Flowers of Sulfur Creep Corrosion Testing of Populated Printed Circuit Boards

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Abstract

Creep corrosion testing of printed circuit boards (PCBs) using a specially designed flowers of sulfur chamber has been developed by an iNEMI technical committee. The iNEMI test is based on a chamber that is 300-mm cube acrylic box with 8-paddle wheels rotating at 20 RPM that can accommodate 8 PCBs. In one embodiment of the test setup, the sulfur vapor with controlled concentration is provided by two 100-mm diameter petri dishes containing beds of sulfur and by maintaining the chamber temperature at 50ºC. 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 household bleach in a 100-ml beaker. The creep corrosion qualification test has successfully predicted creep corrosion on specially designed and manufactured unpopulated printed circuit boards of various finishes, soldered with rosin or with organic acid flux. Creep corrosion similar in morphology to that observed in the field has been reproduced in the iNEMI tests. This paper describes the iNEMI creep corrosion testing of a number of fully populated PCBs of various technologies and vintages of known field reliability. The results confirm the finding that prebaking the PCBs is a necessary condition for creep corrosion to occur in the iNEMI flowers of sulfur chamber. The creep corrosion results on prebaked PCBs of 7 different technologies agreed with the field reliability experiences. The PCBs from lots that suffered creep corrosion in the highly polluted geographies showed creep corrosion of similar morphology in the flowers of sulfur creep corrosion test; whereas, the PCBs from lots that did not suffer creep corrosion in the field, survived the flowers of sulfur test with little or no creep corrosion. The iNEMI PCB creep corrosion qualification test is now sufficiently well developed to be adopted as an industry standard test. The paper will also show some evidence that long-term storage before usage may eliminate creep corrosion.

1. **Introduction**

Creep corrosion on printed circuit boards (PCBs) is the corrosion of copper (and sometimes silver) metallization and the creeping of the corrosion products (mostly sulfide of copper and sometimes silver) on the PCB surfaces. Creep corrosion can be extensive enough to cause the electrical short circuiting of neighboring features on PCBs, such as the plated through holes (PTHs). The history of creep corrosion has been extensively covered in the literature **[1-5]**. Mixed-flowing gas (MFG) and the flowers of sulfur (FOS) are the two main tests for creep corrosion. The MFG test was developed in the 1980s for the study of electrical connector corrosion **[6]** and has since been applied to the study of creep corrosion **[3, 5, 7-9]**. A 105ºC FOS test has been used successfully for the qualification of miniature surface-mount resistors [**10**]. A FOS test has been developed by an iNEMI subcommittee to test for creep corrosion on PCBs [**12-16**]. The low cost and the easy of control of the test variables was the main motivation for developing the FOS-based creep corrosion qualification test. The test chamber is shown in **Figure 1**. The test conditions are as follows:

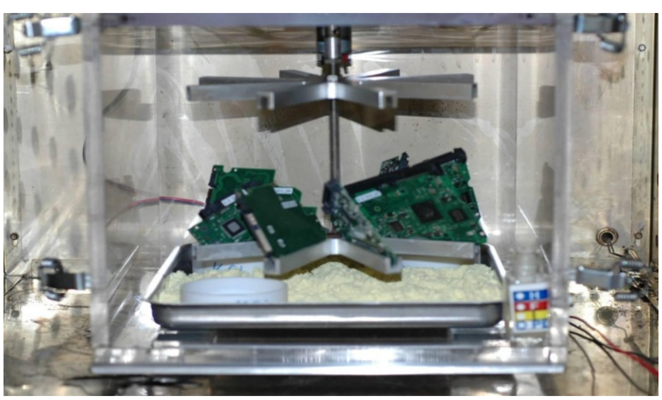


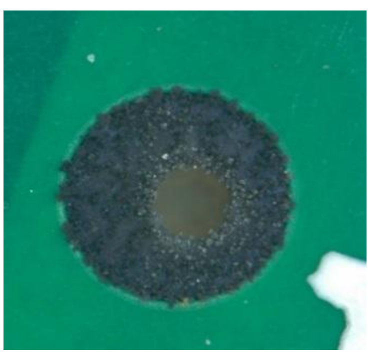
Figure 1: iNEMI flowers of sulfur creep corrosion setup with KCl saturated salt in petri dishes and sulfur in a stainless-steel tray. The 40-ml household bleach in 100-ml beaker is behind the paddle wheels and is not visible.

(a) The test PCBs are baked in flowing nitrogen gas at 100°C for 24 hours. The flowers-of-sulfur test chamber is 300-mm cube made of 12.7-mm thick acrylic that has a front-loading door sealed with a silicone coated rubber gasket.
(b) Relative humidity is maintained at about 81% in the chamber using two 80-mm diameter petri dishes filled with KCl saturated solution.
(c) The sulfur concentration is maintained using flowers of sulfur bed in two 100-mm diameter petri dishes or in a 300x300-mm tray and by maintaining the chamber temperature at 50°C.
(d) Chlorine is provided using 40-ml household bleach containing 6.25% sodium hypochlorite in a 100-ml beaker.
(e) Eight test PCBs can be mounted on the paddle wheel setup that is rotated at 20 RPM to circulate the air in the chamber and have some airflow over the test PCBs.
(f) The test duration of 10 days is adequate. Susceptible PCBs often suffer creep corrosion within 5 days.
(g) Any spread of the corrosion product over the test PCBs is an indication of creep corrosion.

This paper describes the creep corrosion testing of 7 fully populated printed circuit boards (PCBs) of various technologies and vintages of known field reliability histories. The paper also confirms the earlier discovered necessity of prebaking the test PCBs **[14]**. Early in the phase 2 of the iNEMI project on FOS testing for creep corrosion, it was discovered that loading the FOS chamber with test PCBs lowered the corrosion rates of copper and silver foils **[13]**. It was speculated that volatiles were coming off the test PCBs and contaminating the chamber environment, thus, reducing the copper and silver corrosion rates. Prebaking the PCBs at 100°C under flowing nitrogen gas for 24 hours was tried as a means of "flushing out" the volatiles from the test PCBs. As published in **reference 14**, creep corrosion test runs on PCBs with and without prebake proved the necessity of the prebake: Test PCBs known from field experience to be susceptible to creep corrosion, suffered creep corrosion in the test when prebaked, whereas the unbaked PCBs from the same manufacturing lots did not suffer any creep corrosion as shown in **Figure 2.**

2. **Experimental procedure and results**

The creep corrosion testing was done using the iNEMI technique described above. The silver corrosion rates during the FOS testing were measured by exposing a silver foil mounted on a rotating paddle wheel and measuring the thickness of the corrosion product using the coulometric reduction method. The silver corrosion rate was also measured using the electrical resistivity method on stationary silver thin films. The silver corrosion rates are shown in **Figure 3**. The discrepancy between the two may be due to the fact that the corrosion rate on moving silver foils with air flow across them would be higher than on stationary foils


Without prebake

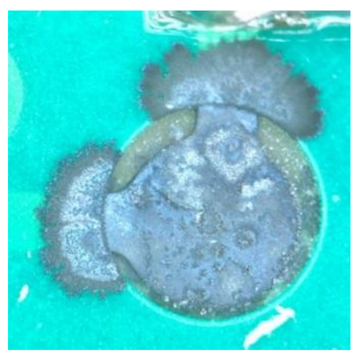

With prebake

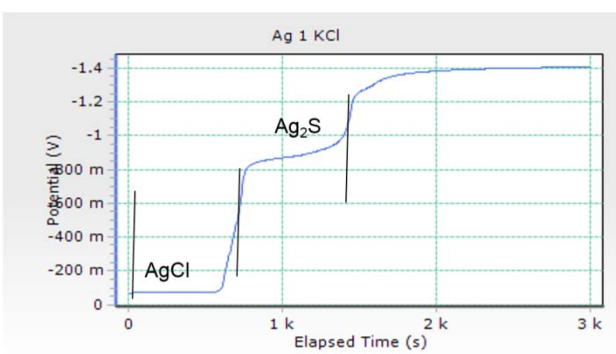
Figure 2: Effect of prebake on the occurrence of creep corrosion on test PCBs. [**14**].

Table 1: Summary of the FOS creep corrosion test. The even numbered test PCBs shown in highlighted rows were prebaked. The odd numbered PCBs were not prebaked.

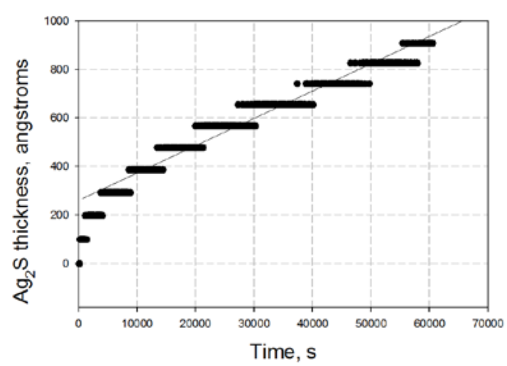
Test PCB #	ID	Name	Prebake	Corrosion results
1	2.5 DV1_10	SPF	No	No creep corrosion
2	2.5 DV1_11	SPF	Yes	No creep corrosion.
3	2.5 DV1_20	OSP Rosin	No	No creep corrosion
4	2.5 DV1_21	OSP Rosin	Yes	No or minor creep corrosion.
5	2.5 DV2_01	SCI	No	Minor creep corrosion
6	2.5 DV2_02	SCI	Yes	Heavy creep corrosion
7	3.5 DV1_01	SCI	No	No creep corrosion
8	3.5 DV1_02	SCI	Yes	Moderate creep corrosion
9	3.5 DV2_01	SCI	No	Minor creep corrosion
10	3.5 DV2_02	SCI	Yes	Heavy creep corrosion
11	3.5 DV3_10	SPF	No	No creep corrosion
12	3.5 DV3_11	SPF	Yes	Low creep corrosion
13	3.5 DV3_20	OM	No	No creep corrosion
14	3.5 DV3_21	OM	Yes	Heavy creep corrosion

Seven 7 fully populated PCBs, listed in **Table 1**, from 7 part numbers, that were not baked were subjected to the iNEMI creep corrosion FOS test described above. The test duration was 5 days. Of the 7 PCBs tested, only two PCBs (# 5 and #9) suffered very minor creep corrosion; the rest did not suffer any creep corrosion. **Figure 4** shows the extent of creep corrosion on PCBs #5 and #9. These test results did not agree with the field experience.

Earlier research on FOS testing of iNEMI test PCBs had shown that prebaking the PCBs in flowing nitrogen gas at 100°C for 24 hours is necessary to cause creep corrosion similar in morphology to that experienced in the field **[14]**. Therefore, the FOS test was repeated on 7 fully populated PCBs with the same 7 PCB part numbers, but this time the PCBs were prebaked at 100°C in flowing nitrogen gas for 24 hours to flush out the volatiles from the PCBs. Test duration was 6 days. Of the 7 PCBs tested, 5 suffered creep corrosion in agreement with the field experience on these families of PCBs, as shown in **Figure 5**. **Table 1** is a summary of the FOS testing of PCBs with and without prebaking.

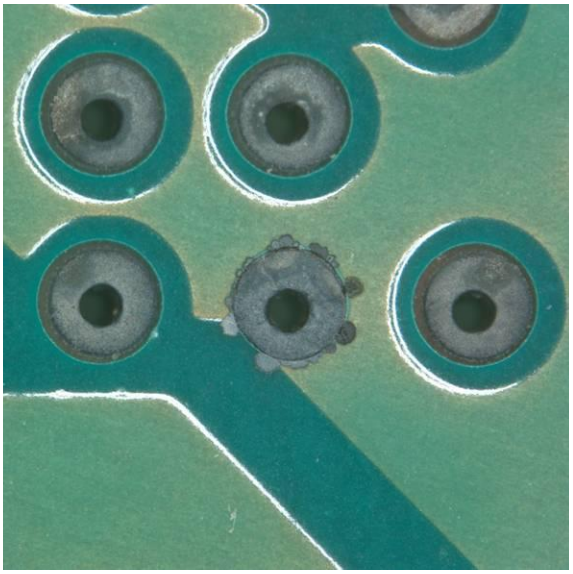


Ag_2S = 657 Å/day; AgCl = 1046 Å/day

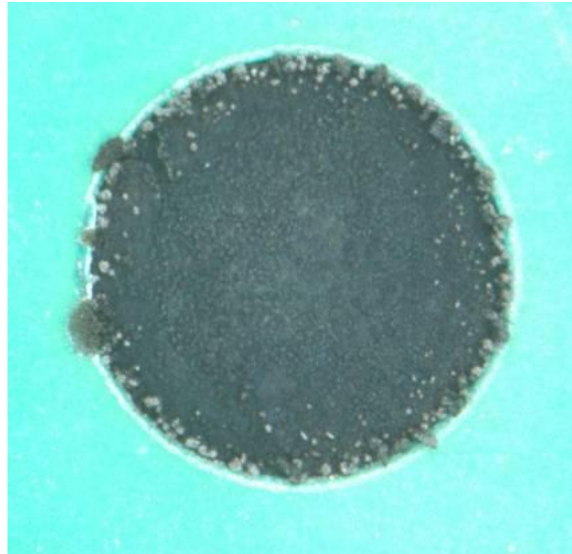


Silver corrosion rate =((940-270)/60000)(2600x24)=697 Å/day, coupon is stationary.

Figure 3: Corrosion rate of silver in the FOS test chamber:



PCB #5: 2.5 DV2-01



PCB #9: 3.5 DV2-01

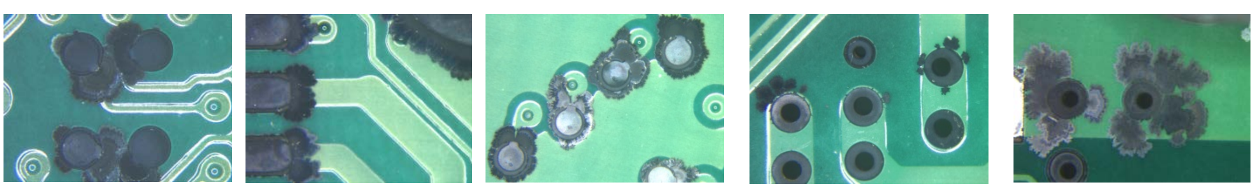
Figure 4: Of the 7 families of PCBs that were not baked, only two (PCB #5 and 9) suffered minor extent of creep corrosion. The remaining 5 suffered no creep corrosion.

Two PCB part numbers that had suffered creep corrosion in the field and that had failed in the iNEMI flowers of sulfur test were retested after more than 2 years in storage. Neither part number PCB suffered creep corrosion after more than 2 years in storage. **Figure 6** shows that creep corrosion test results before and after the 2-year storage.

3. Discussion

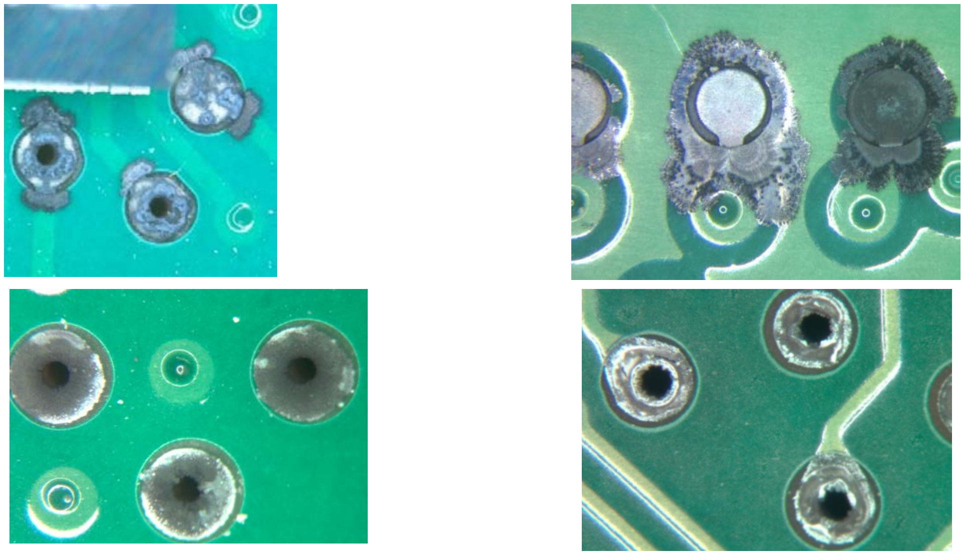
The results of the above tests clearly demonstrate the validity of the iNEMI FOS test for measuring the creep corrosion propensity of circuit boards. The tests confirm the necessity of prebaking the test PCBs in flowing nitrogen gas at 100ºC for 24 hours. **Table 1** shows that the PCBs that were not prebaked suffered minor to no creep corrosion; whereas prebaking the PCBs led to creep corrosion in the FOS chamber similar to that experienced in the field. The reason for the necessity to prebake has been described earlier **[14]** and is most probably as follows: The FOS test chamber is a sealed chamber of limited volume. The volatile organic compounds coming off the test PCBs contaminate the chamber and the PCBs surfaces. The contamination on the PCBs surfaces may not be conducive to creep of the corrosion products. Prebaking the test PCBs in flowing nitrogen gas at 100ºC for 24 hours releases the volatile organic compounds from the PCBs and sweeps them away,not letting them redeposit back on the PCBs. Prebaked PCBs are thus less prone to contaminate the FOS chamber and affect the creep of the corrosion products on the PCB surfaces. On the other hand, creep corrosion testing in mixed-flowing gas (MFG) chambers does not require the prebaking step because in the MFG test gases are flowing into and out of the chamber, thus, not allowing the buildup and contamination of the chamber with the volatile organic compounds coming off the PCBs.

The reason for the observation that 2-year storage of soldered PCBs eliminates creep corrosion in the FOS test may be due to the oxidation of the copper building up a protective corrosion barrier preventing the copper from being attacked by the sulfur and chlorine gases and, therefore, not allowing any creep corrosion.



Heavy creep corrosion PCB#6	Moderate creep corrosion PCB#8	Heavy creep corrosion PCB #10	Moderate creep corrosion PCB #12	Heavy creep corrosion PCB #14

Figure 5: Creep corrosion of five of the seven prebaked PCBs that suffered creep corrosion.



(a) NT test PCBs: (b) 3.5DV2 test PCBs

Figure 6: Evidence that 2-year storage eliminates creep corrosion in the iNEMI creep corrosion test. The top micrographs show creep corrosion on relatively freshly manufactured PCBs. The bottom micrographs show that there was no creep corrosion after the PCBs had been in storage for 2 years.

The iNEMI test described in this paper used an outdated setup that had the sulfur and the saturated salt solution in petri dishes and the household bleach in a beaker. The iNEMI test has since been updated to a setup that is described in detail in an accompanying paper in this conference [**16**]. In this updated setup, the release of the chlorine gas from the household bleach is throttled to pass through a narrow 1-mm gap. The chlorine and the water vapor coming off the bleach are forced horizontally over a KCl saturated salt solution bath so that the relative humidity in the chamber is essentially the deliquescent relative humidity of KCl.

4. Conclusions

The iNEMI creep corrosion test is sufficiently well developed to be an industry standard test for the qualification of printed circuit board technologies and production lots to ensure that they are free from creep corrosion in the field. The test includes a necessary prebaking step to flush out the volatile organic compounds that would otherwise be released in the flowers of sulfur test chamber, contaminating the test PCBs surfaces and making them less conducive to the creep of the corrosion products.

There is evidence that the storage of soldered PCB assemblies for 2 years eliminates creep corrosion in the iNEMI flowers of sulfur test.

5. References

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Flowers-of-sulfur Creep Corrosion Testing of Populated Printed-Circuit Boards

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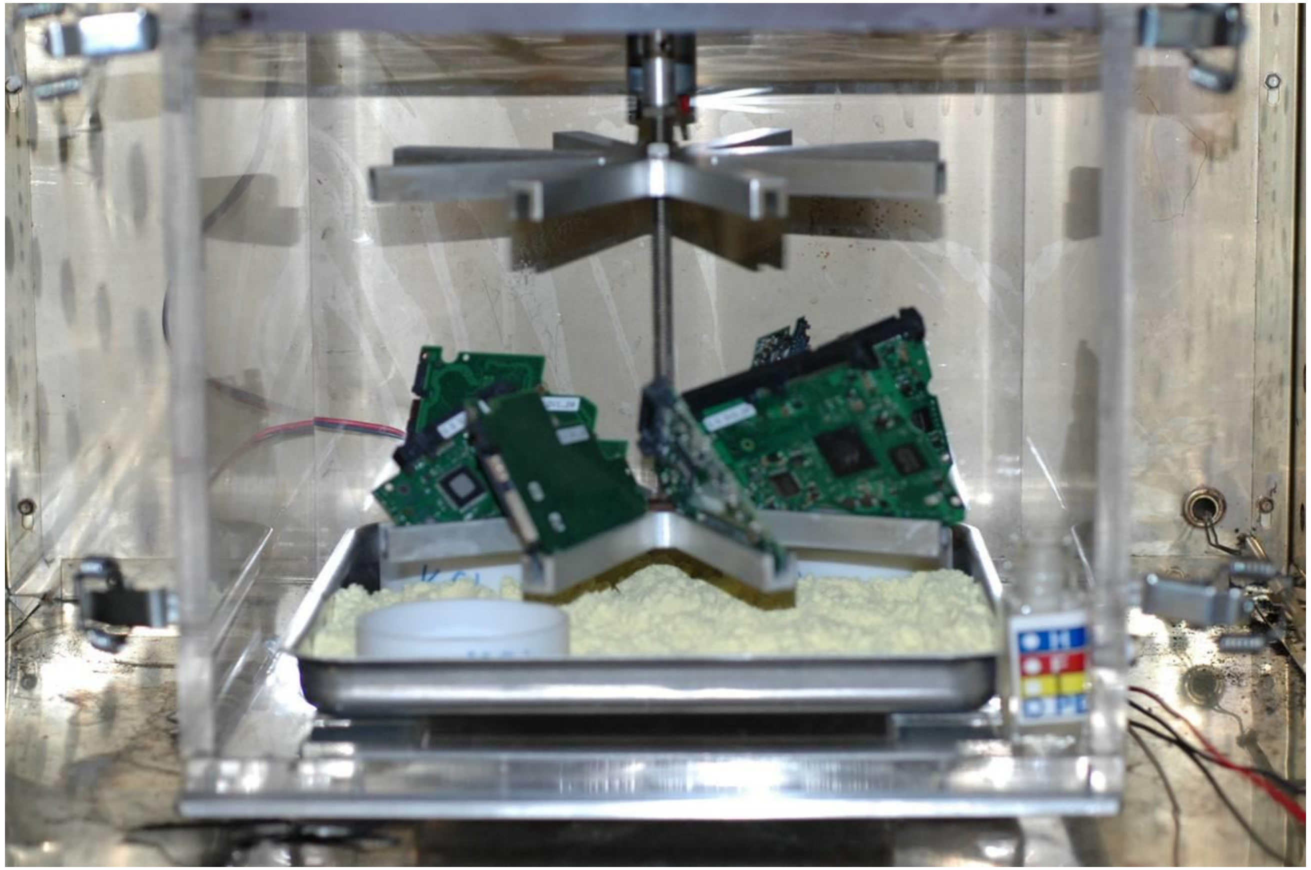
Agenda

- Flowers of sulfur chamber and the iNEMI test procedure
- Effect of prebake
- Corrosion rate measurement
- Creep corrosion testing of 7 part number soldered PCBs
- Effect of 2-year storage
- Conclusions

FOS setup with test PCBs



iNEMI creep corrosion FOS chamber

- 300-mm cube acrylic box with 8-paddle wheels rotating at 20 rpm that can accommodate 8 printed circuit boards under test.
- The sulfur vapor with controlled concentration is provided by two 100-mm diameter petri dishes containing beds of sulfur and by maintaining the chamber temperature at 50^{o}C.
- The relative humidity is maintained at about 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 household bleach in a 100-ml beaker.

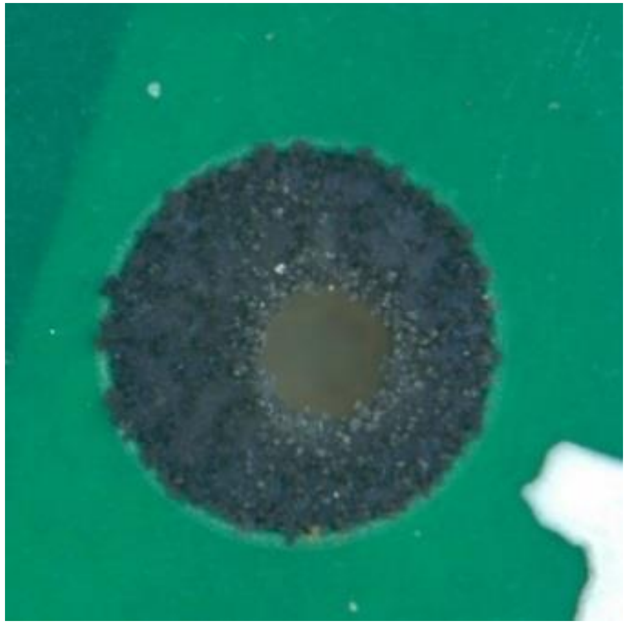
iNEMI creep corrosion qualification test procedure

- The test PCBs are prebaked in flowing nitrogen gas at 100°C for 24 hours to drive off the volatiles that would otherwise contaminate the limited volume, sealed FOS chamber.
- Up to 8 test PCBs can be placed on the paddles and rotated at 20 rpm in the FOS chamber at 50°C.
- Test period of 10 days is sufficient.
- Creep corrosion is observable under a low magnification microscope.

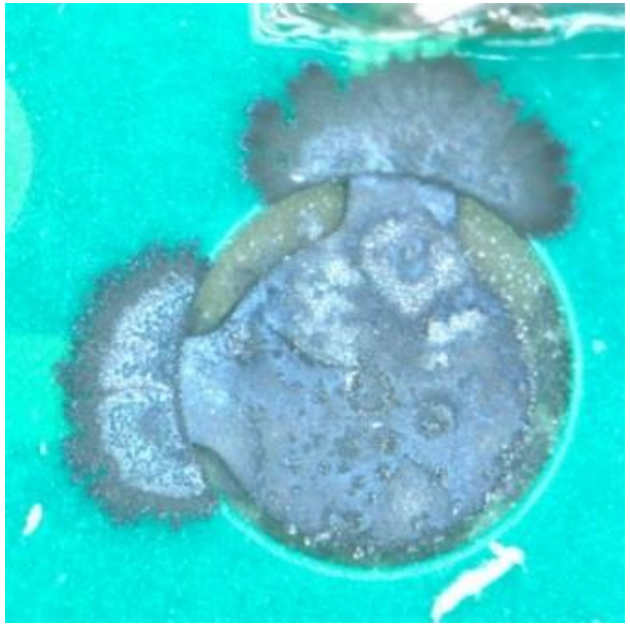
Effect of prebake

- Prebake is done at 100ºC in flowing nitrogen gas for 24 hours to drive off the volatiles that may otherwise contaminate the sealed FOS chamber.

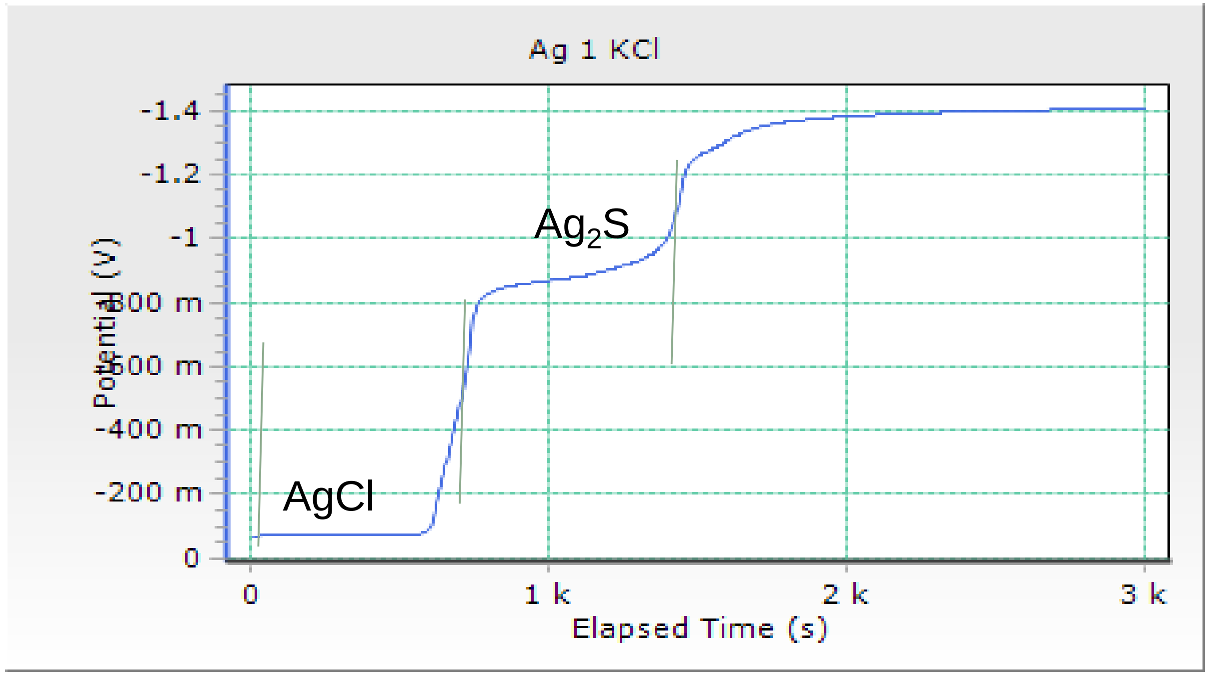
Without prebake



With prebake

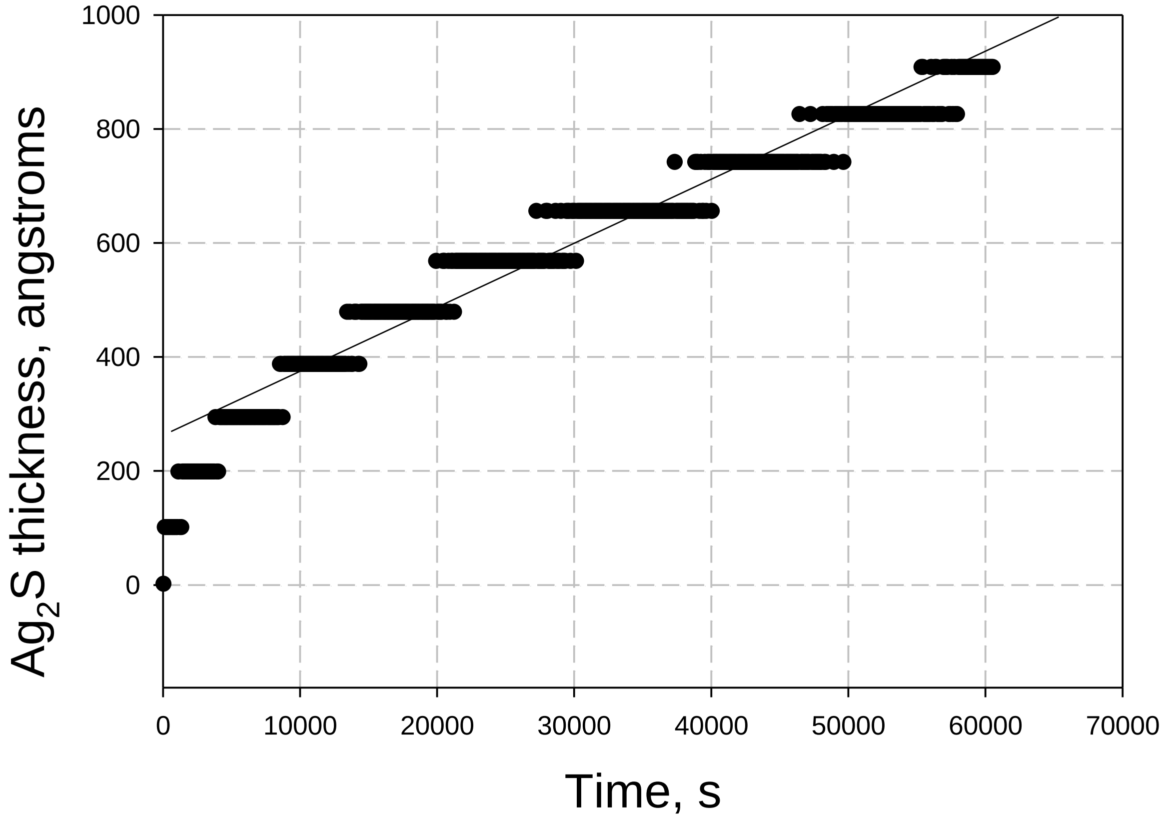


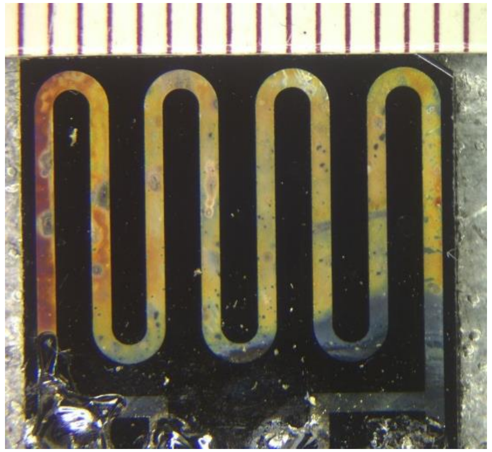
Silver corrosion rate measurement



Silver corrosion product	Seconds	Thickness of corrosion product, angstroms	Exposure days	Silver corrosion rate, angstroms/day
Ag2S	676	657	1	657
AgCl	705	1046	1	1046

Silver corrosion rate measurement





Silver corrosion rate =((940-270)/60000)(2600x24)=697 A/day.

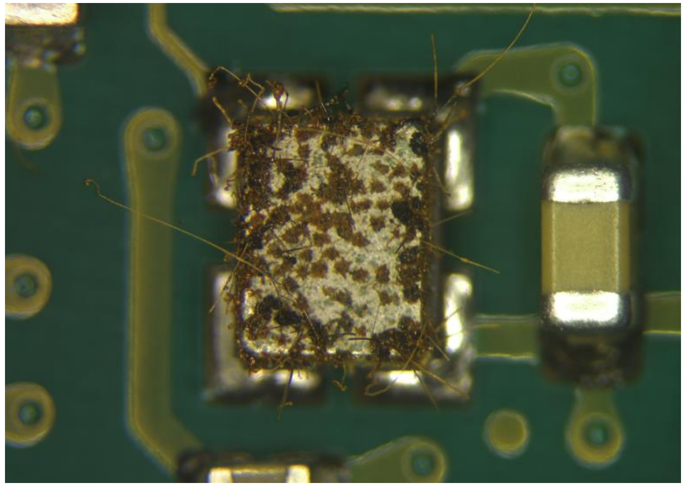
Summary of test results

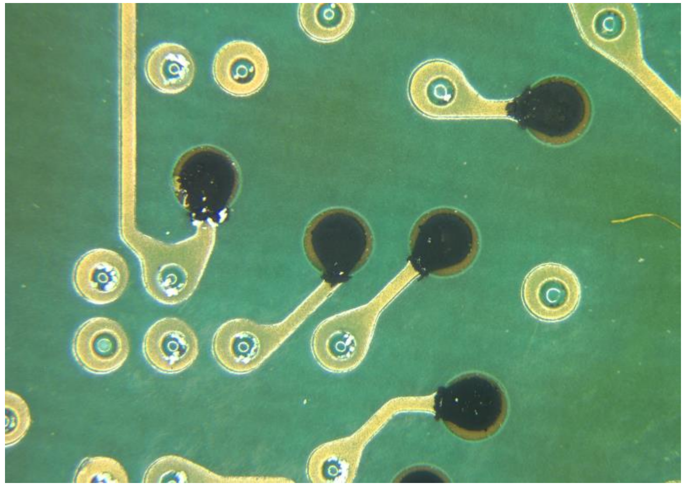
	ID	Name	Prebake?	
1	2.5 DV1_10	SPF	No	No creep corrosion
2	2.5 DV1_11	SPF	Yes	No creep corrosion.
3	2.5 DV1_20	OSP Rosin	No	No creep corrosion
4	2.5 DV1_21	OSP Rosin	Yes	No or minor creep corrosion.
5	2.5 DV2_01	SCI	No	Minor creep corrosion
6	2.5 DV2_02	SCI	Yes	Heavy creep corrosion
7	3.5 DV1_01	SCI	No	No creep corrosion
8	3.5 DV1_02	SCI	Yes	Moderate creep corrosion
9	3.5 DV2_01	SCI	No	Minor creep corrosion
10	3.5 DV2_02	SCI	Yes	Heavy creep corrosion
11	3.5 DV3_10	SPF	No	No creep corrosion
12	3.5 DV3_11	SPF	Yes	Light creep corrosion
13	3.5 DV3_20	OM	No	No creep corrosion
14	3.5 DV3_21	OM	Yes	Heavy creep corrosion

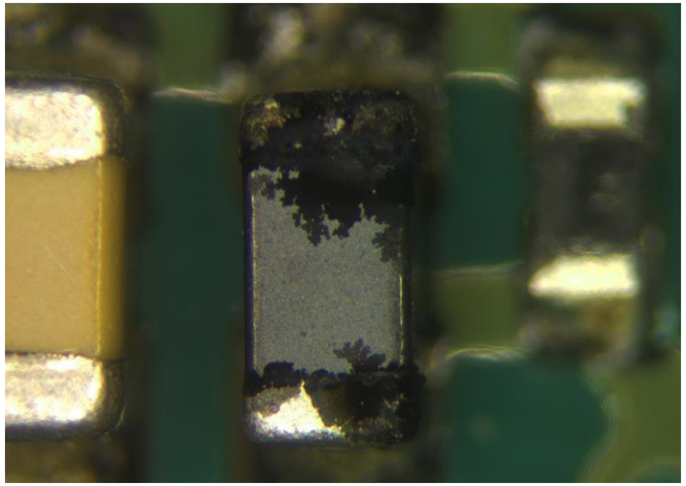
2.5 DV1_11

No creep corrosion

(Prebaked PCBs)

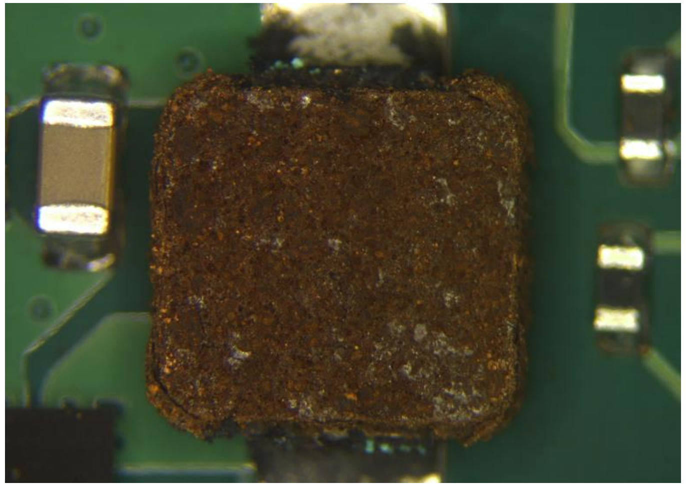


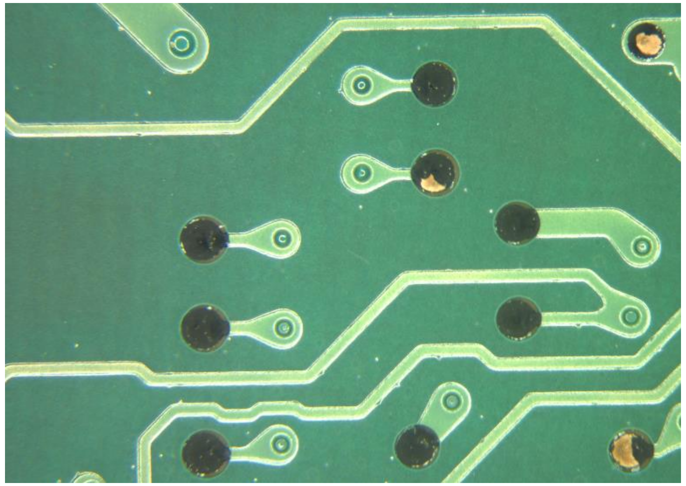


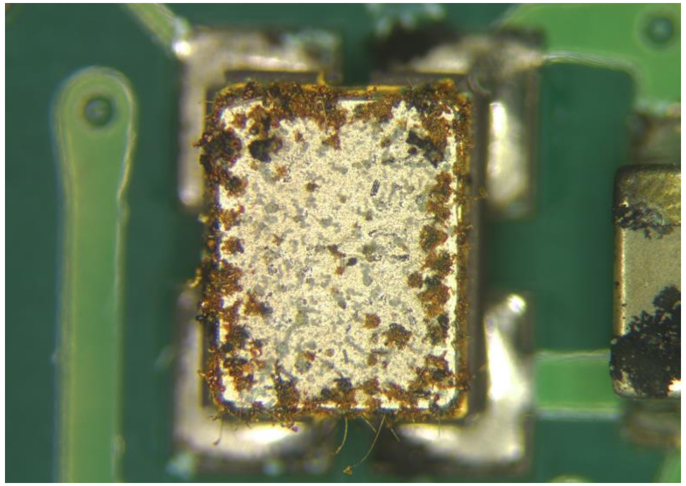


2.5 DV1_21

No or minor creep corrosion (Prebaked PCBs)



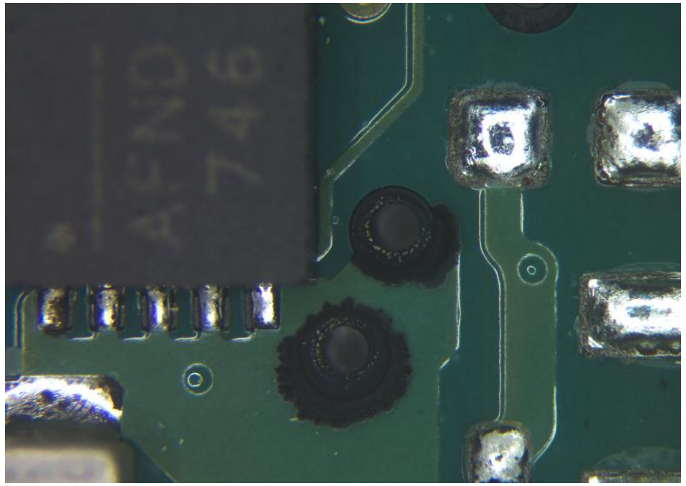


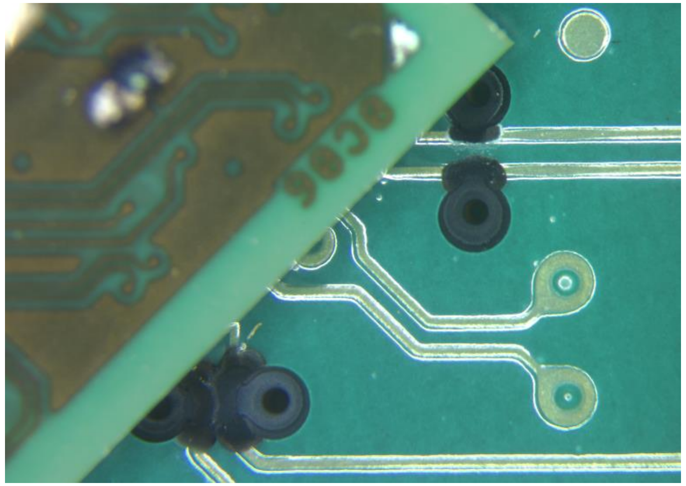


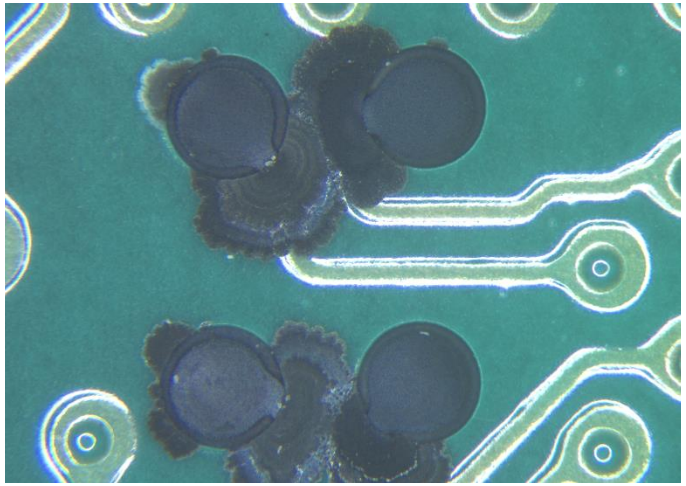
2.5 DV2_02

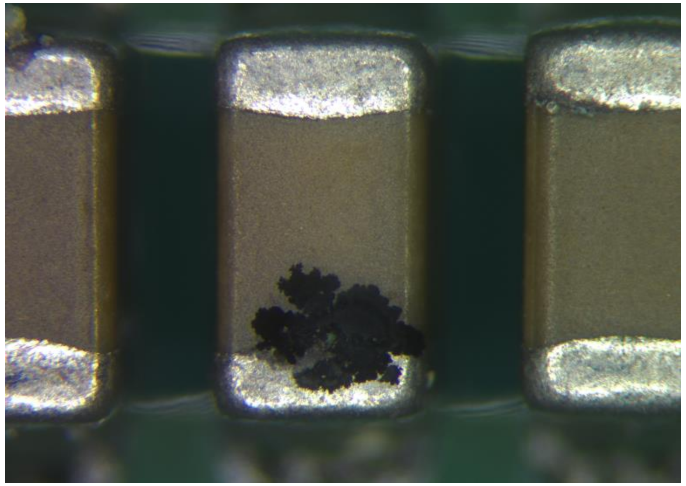
Heavy creep corrosion

(Prebaked PCBs)





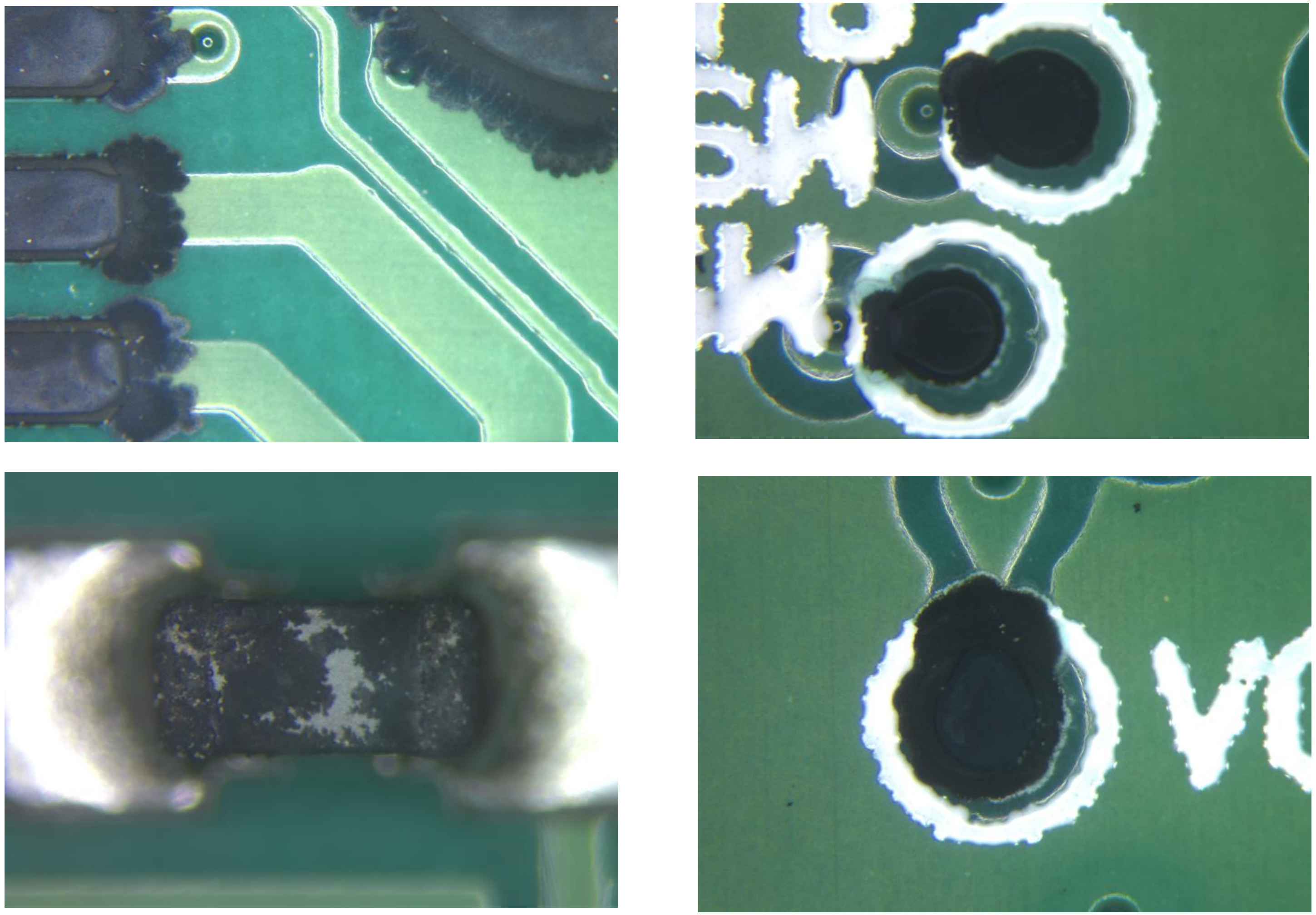




3.5 DV1_02

Moderate creep corrosion

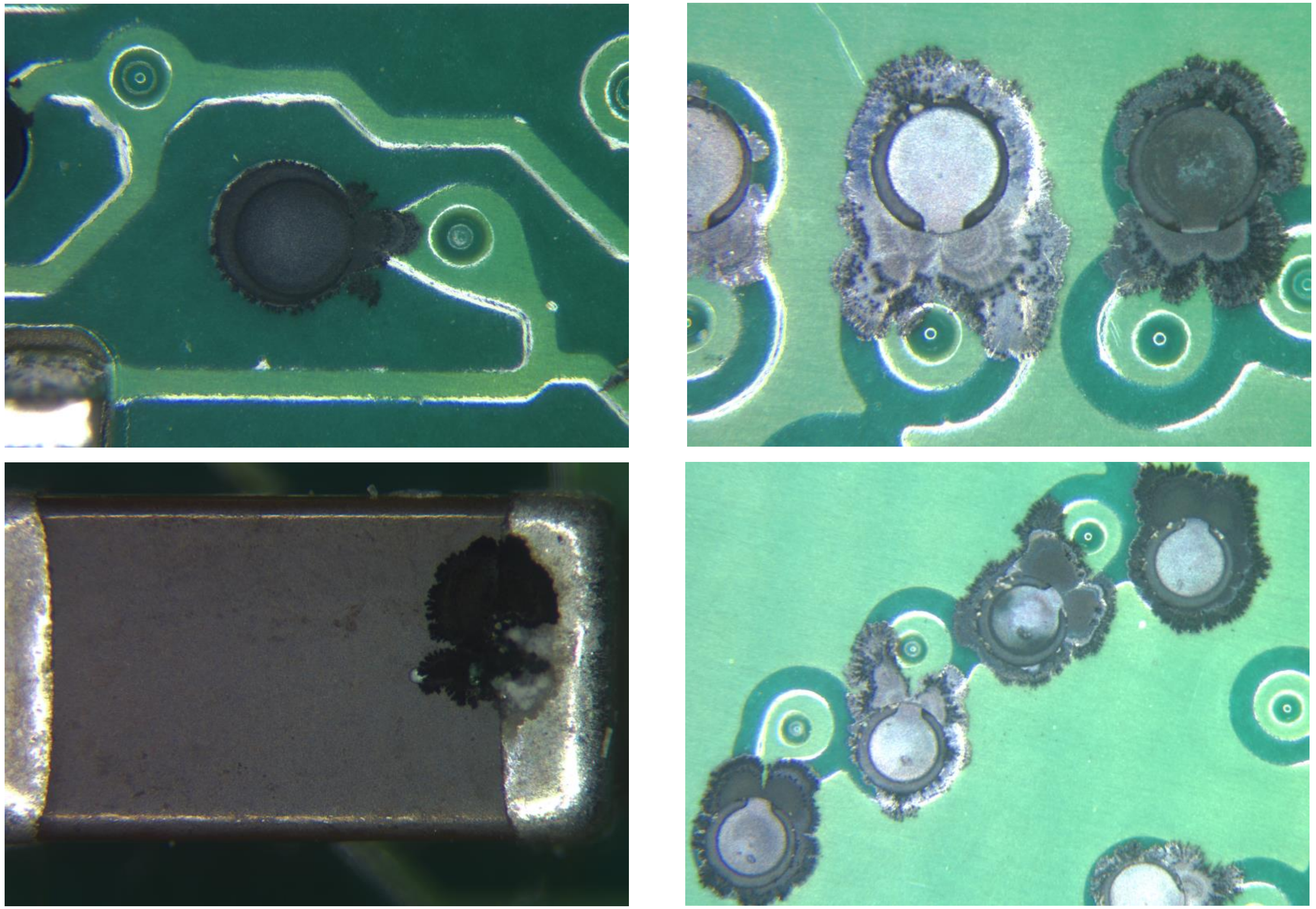
(Prebaked PCBs)



3.5 DV2_02

Heavy creep corrosion

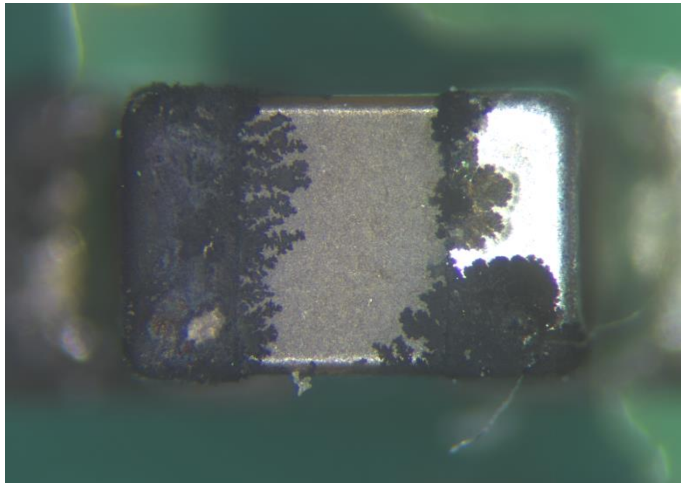
(Prebaked PCBs)

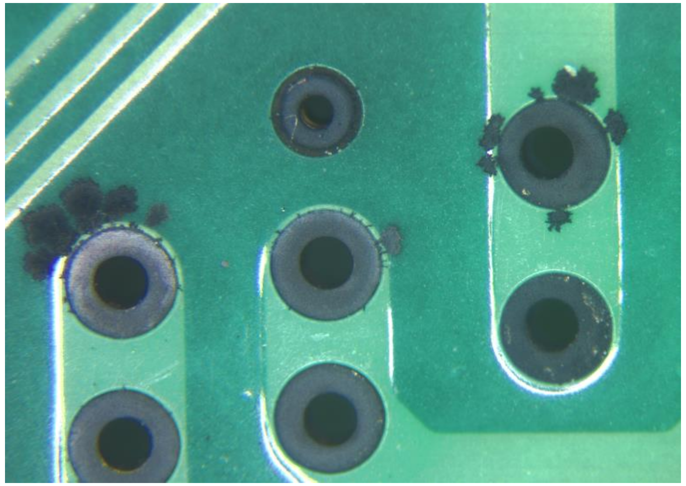


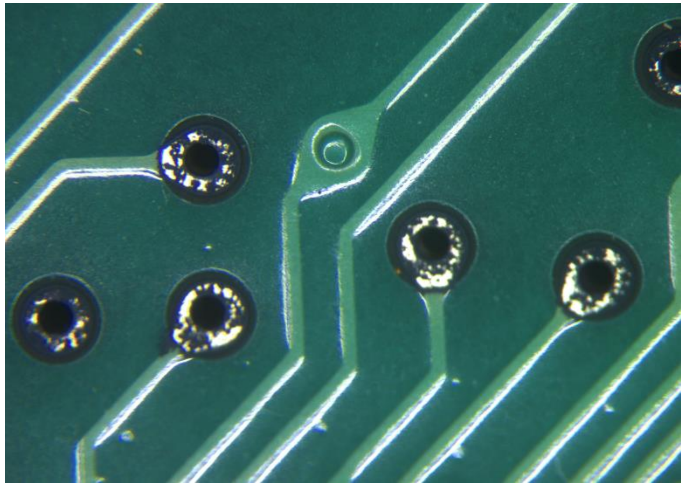
3.5 DV3_11

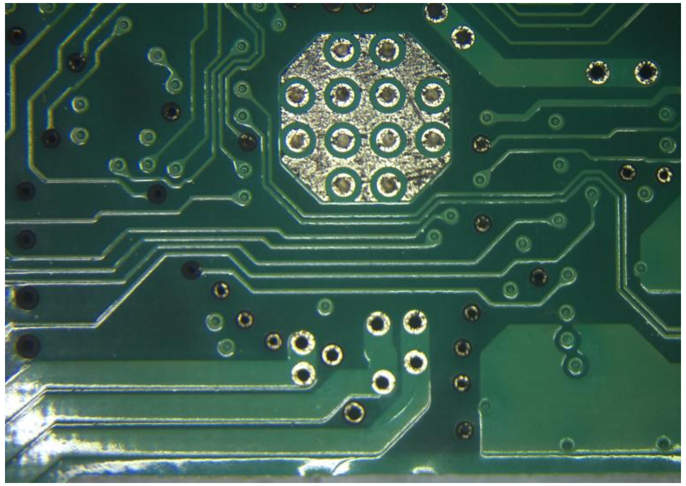
Light creep corrosion

(Prebaked PCBs)





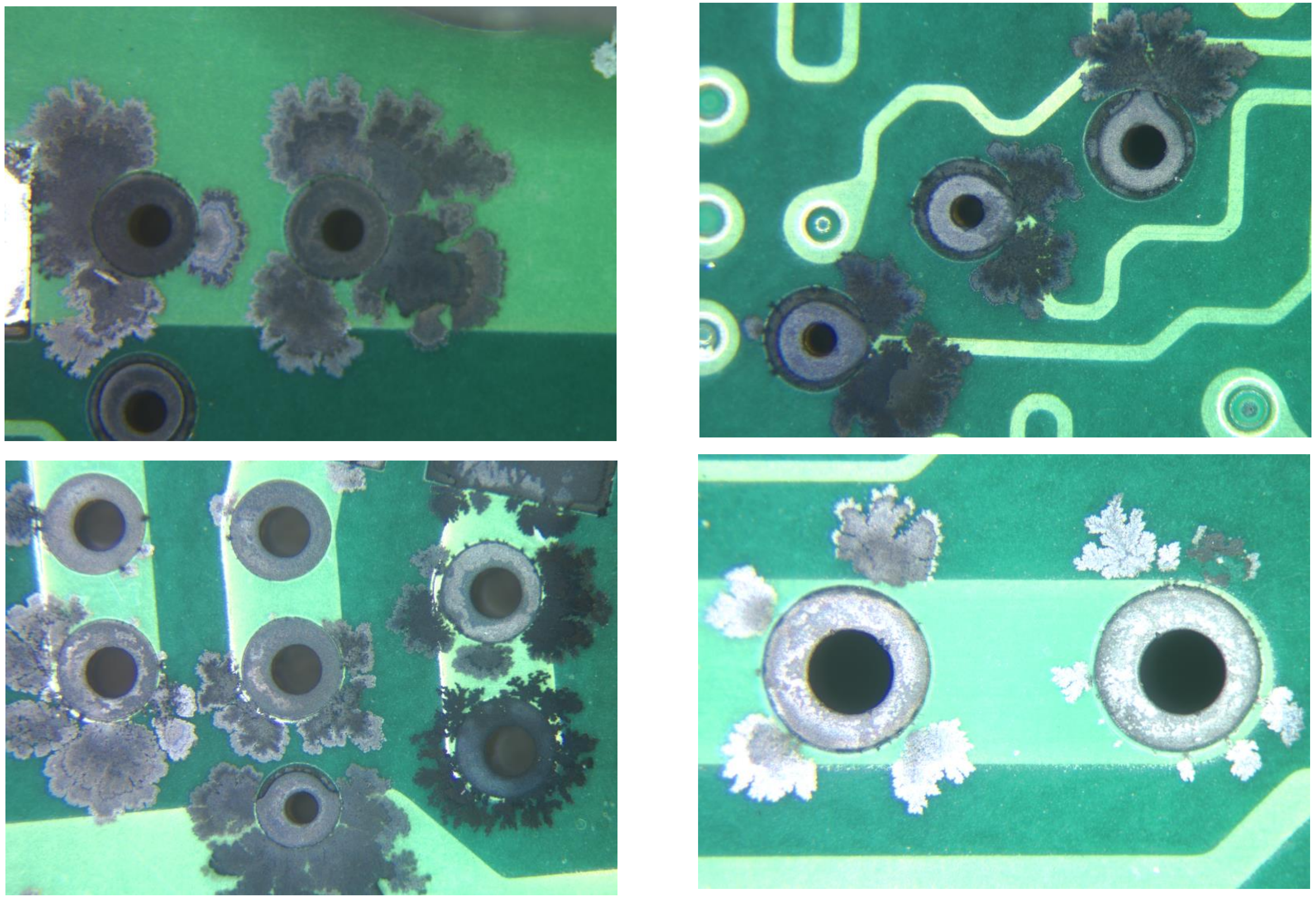




3.5 DV3_21

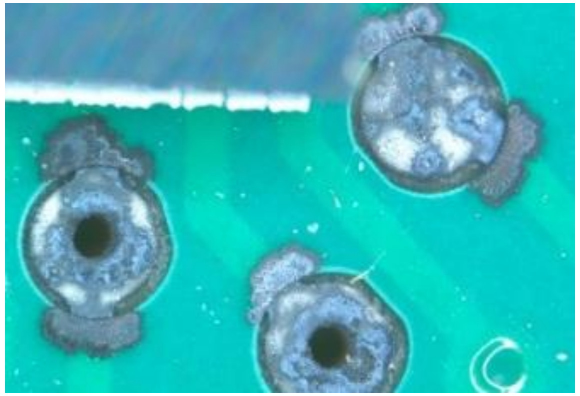
Heavy creep corrosion

(Prebaked PCBs)

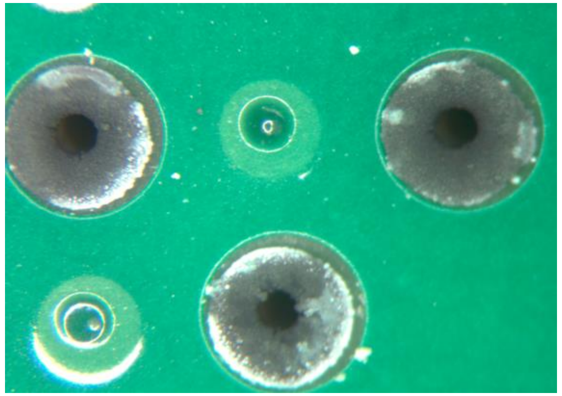


Effect of 2-year storage

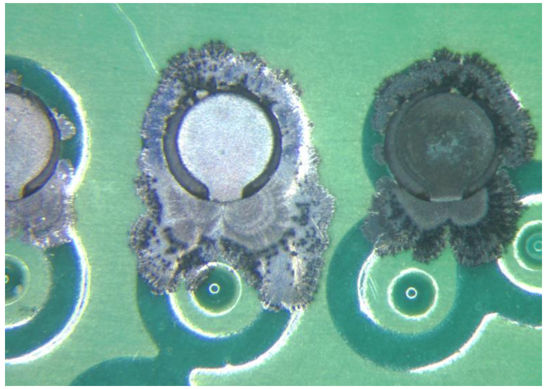
- There is evidence based on two PCB part numbers that storage of 2 years or more eliminates creep corrosion in the iNEMI FOS test



Fresh



2-year storage



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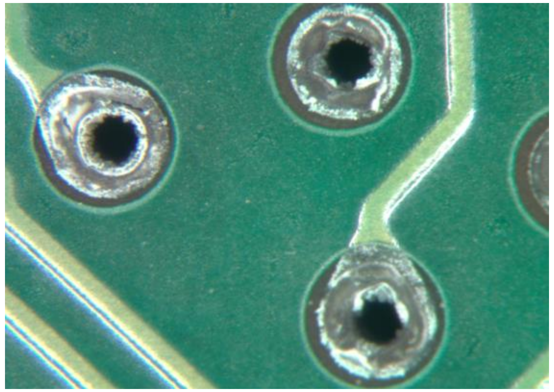

2-year storage

Conclusions

- The iNEMI creep corrosion test is sufficiently well developed to be an industry standard test for the qualification of PCBs technologies and production lots to ensure that they are free from creep corrosion in the field.
- Prebaking is necessary to drive off the volatiles that would otherwise contaminate the limited volume, sealed FOS chamber.
- There is evidence that the storage of soldered PCB assemblies for 2 years eliminates creep corrosion in the iNEMI FOS creep corrosion qualification test.