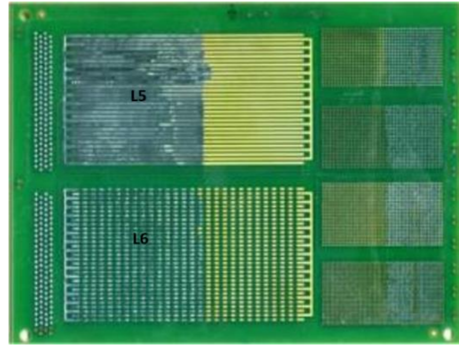


Figure 4: Copper and silver corrosion rates in a FOS chamber with no test PCB loading. The corrosion rates were measured using coulometric reduction on Cu and Ag foils exposed to the chamber environment for one day. The corrosion rates versus setup gap were measured at 80% relative humidity.





(a) Top view **(b Bottom view**

Figure 5: Layout of the test PCBs.

A number of corrosion rate test runs were conducted in the FOS chamber, without test PCB loading, as function of relative humidity and setup gap. **Figure 4** shows that the copper corrosion rates increased with relative humidity much more so than the silver corrosion rate. The AgCl formation rate decreased with relative humidity may be because of the chlorine gas being absorbed by the moisture adsorbed on the chamber walls at high humidity. Both silver and copper showed some increase in corrosion rates as a function of setup gap at 80% relative humidity; whereas, the AgCl formation rate was a strong function of setup gap with the formation rate being almost zero at 1-mm setup gap. The copper and silver corrosion rates in a chamber loaded with test PCBs showed a decrease in corrosion rates as a function of relative humidity probably because the loading with 5 test PCBs increased the area on which the absorption of the corrosive gases could occur by the moisture adsorbed on the test PCB and the chamber walls. The AgCl formation rate also decreased with relative humidity as it did in the chamber with no test PCB loading, indicating that the chlorine gas may have a greater propensity of being absorbed by the surface moisture compared to the sulfur gas.

The results of the first of its kind study of creep corrosion propensity on PCBs with 5 different finishes, soldered with organic acid flux, as a function on relative humidity, shown in **Table 1**, indicates that there is no data center relative humidity threshold below which PCBs will not suffer creep corrosion. The results of the study should be valid for PCBs soldered with organic acid flux exposed to 50ºC ambient environments high in sulfur and chlorine gases. The OSPA finished test PCBs were free from creep corrosion at all humidity levels. Severe creep corrosion was observed on OSP-B and on ImAg finished PCBs at relative humidity as low as 11-17% and on ENIG finished PCBs in the 31-46% relative humidity range.

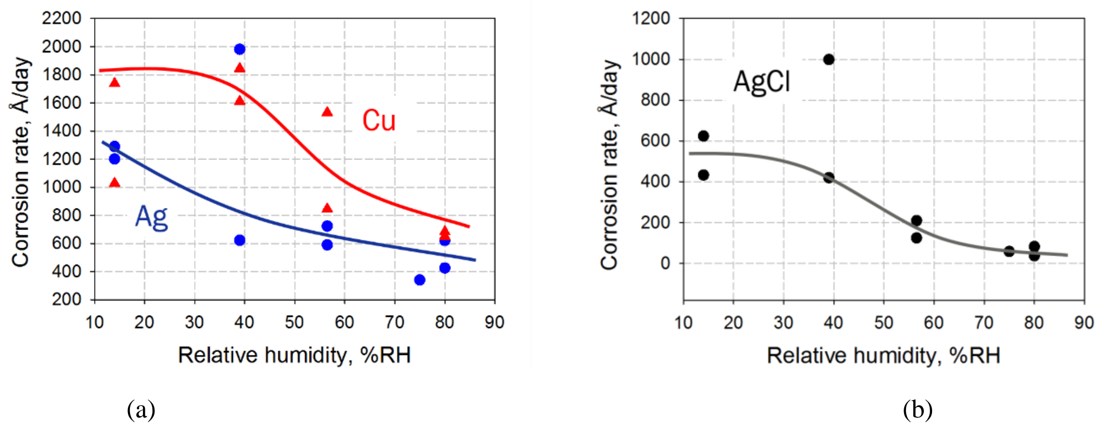


Figure 6: Corrosion rates in FOS chamber loaded with 5 test PCBs and one set of 25x50-mm copper and silver foils. (a) Cu and Ag corrosion rates, (b) AgCl formation rate.

Table 1: Creep corrosion occurrence as a function of PCB finish and relative humidity. The micrographs showing creep corrosion are highlighted with red background.

Finish	Day	Relative humidity				
		11-17%	**31-46%**	**57-62%**	**74-77%**	**78-81%**
OSP A	5		No corrosion			
	10		No corrosion			
OSP B	5			No corrosion		
	10					
ImAg	5					
	10	Did not continue				
ENIG	5					
	10		Did not continue			
ENIG with post organic coating	5					
	10		Did not continue			

This result provides the first experimental evidence of the previous assertion that “creep corrosion can occur on a dry This result provides the first experimental evidence of the previous assertion that “creep corrosion can occur on a dry surface” if certain types of contaminants are present to make the PCB surfaces susceptible to creep corrosion **[17, 18]**.

In this particular case, the susceptibility to creep was promoted probably by the presence of un-deactivated organic acid flux residues. The amount of the un-deactivated flux residue depends on the flux application method, the reflow and the wave soldering thermal profiles. The lack of a common relative humidity threshold and the finding that some finishes on PCBs make them susceptible to creep corrosion at low humidity levels whereas as other finishes make the PCBs susceptible to creep corrosion at high humidity levels calls for a modification of the iNEMI creep corrosion qualification test. The modification to the qualification test would be to conduct creep corrosion tests at both high and low humidity levels of say 15% (using $ZnCl_2$ saturated solution) and 80% (using KCl saturated solution).

4. Conclusions

The relative humidity in FOS chambers can be controlled at any humidity level in the 15-80% range in the presence of household bleach by throttling the flow of moisture evaporating off the household bleach and forcing the moisture to flow over a saturated salt solution so that the salt solution can dominate and control the relative humidity at its deliquescence relative humidity value.

The corrosion rates of copper and silver and the rate of formation of AgCl in a sealed FOS chamber, loaded with test PCBs, decrease with rising relative humidity most probably because of the absorption of the sulfur and chlorine gases by the moisture adsorbed on the test PCB and the chamber walls.

Test PCBs soldered with organic acid flux showed high propensity to creep corrosion at relative humidity levelsas low as 11-17%. This result provides the first direct experimental evidence of creep corrosion occurring on “dry” surfaces on PCBs that are likely contaminated with un-deactivated flux residues.

There is probably no common threshold relative humidity level below which creep corrosion will not occur.

Creep corrosion of OSP, ImAg and ENIG finished test PCBs soldered with rosin flux will be studied as a function of relative humidity and reported in the near future. Following this study, the iNEMI creep corrosion qualification test relative humidity condition may be revised.

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Prabjit Singh, IBM Corporation

Poughkeepsie, New York

iNEMI creep-corrosion taskforce

- Haley Fu, iNEMI, Shanghai, China
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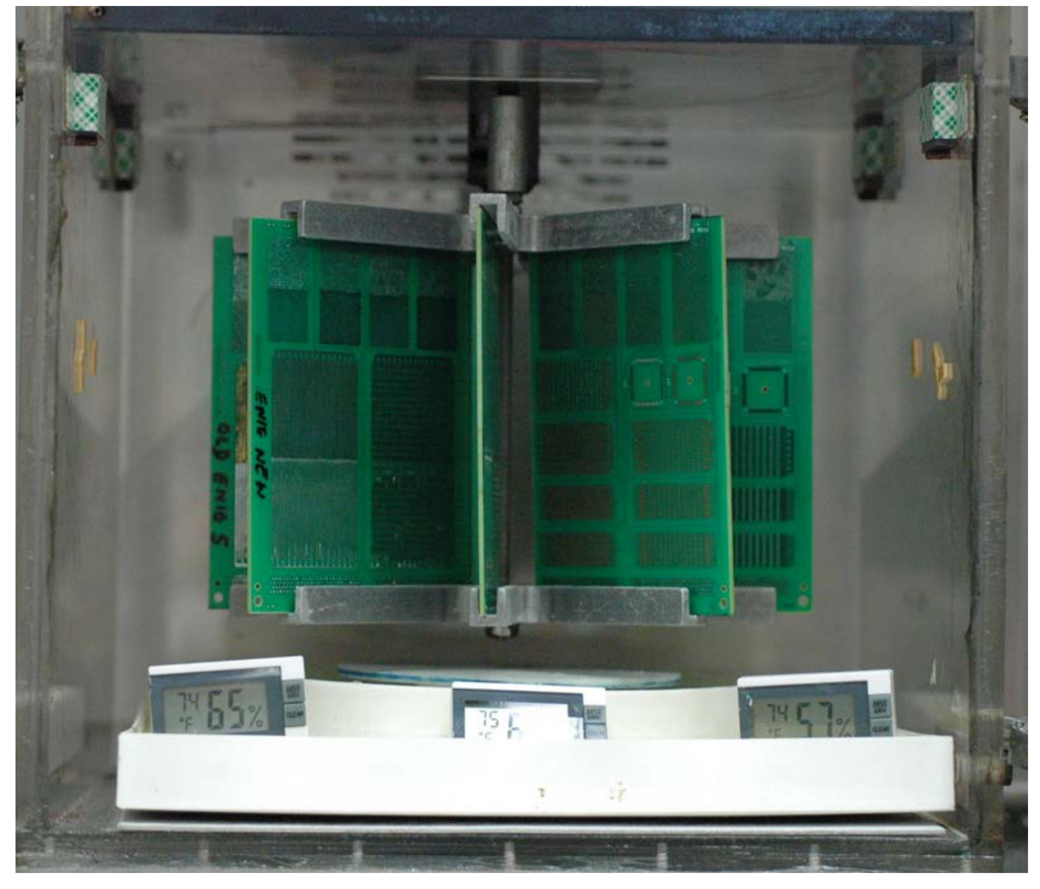
Agenda

- FOS chamber design and the bleach setup and gap
  - *Cu and Ag corrosion rates as function of humidity*
  - *Cu and Ag corrosion rates as a function of bleach setup gap*
- 5 and 10 day creep corrosion as a function of relative humidity
  - *Cu and Ag corrosion rates*
  - *Creep corrosion summary*
- Conclusions

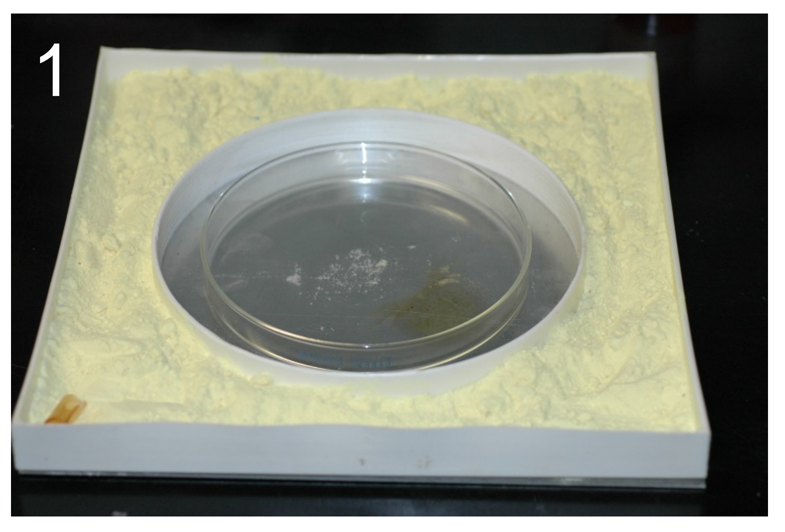
The modified iNEMI FOS chamber



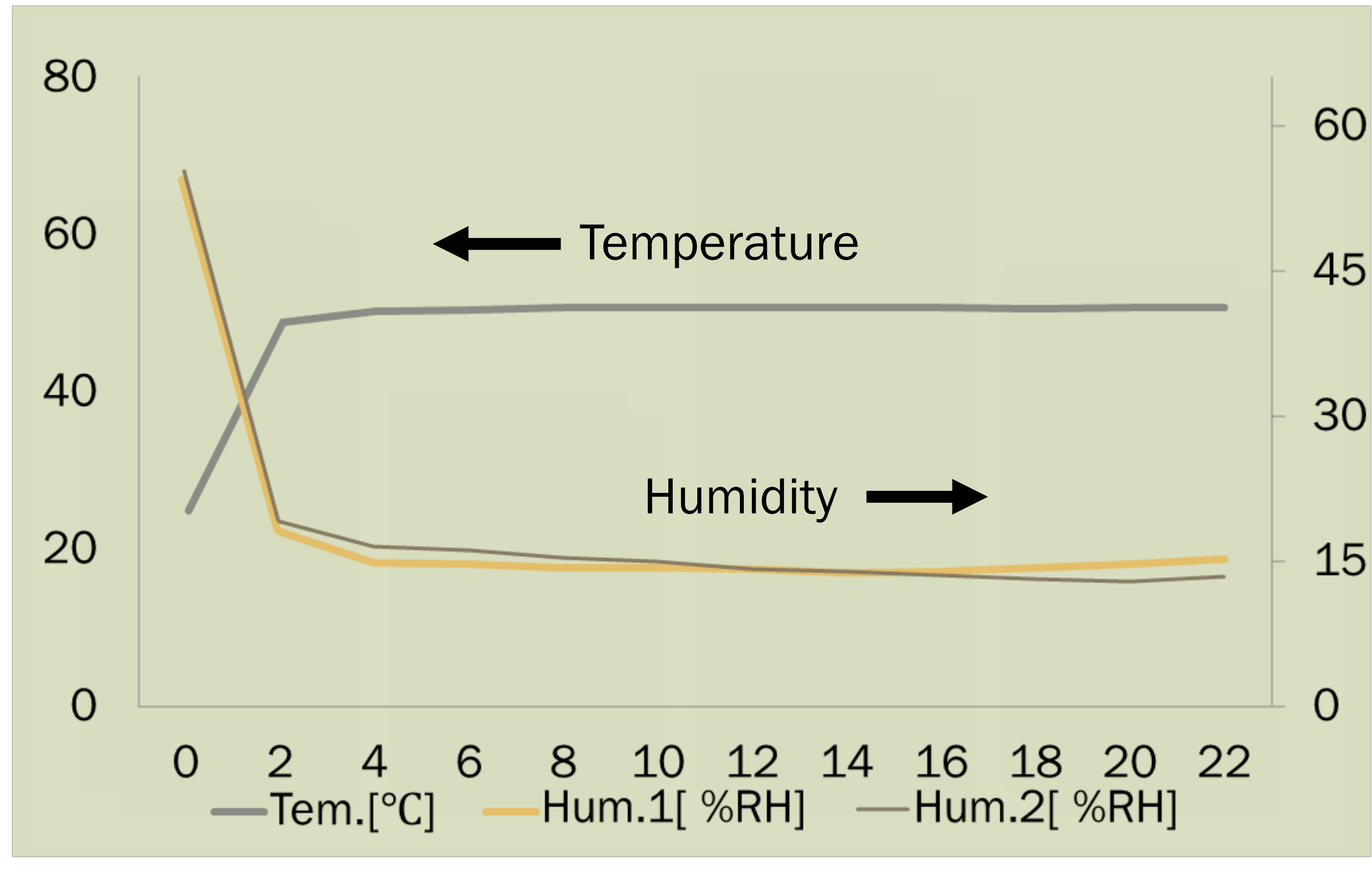
Setup to control humidity, sulfur and chlorine

Setup dimensions

The sulfur tray is 275 mm square, with an inner diameter of 195 mm and 20 mm high on the inside.
The glass petri dish has 145 mm inner diameter and is 15 mm high.
The salt dish has 185 mm outer dia and 67 mm inner diameter and is 20 mm deep.
The cover is 125 mm in diameter.
The cover is 1mm off the salt dish using 1-mm diameter wires in tripod fashion.
(The screws shown in the cover are no longer used.)



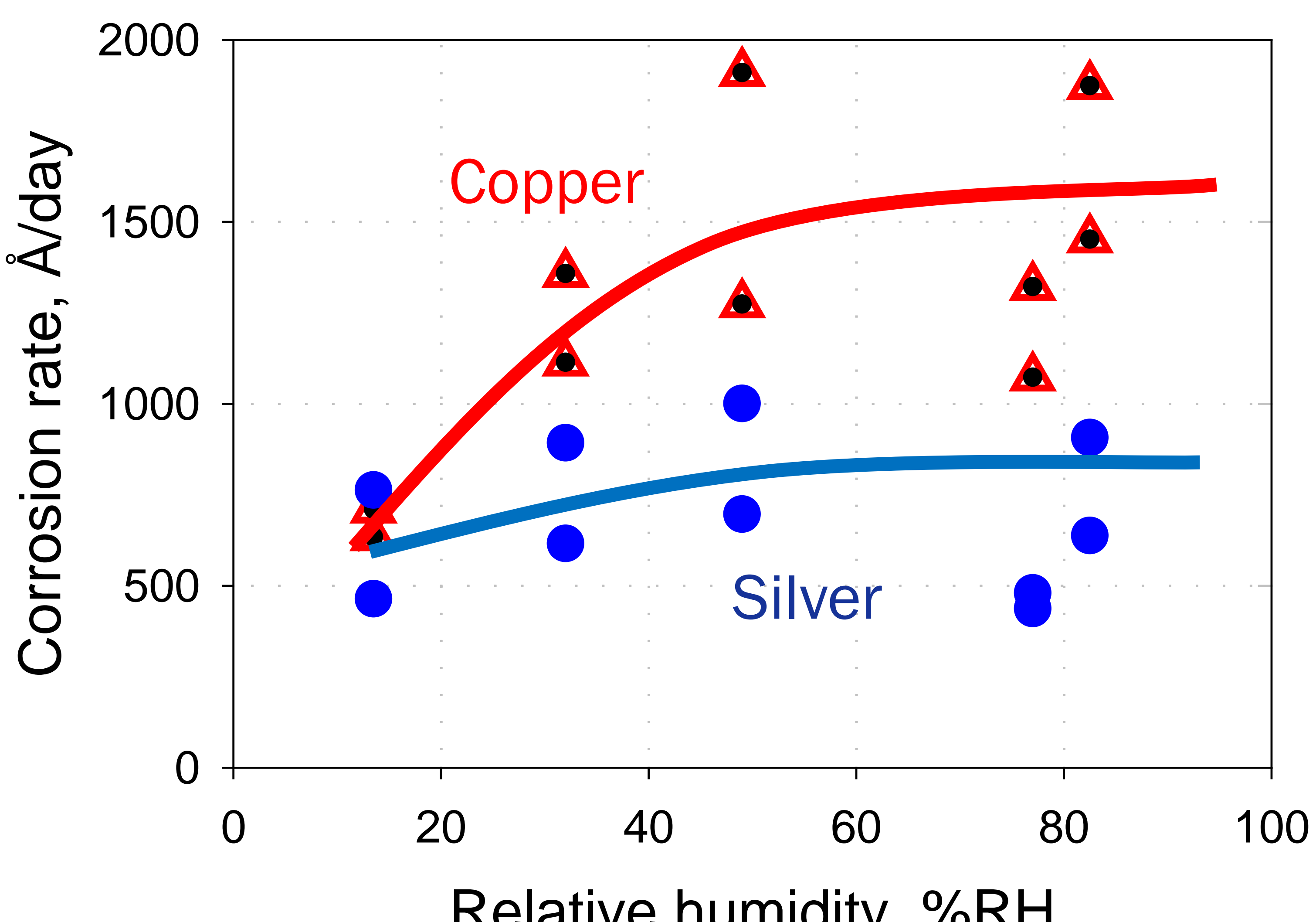
Example of how long it takes for the FOS chamber to reach steady state: $ZnCl_2$ saturated salt solution



Effect of setup gap with KCl saturated salt solution without PCB loading

	1-mm gap (run #16)			1.5-mm gap (run #15)			2-mm gap (run #19)			3-mm gap (run #20)	
%RH	77, 80, 80, 75			76, 79, 79 75			77, 79, 80, 75			79, 80, 81, 78	
	By mass	CR Inner	CR Outer	My mass	CR Inner	CR Outer	By mass	CR Inner	CR Outer	By mass	CR Middle
Cu_2O		380	272		324	369		253	266		492
CuO		85	113		43	34		0	0		61
Cu_2S		644	860		691	900		900	1032		770
Total Cu	876	1109	1245	1014	1073		967	1153	1298	1116	1323
Ag_2S		359	472		405	431		732	962		646
AgCl		0	0		38	46		78	104		72
Total Ag	411	359	472	665	443	469	749	810	1066	864	718

Cu and Ag corrosion rate as a function of humidity in FOS chamber at 50°C, 20 rpm, bleach and 1-mm gap except for 78-81%RH (KCl) with 1.5-mm gap. (without PCB loading)



AgCl growth rate as a function of humidity in FOS chamber at 50°C, 20 rpm, bleach and 1-mm gap except for 78-81%RH (KCl) with 1.5-mm gap(without PCB loading)

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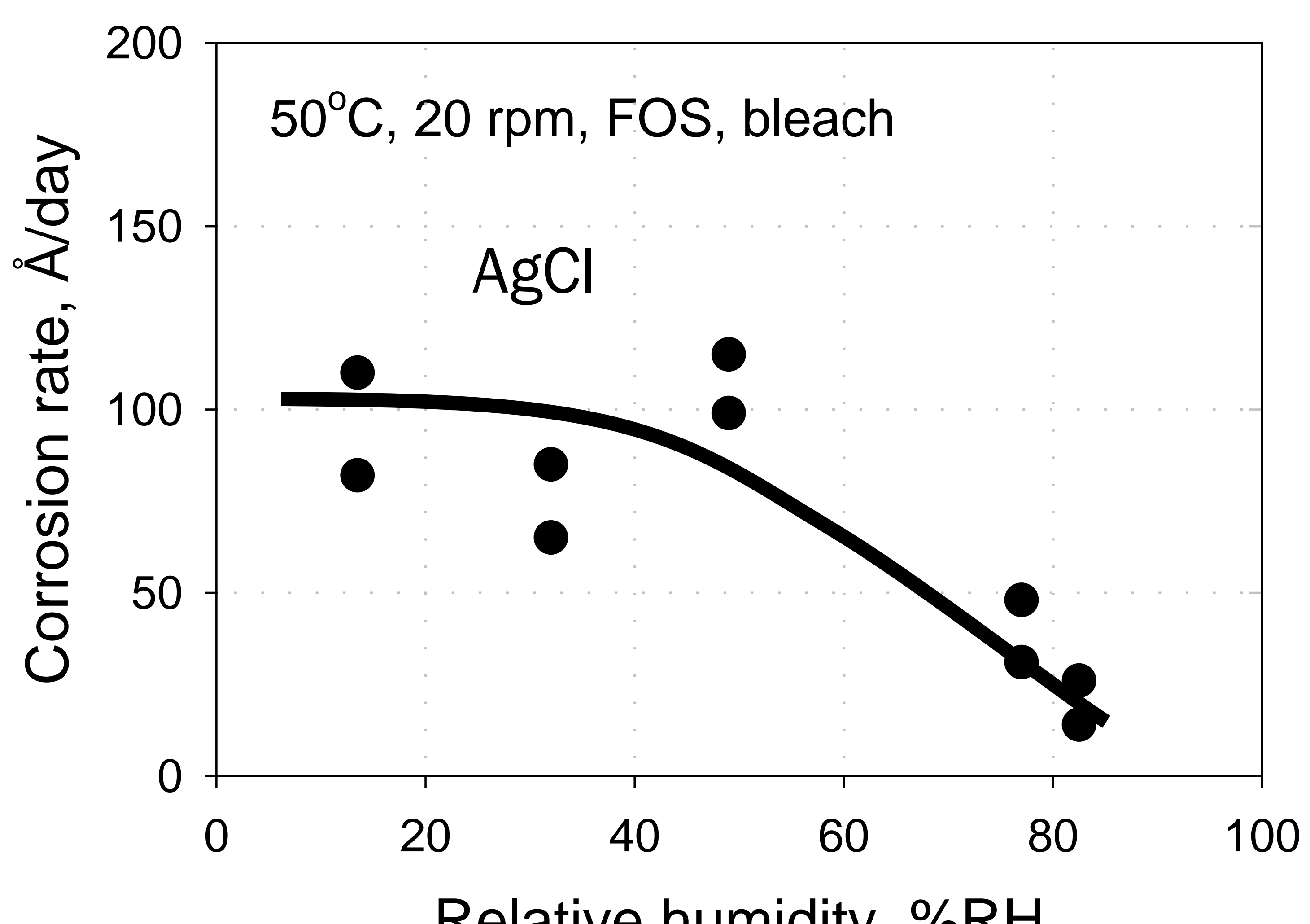
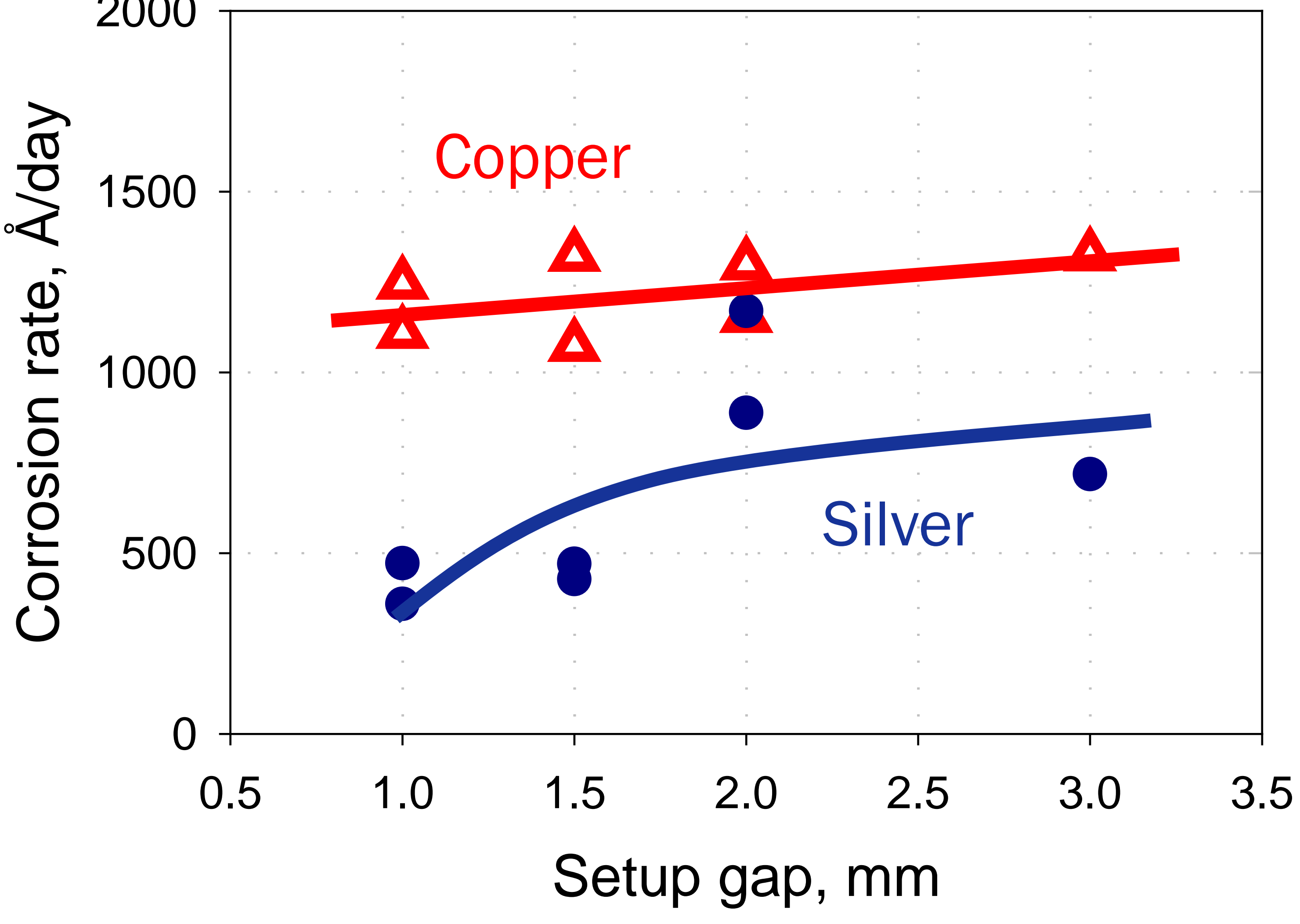
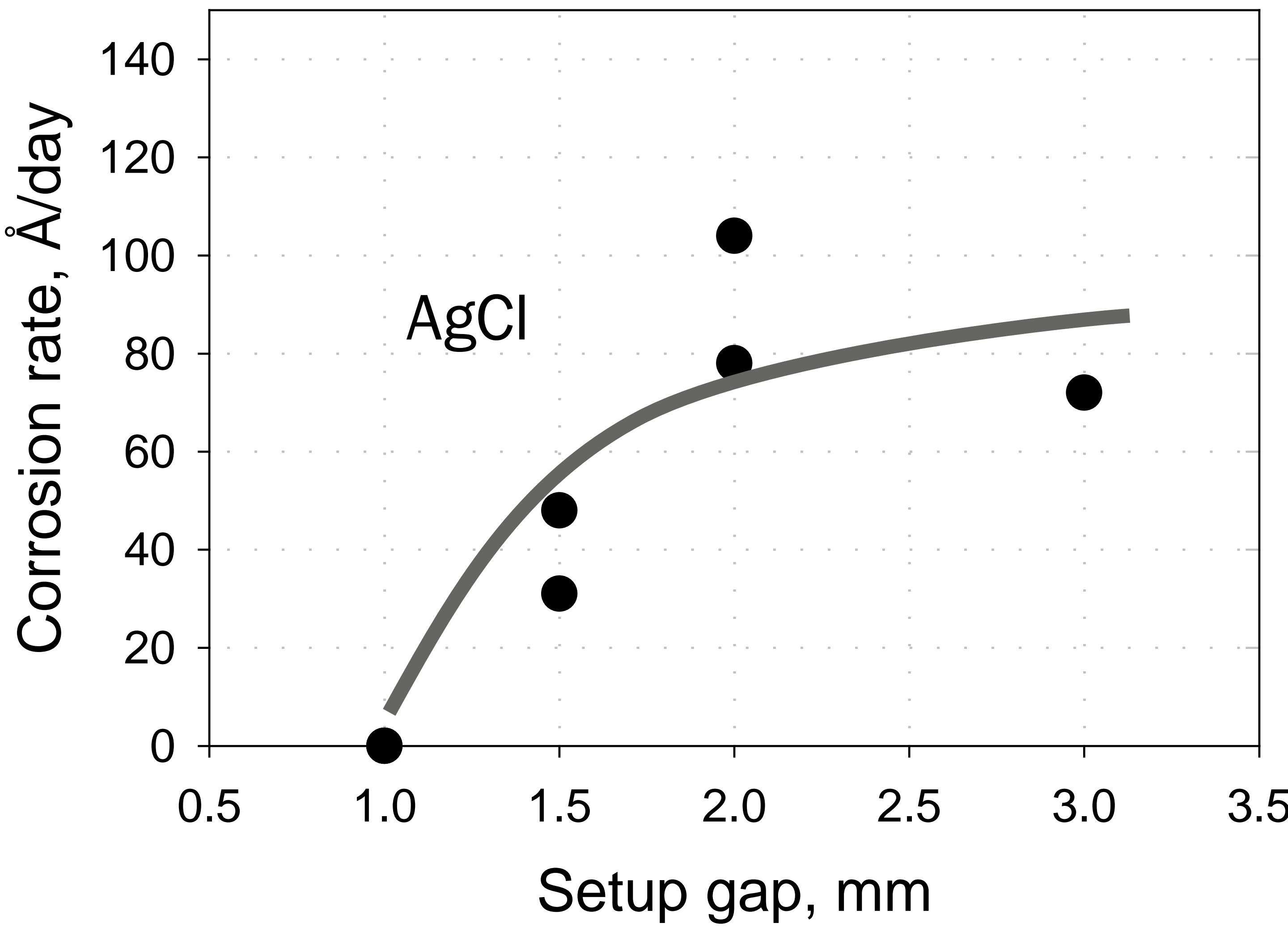


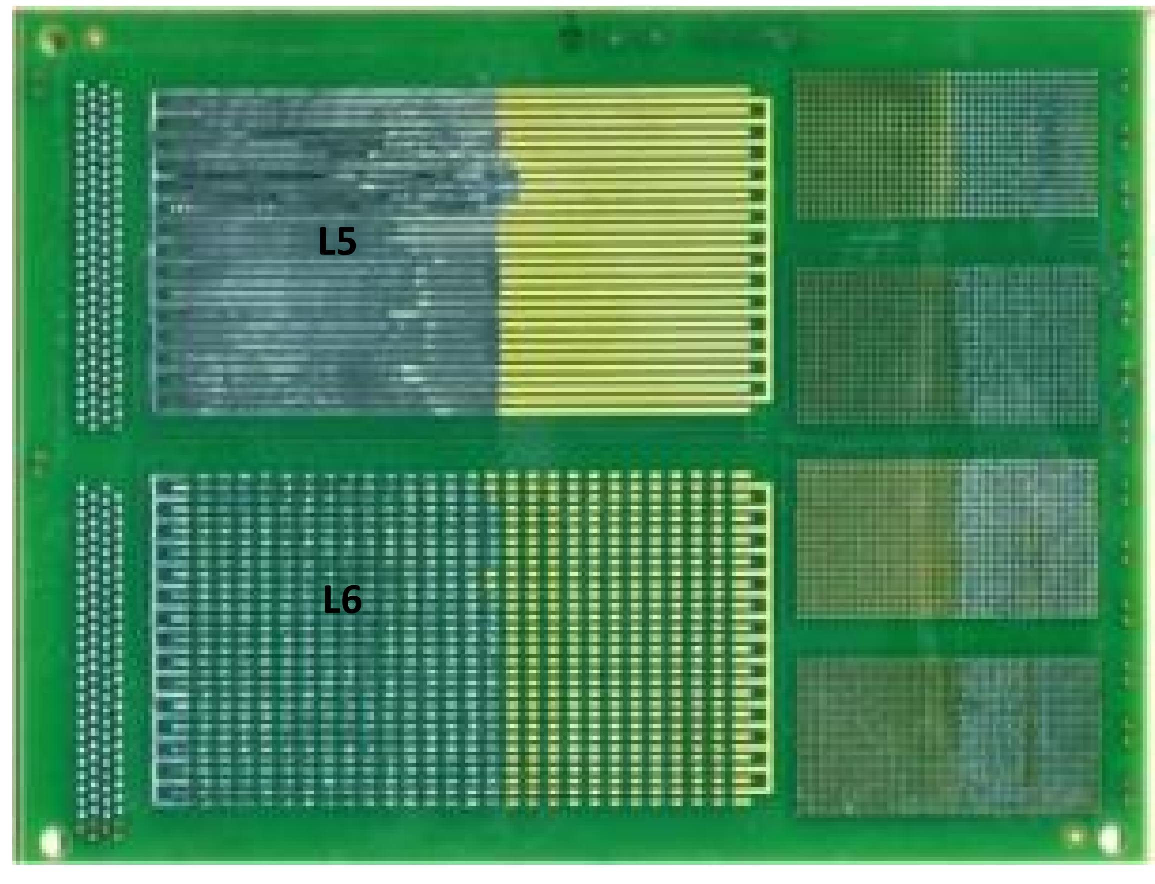
Cu and Ag corrosion rate as a function of gap in FOS chamber at 80%RH (KCl) 50°C, 20 rpm with bleach. (without PCB loading)



AgCl growth rate as a function of gap in FOS chamber at 50°C, 80%RH (KCl), 20 rpm with bleach. (without PCB loading)



Bottom side (wave soldering side)



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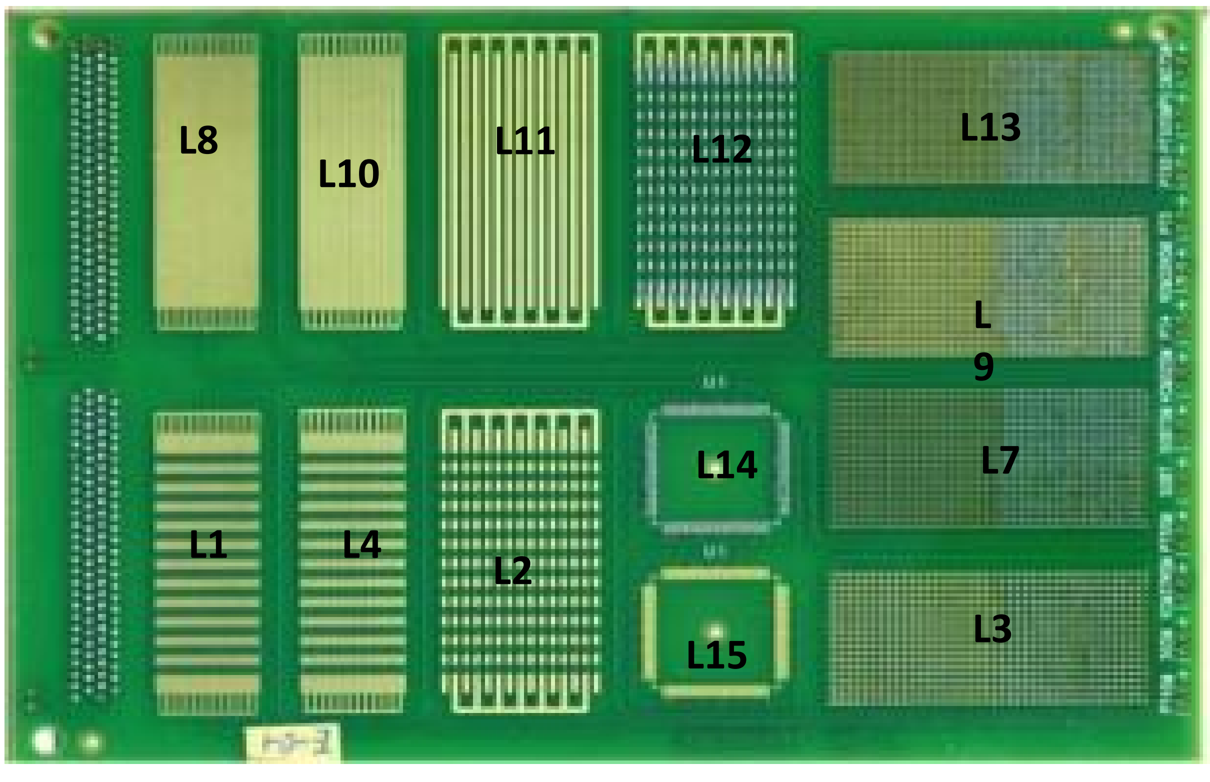
Top side



Cu and Ag corrosion rates during the creep corrosion runs

Run - chmaber	Saturated salt	%RH	Corrosion rate via coulometric reduction Å/day			Corrosion rate via mass gain Å/day	
			Cu total	Ag total	AgCl	Cu total	Ag total
2A-1 2B-1	$ZnCl_2$	11-17%	1028 1738	1201 1289	433 624	1049 2260	2389 1771
3A-2 3B-2	$MgCl_2$	33-45 30-32	1611 1844	1981 622	999 420	2630 4226	1934 987
4A-1 4B-1	$NaNO_2$	55-58	845 1531	723 589	124 209	1077 1126	818 710
710	NaCl	74-77	536 554	342 414	58 71	763 759	447 481
1A-1 1B-1	KCl with 3-mm gap	78-81	683 650	621 425	82 37	719 512	1045 442

Corrosion summary

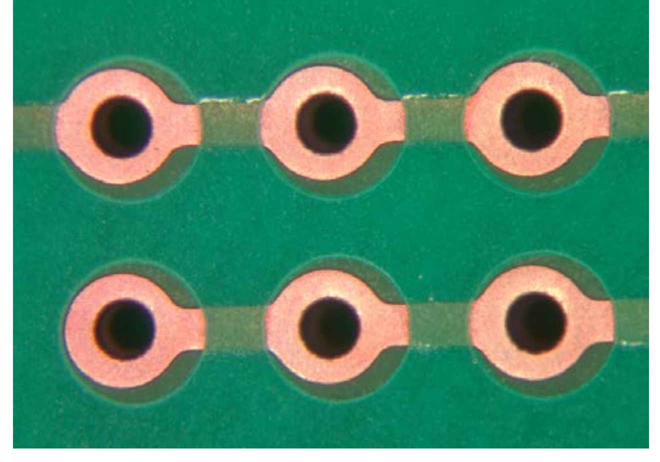
Finish	Day	Relative humidity				
		11-17%	31-46%	57-62%	75%	78-81%
OSP A	5		No corrosion			
	10		No corrosion			
OSP B	5			No corrosion		
	10					
ImAg	5					
	10	Did not continue				

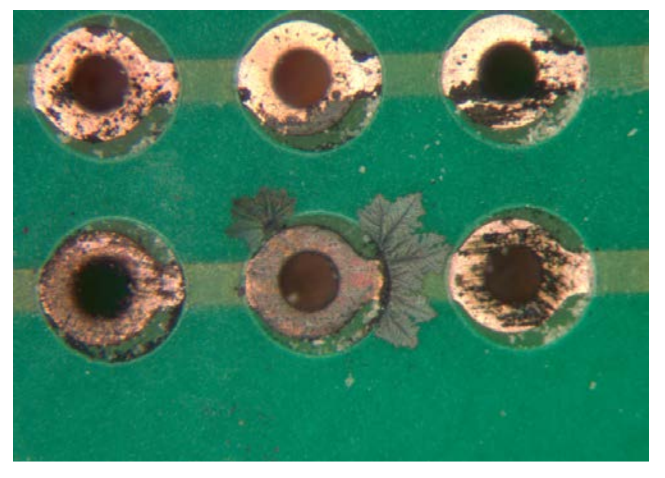
Corrosion summary

Finish	Day	Relative humidity				
		11-17%	31-46%	57-62%	75%	78-81%
ENIG	5					
	10		Did not continue			
ENIG wth post organic coating	5					
	10		Did not continue			

OSP-B at 5 and 10 days in 11-17%RH

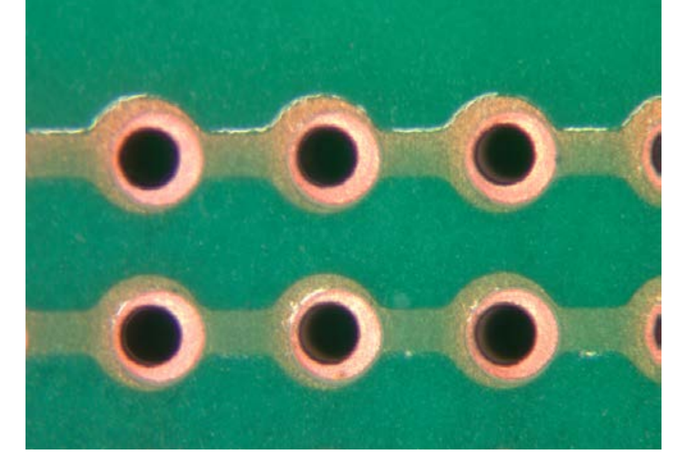
L3 – 5 days

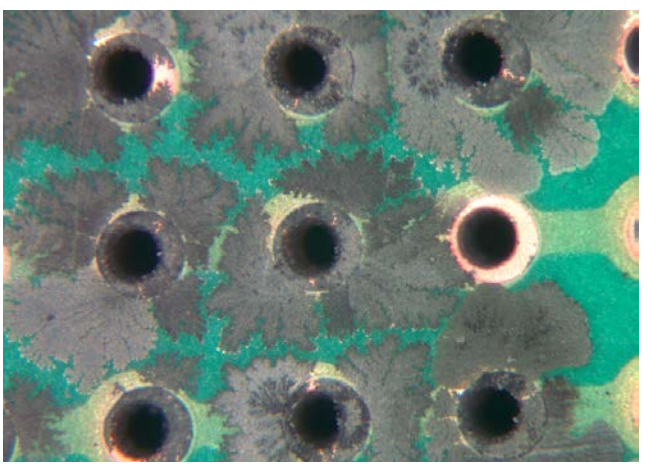




L3 – 10 days

L7 – 5 days



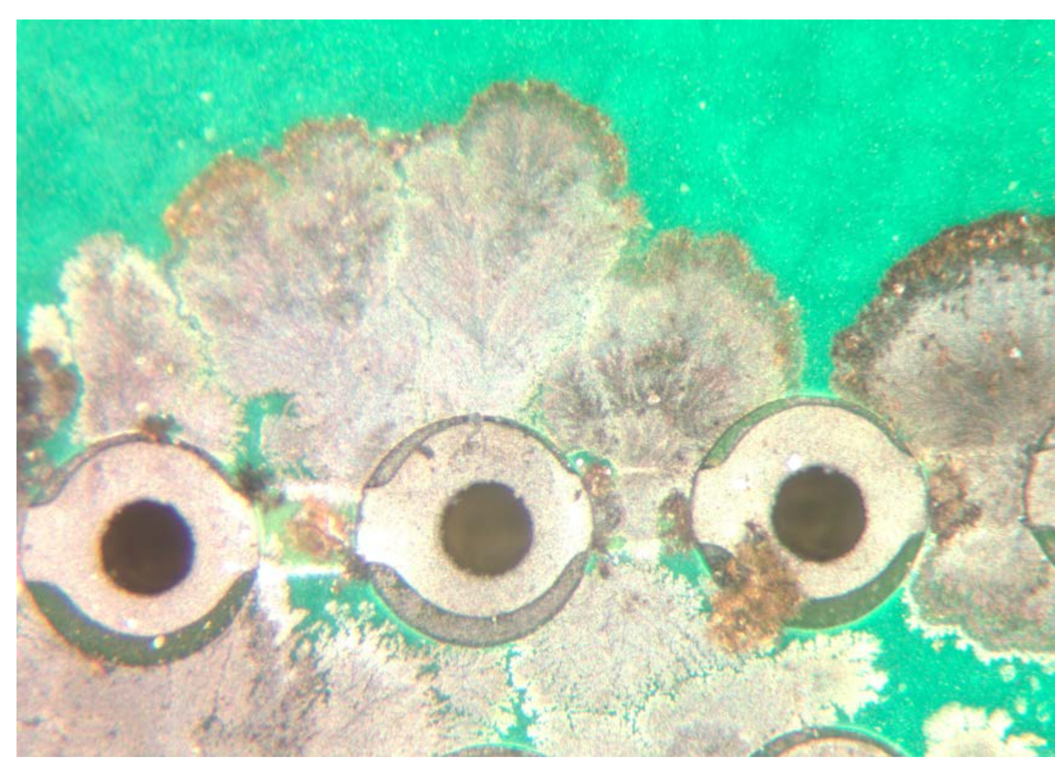


L7 – 10 days

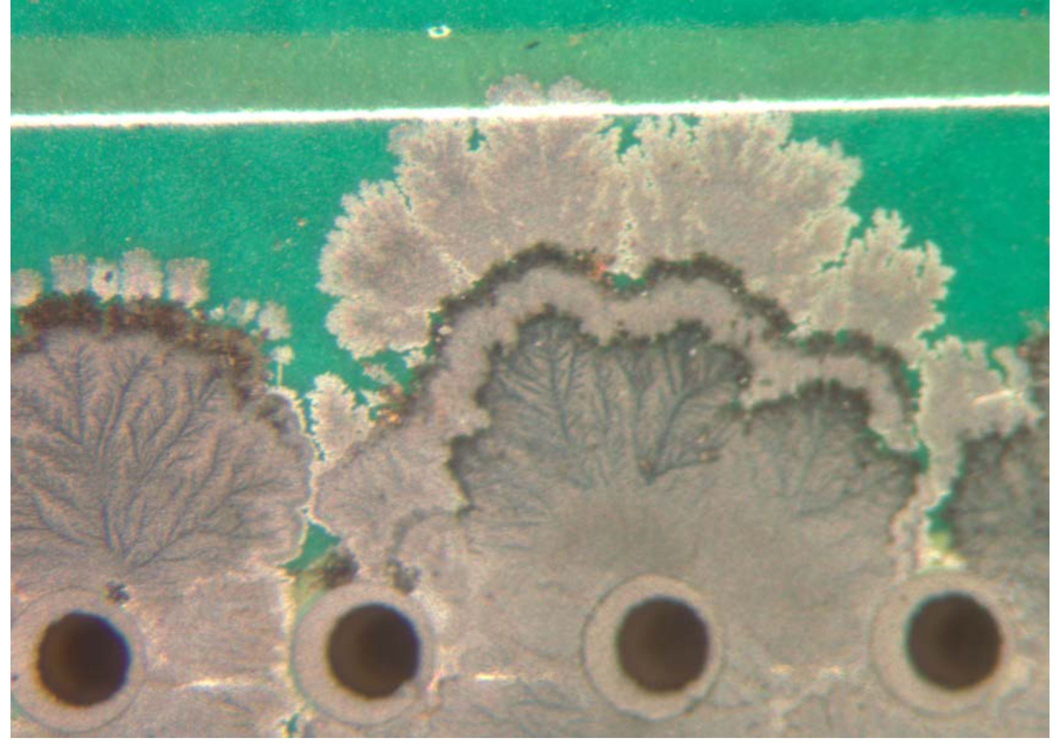
L3 – 10 days

ImAg at 5 days in 11-17%RH

L3 – 5 days

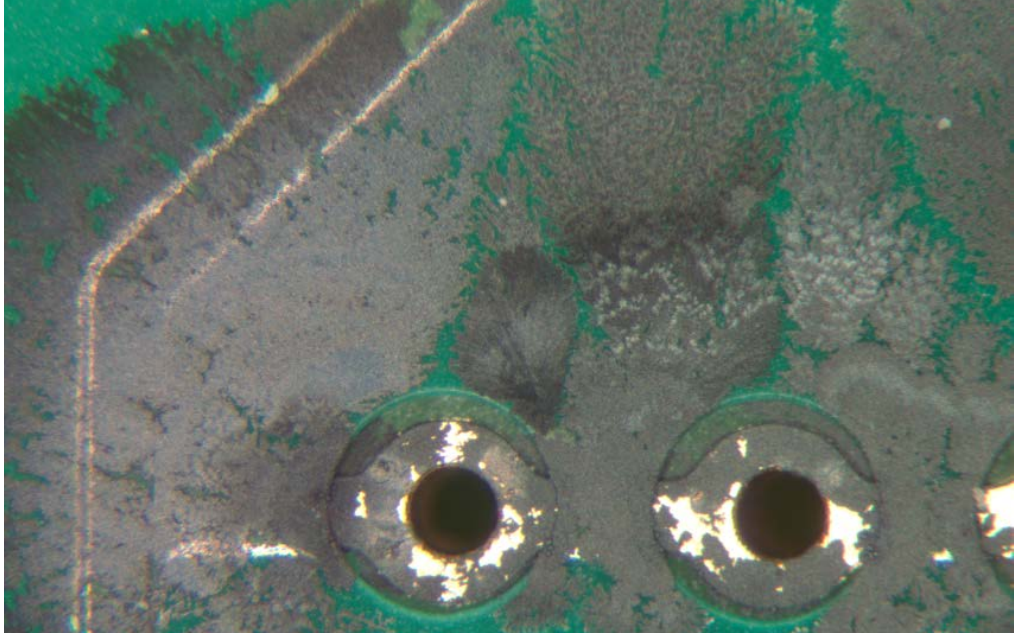


L7 – 5 days

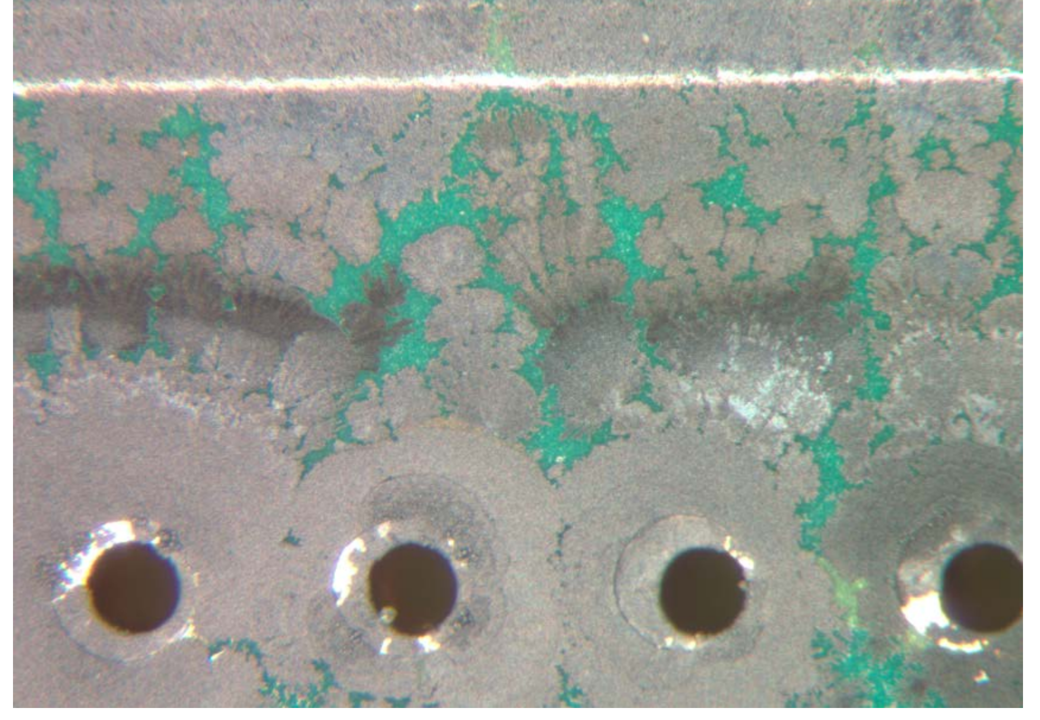


ENIG at 5 days in 33-47 %RH

L3 – 5 days

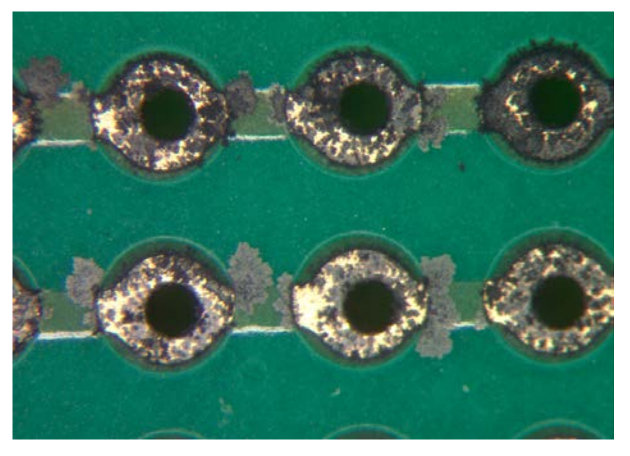


L7 – 5 days



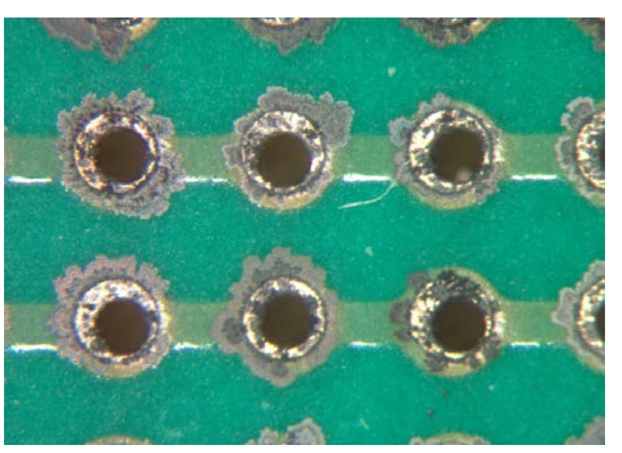
ENIG at 5 and 10 days in 78-81%RH

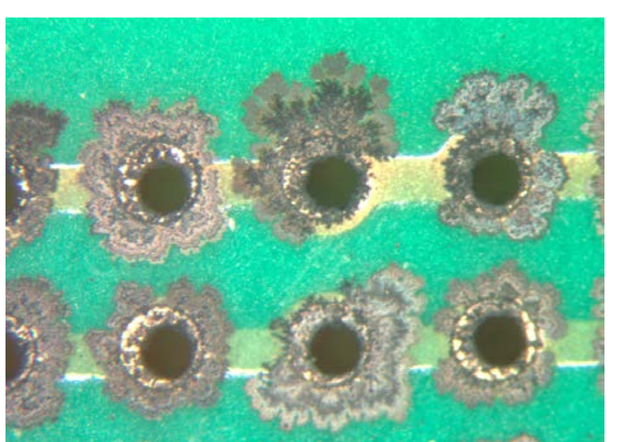
L3 – 5 days



L3 – 10 days

L7 – 5 days

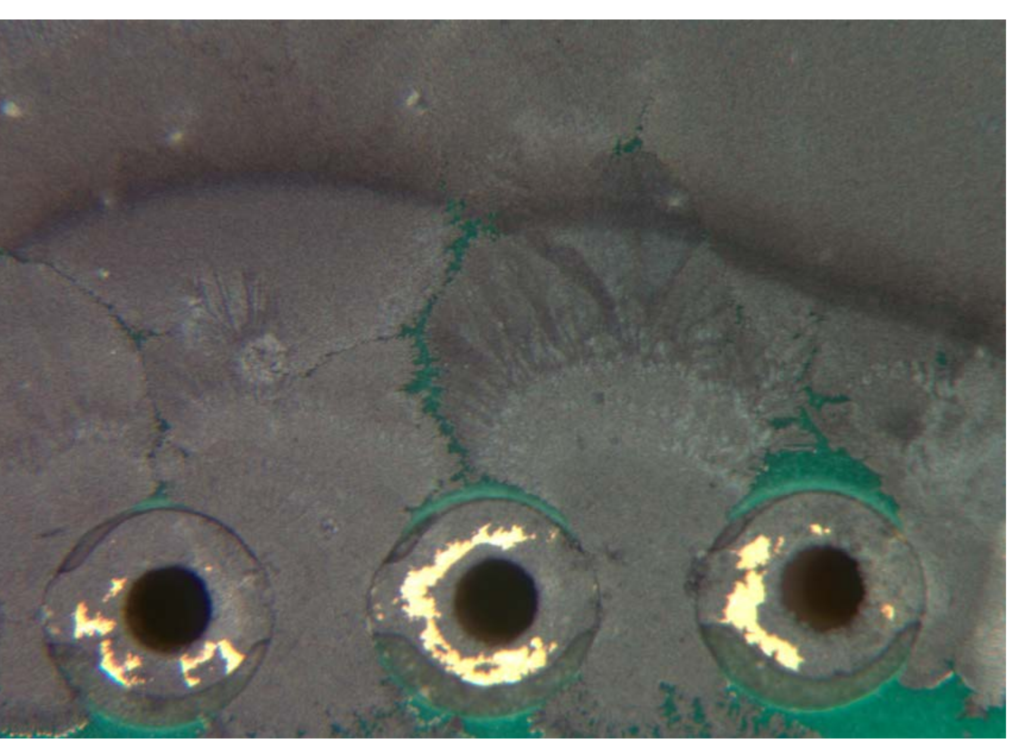




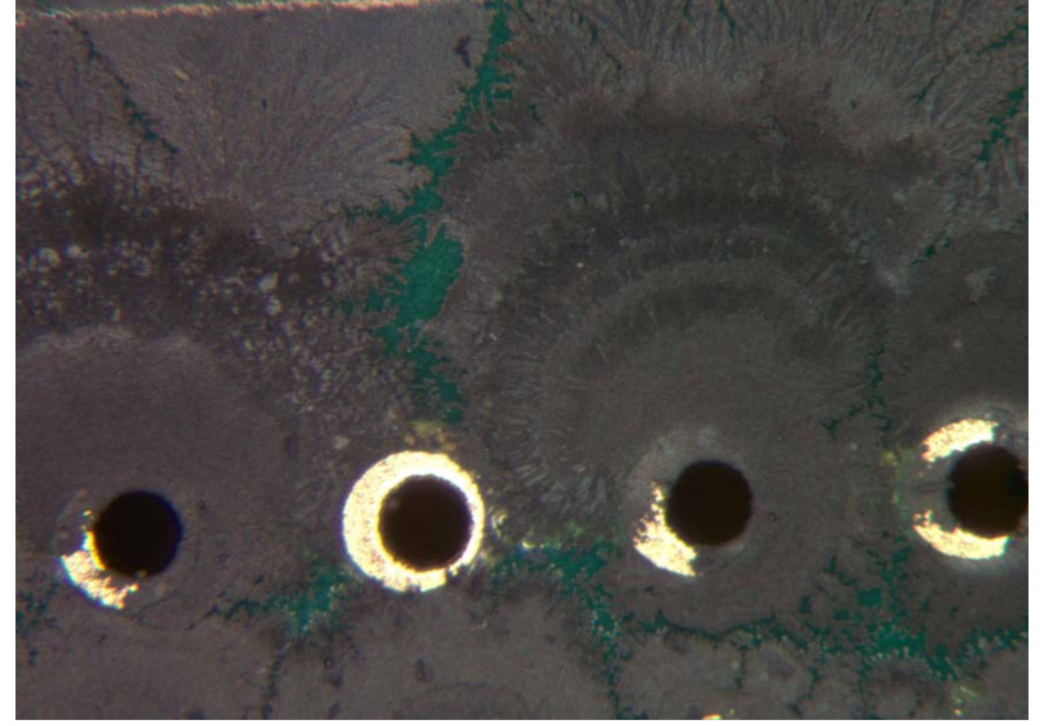
L7 – 10days

ENIG with organic coating at 5 days in 33-47 %RH

L3 – 5 days

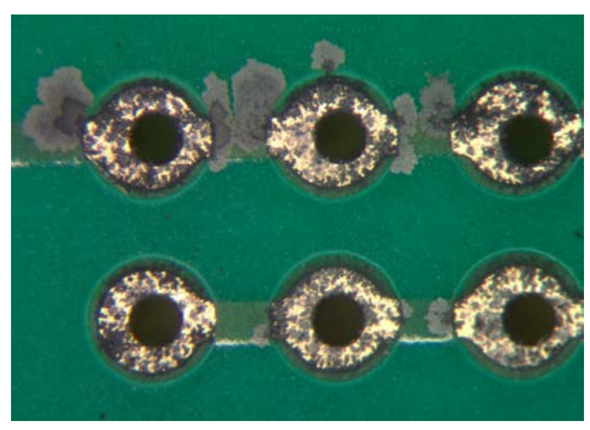


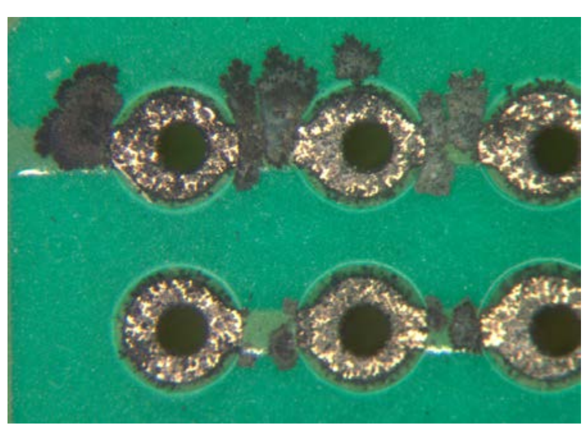
L7 – 5 days



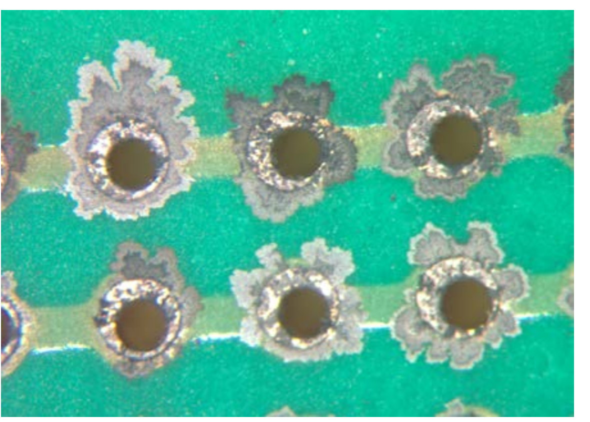
ENIG with organic coating at 5 and 10 days in 78-81%RH

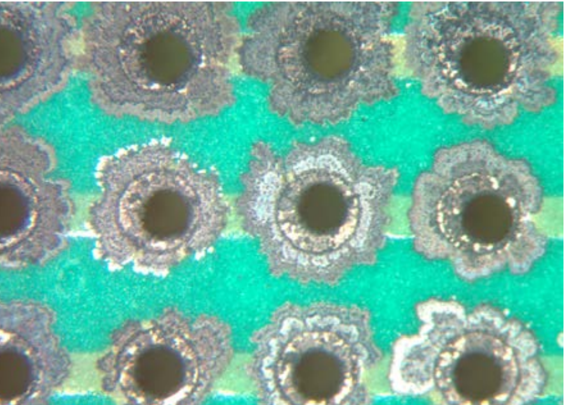
L3 – 5 days





L7 – 5 days





L7 – 10 days

Conclusions

- Relative humidity in FOS chambers can be controlled at any humidity level in the 15-80% range, even in the presence of aqueous bleach solution.
- The corrosion rates of copper and silver and the rate of formation of AgCl in a sealed FOS chamber, loaded with PCBs, decrease with rising relative humidity.
- Test PCBs soldered with organic acid flux showed high propensity to creep corrosion at relative humidity levels as low as 11-17%. This result provides the first direct experimental evidence of creep corrosion occurring on "dry" surfaces on PCBs that are likely contaminated with un-deactivated flux residues.
- There is probably no common threshold relative humidity level below which creep corrosion will not occur.

Thank You!

Questions?