COMPARING FLOWERS-OF-SULFUR AND MIXED-FLOWING GAS CREEP CORROSION TESTING OF PRINTED CIRCUIT BOARDS

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ABSTRACT

Creep corrosion testing of printed circuit boards (PCBs) using a specially designed iNEMI flowers-of-sulfur (FOS) chamber was compared with a mixed-flowing-gas (MFG) test that used the iNEMI proposed gas composition. The iNEMI FOS test chamber is a 300-mm cube acrylic box with an 8-paddle wheel rotating at 20 rpm that can accommodate 8 PCBs. The sulfur vapor with controlled concentration was achieved by a bed of flowers-of-sulfur covering most of the chamber floor and by maintaining the chamber temperature at 50°C. The relative humidity was maintained at 81% using two 80-mm diameter beakers containing KCl saturated solution. The source of chlorine was 40-ml of Clorox in a 100-ml beaker. The iNEMI MFG chamber gas composition consisted of H_2S=1200 ppb, NO_2=200 ppb, Cl_2=20 ppb and SO_2=200 ppb. The MFG chamber was kept at 40°C and 70-75% relative humidity. The PCB finishes tested were organic surface preservative (OSP), immersion silver (ImAg) and gold on electroless nickel (ENIG). Identical bare PCBs and fully populated PCBs were tested to eliminate the effect of assembly process variables on corrosion. The exposure times were 5 to 20 days in the MFG test and 12 days in the FOS test.

In the MFG test, the ENIG PCBs suffered the most creep corrosion followed by the ImAg PCBs, with the OSP PCBs suffering the least amount of creep corrosion. In the FOS testing, the ENIG PCBs were the only ones that suffered significant creep corrosion, with only slight extent of creep corrosion observed on the ImAg PCBs. In the FOS test, chlorine gas was confirmed to be necessary for creep corrosion. The morphology of the creep corrosion on the ENIG PCBs tested in the FOS chamber more closely resembled that observed in the field, compared to the creep corrosion morphology generated in the MFG chamber. The creep corrosion morphology generated in the FOS chamber on ENIG PCBs showed a better defined banding structure, often seen on PCBs returned from the field.

Key words: Creep corrosion, flowers-of-sulfur, mixed-flowing gas, iNEMI

INTRODUCTION

Creep corrosion is the corrosion of copper and sometimes silver metallization on PCBs in environments high in sulfur-bearing gaseous contamination and the spreading of the sulfide corrosion products across the PCB surfaces to the extent that they may electrically short circuit neighboring features on the PCBs [1-3]. It is generally agreed that the adoption of the European Union Restriction of Hazardous Substance (RoHS) directive in February 2003 and its taking effect on 1 July 2006 [4] and the expansion of the electronic goods markets in Asia resulted in a dramatic increase in the occurrence of creep corrosion on PCBs [5]. RoHS restricted the use of six hazardous materials in electronics [4]. The restriction of lead in solders forced the PCB industry to abandon Pb-Sn hot-air-solder-level (HASL) surface finish. Immersion Ag (ImAg) surface finish was a popular initial replacement for Pb-Sn HASL because of its compatibility with Sn-Ag-Cu (SAC) solders [6]. The replacement of HASL with ImAg impacted PCB reliability, rendering the PCBs more prone to creep corrosion. The lead-free solders that became popular, such as SAC305, have much higher melting ranges than the Pb-Sn eutectic solder that was banished by RoHS. Although lead-free HASL is an acceptable surface finish for consumer products and mitigates copper creep corrosion, it poses other risks for PCBs used in high complexity, high reliability applications due to its high processing temperature [6]. Organic surface preservative (OSP) has gained popularity as a surface finish for lead-free soldering. While demonstrating improved creep corrosion performance over ImAg, it does not completely eliminate the concern. [6]

A need arose to develop a convenient qualification test that PCB assembly suppliers could use to satisfy their customers that their electronic assemblies will not suffer creep corrosion. Initially a lot of effort was directed to the use of MFG testing of PCBs [7-8], but more recently the focus has shifted to developing the much more cost-effective and convenient approach of FOS testing which has been successful in many case studies in being able to reproduce creep corrosion similar in morphology to that occurring in the field [9-11].

This paper is the first of its kind comparing the creep corrosion results of MFG and FOS testing on the same PCBs. The confidence in the ability of the FOS test to be equally or more successful in predicting creep corrosion, compared to the MFG test, will greatly aid in its wider acceptance as a test that PCB suppliers can depend on to qualify their products against creep corrosion.

BACKGROUND

As mentioned in the introduction, sulfur induced creep corrosion of printed circuit boards became a more significant issue for the electronics industry in the late 2000's. The conversion to ImAg surface finish for PCBs and lead-free soldering for assemblies as part of the 2006 RoHS transition made the hardware more vulnerable to creep corrosion. The lead-free transition coincided with the expansion of the IT industry into growth market geographies where the atmospheric sulfur tends to be higher (Figure 1), particularly near coal-burning power plants. Additionally, the trend toward the use of air side economizers that bring outdoor air into the data centers to reduce HVAC energy costs aggravated the situation.

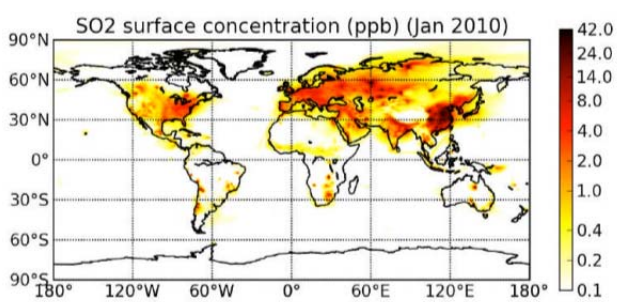


Figure 1: Worldwide SO2 concentration **[12]**

One of the first studies to evaluate PCB surface finishes such as ImAg and OSP for susceptibility to sulfur induced creep corrosion was conducted by Veale [2]. The study used MFG testing to compare the performance of ImAg, OSP, ImSn and ENIG surface finishes at conditions roughly equal to the Battelle Class III of H_2S = 100 ppb, NO_2 = 200 ppb, and Cl_2 = 20 ppb at 30°C in 75% RH for 20 days, with the addition of SO_2 = 200 ppb, similar to the EIA Class IIIA. Veale concluded that ImAg and ENIG would be susceptible to failures in a G2 environment (Table 1), while OSP and ImSn should have acceptable performance. Hannigan **[13]** has since clarified that the Battelle Class III MFG condition is more consistent with the ISA G1 environment, based on a comparison of copper coupon corrosion rates. With a focus on industrial environments such as steel, paper and tire manufacturing plants, concerns with data center environments were not discussed by Veale.

Table 1: Gaseous Corrosivity Levels per ISA-71.04 (ISA 1985)

Severity Level	Copper Reactivity Level, A/month	Description
G1 Mild	300	An environment sufficiently well-controlled such that corrosion is not a factor in determining equipment reliability.
G2 Moderate	300-1000	An environment in which the effects of corrosion are measurable and may be a factor in determining equipment reliability.
G3 Harsh	1000-2000	An environment in which there is high probability that corrosive attack will occur.
GX Severe	>2000	An environment in which only specially designed and packaged equipment would be expected to survive.

Shortly after the RoHS Directive entered into force in 2006, Mazurkiewicz [3] documented field failures due to copper creep corrosion in several unique high sulfur environments. Two examples pre-dated the transition to lead-free and were attributed to the use of ENIG PCB surface finish. Two examples, however, were directly linked to the implementation of ImAg PCB surface finish adopted with the lead-free soldering required by RoHS for consumer products. High sulfur in a clay modeling center and a sulfur refining and distribution facility both had PC failures attributed to sulfur induced creep corrosion, where previous PC technologies had performed adequately.

Schueller published the first paper specific to the issue of field failures in data center environments due to copper creep corrosion of lead-free printed circuit boards using ImAg PCB surface finish [1] a little over a year after the RoHS transition date. The prevalence of the failure of hard disk drives (HDD), graphic cards and motherboards in desktop and work station systems, as compared to notebook systems, was attributed to the air flow across the PCB assemblies. By comparison, HDDs with OSP PCB surface finish were not failing. Schueller also found that solder mask design and quality could contribute to the incidence of creep corrosion.

Schueller had noted that MFG testing at typical industry conditions had not uncovered the susceptibility of ImSn PCB surface finish to copper creep corrosion. Xu, working with Hannigan and others, led several studies to evaluate MFG conditions to more closely match the sulfur atmospheric environments found in the growth market data centers and drove to define a new industry standard condition through iNEMI. Initially focused on Battelle Class IV conditions, Xu went on to recommend an increase in the concentration of H_2S [13, 14] as shown in Table 2. Xu was also among the first to note process interactions, such as the effect of soldering flux.

Table 2: Mixed Flowing Gas Test Conditions

Gas	Battelle Class IV	EIA Class IIA	Xu Proposal
H_2S	200	100	1500-1700
NO_2	200	200	200
SO_2		200	200
Cl_2	50	20	20

The iNEMI corrosion project team continued the exploration of MFG test conditions and process interactions on a variety of surface finishes [7, 8]. The team ultimately recommended the conditions used in the study described by this paper. As mentioned above, seeking a more user friendly test method, the iNEMI team developed an FOS test that has been able to replicate the desired outcome.

Solid state drives (SSD) are becoming increasingly complex with higher density boards and more layers. Increasing performance is also increasing power consumption and temperatures. Increasing popularity, along with decreasing cost, is increasing volumes. With the introduction of SSDs in high reliability server systems, a reliability testing study was launched to verify that the plan of record OSP PCB surface finish and assembly process chemistry of rosin no clean flux would have good field performance. For comparison purposes, it was decided to include ENIG and ImAg PCB surface finishes. The timing of the study also took advantage of the recent definition of the iNEMI MFG and FOS test conditions to include both stress tests for comparison purposes.

EXPERIMENTAL AND RESULTS

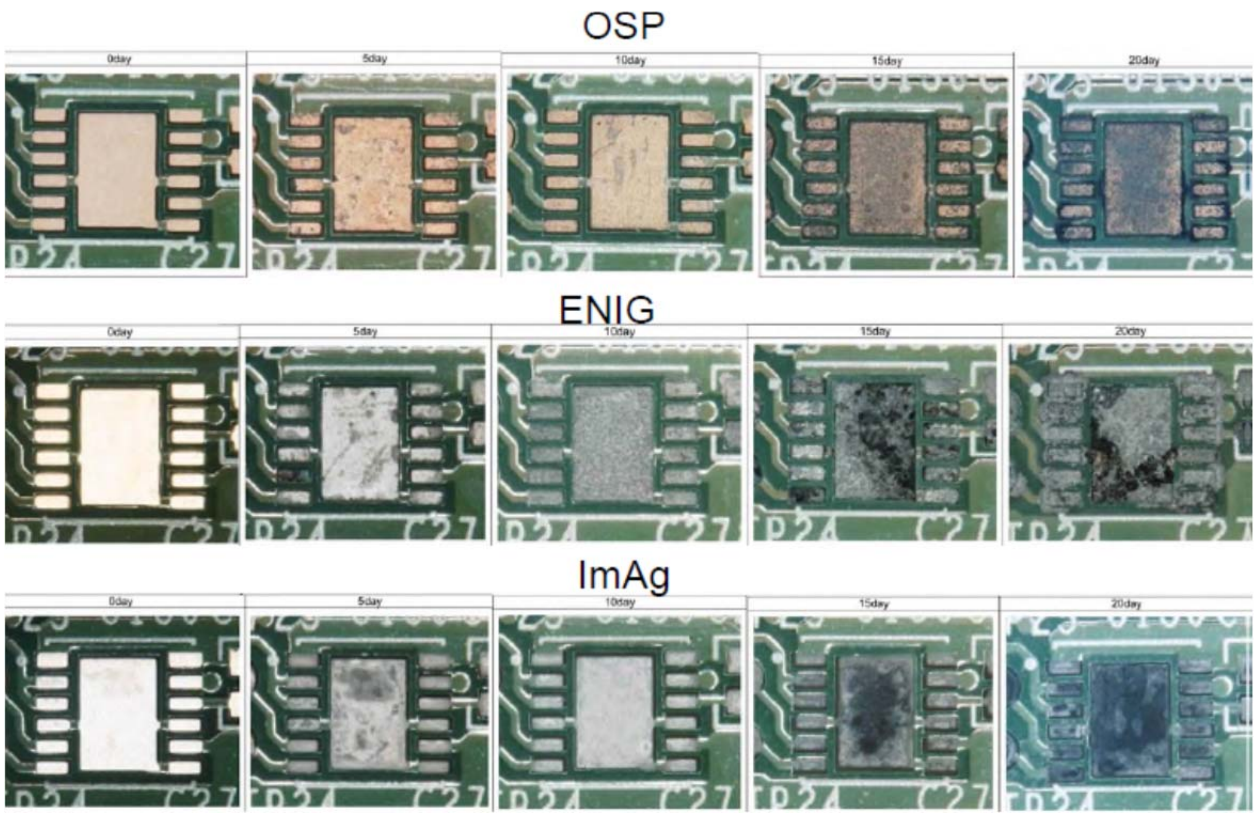
The MFG testing was done using the iNEMI defined conditions consisting of H_2S=1200 ppb, NO_2=200 ppb, Cl_2=20 ppb, SO_2=200 ppb, 40^{o}C and 70-75% relative humidity to achieve 500 nm/day copper corrosion rate. The MFG chamber is shown in Figure 2a. The test PCBs were rotated at 1 rpm. The FOS testing was done in an iNEMI defined flowers of sulfur test chamber (Figure 2b) consisting of a 300-mm cube acrylic box with an 8-paddle wheel rotating at 20 rpm that can accommodate 8 test PCBs. The sulfur vapor with controlled concentration was achieved by a bed of flowers of sulfur covering most of the chamber floor and by maintaining the chamber temperature at 50^{o}C. The relative humidity was maintained at 81% using two 80-mm diameter beakers containing KCl saturated solution. The source of chlorine with repeatable though time varying concentration was provided by 40-ml Clorox in a 100-ml beaker.

The bare and the assembled PCBs had three different finishes: OSP, ImAg and ENIG. Soldering was done with no-clean rosin flux. The sample size of each type of PCB and the periods of exposure in the MFG chamber are listed in Table 3. The bare and the assembled PCBs were exposed to the MFG environments for 5, 10, 15 and 20 days. The corrosion of the bare PCBs as a function of PCB finish and exposure time is summarized in Figure 3. The PCBs with OSP finish fared the best with the ENIG and ImAg finishes showing substantial corrosion. Typical examples of creep corrosion on the printed circuit board assemblies (PCBAs) at the plated-through holes (PTHs) and the capacitor terminals are displayed in Figure 4. The extent of creep corrosion in micrometers is summarized in Table 4. The maximum extent of creep corrosion on the OSP finished PCBAs was 108 µm; whereas the maximum extents of creep corrosion on the ImAg and the ENIG finished PCBAs were 216 and 324 µm, respectively. The creep corrosion product contained mostly Cu and S, in the form of Cu_2S as previously noted. Four PCBAs from each finish group were functionally tested before and after the MFG exposures. The results tabulated in Table 5 show that the PCBAs that had OSP and ImAg finishes survived 5 day of exposure to MFG; whereas some of the PCBAs that had ENIG finish failed within 5 days of exposure to MFG.

(a)

(b)

Figure 2: (a) MFG cham*b*er conditions consist of H_2S =1200 ppb; NO_2 = 200 ppb; Cl_2 =20 ppb; SO_2 = 200 ppb; 40^{o}C; and 70-75% relative humidity. (b) FOS chamber is a 300-mm cube acrylic box with 8-paddle wheels rotating at 20 RPM that can accommodate 8 printed circuit boards under test. A bed of flower covers most of the chamber floor. The chamber temperature is maintained at 50^{o}C. The relative humidity is maintained at 81% using two 80-mm diameter beakers containing KCl saturated solution. The source of chlorine with repeatable though time varying concentration is provided by 40-ml Clorox in a 100-ml beaker.



0 days 5 days 10 days 15 days 20 days

Figure 3: Optical micrographs of PCBs subjected to MFG environment.

Table 3: Sample size and exposure days for the MFG tests.

PCB				PCBA			
Exposure days	OSP	ENIG	ImAg	Exposure days	OSP	ENIG	ImAg
5	2	2	2	5	2	2	2
10	2	2	2	10	2	2	2
15	2	2	2	15	2	2	2
20	4	4	4	20	4	4	4
Total	**10**	**10**	**10**	**Total**	**10**	**10**	**10**

Table 4: Summary of creep corrosion incidents in MFG testing and their extent in micrometers (□m).

	Finish	J lead	PTH	Capacitors	A screw connection on card	Max creep corrosion
FG006APN	OSP	81	27	54	--	81
FG006AML	OSP	--	108, 81	108	81	108
FOCO85FQ	ImAg	216, 108, 135	--	137	--	216
FOCO85FY	ImAg	--	135, 108x	108, 81, 81, 81	--	135
FOCO85FD	ENIG	--	189, 243, 243	162, 162, 108	54, 54	243
FOCO85FJ	ENIG	--	243, 243, 243	324, 324	216	324

OSP

ENIG

ImAg

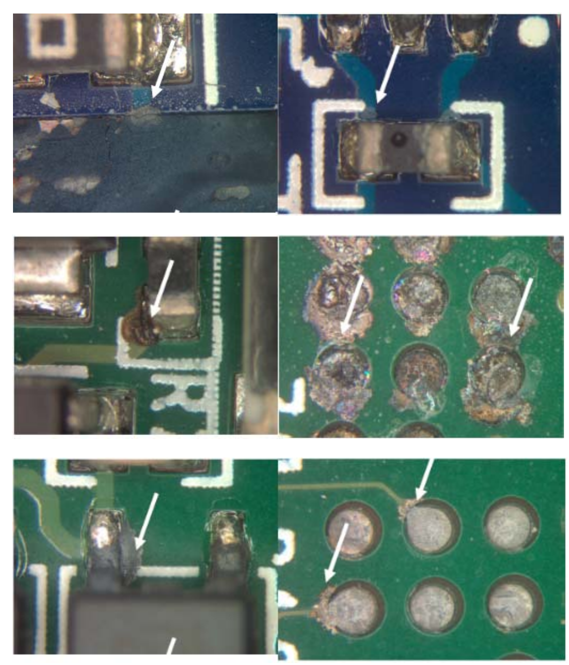


Figure 4: Creep corrosion on PCBAs with the three finishes exposed to 20 days of MFG environment. There was limited creep corrosion on the OSP finished boards, with somewhat more creep corrosion on the ImAg finished boards and substantial creep corrosion on the ENIG finished boards.

Table 5: Performance of the PCBAs in the MFG test.											
Sn	**Material**	**Days**	**Test results**	**Sn**	**Material**	**Days**	**Test results**	**Sn**	**Material**	**Days**	**Test results**
FG006AV9	OSP	5	PASS	FOCO85FA	ENIG	5	ISSUE	FOCO85FS	ImAg	5	PASS
FG006AM4	OSP	10	PASS	FOCO85FB	ENIG	10	PASS	FOCO85FM	ImAg	10	PASS
FG006AZW	OSP	15	ISSUE	FOCO85FH	ENIG	15	ISSUE	FOCO85FW	ImAg	15	ISSUE
FG006AQ3	OSP	20	ISSUE	FOCO85FE	ENIG	20	ISSUE	FOCO85FX	ImAg	20	ISSUE

In an attempt to compare creep corrosion testing in a MFG chamber to that in a FOS chamber, PCBAs with the three finishes were also subjected to FOS testing. Since all the test PCBAs had already been exposed to the MFG environment, the best candidates for FOS testing were the test PCBAs exposed to just 5 days of the MFG environment. The PCBAs were first baked in flowing nitrogen gas at 105°C to drive off the volatiles that would otherwise contaminate the sealed FOS chamber. Studies have shown that unbaked circuit boards contaminate the FOS chamber suppressing the metal corrosion rates and do not allow creep corrosion to occur [10]. In the first 10-day FOS test run, the Clorox beaker was inadvertently left out. As expected, creep corrosion did not occur on any of the circuit boards. The next 12-days of the FOS test included 40ml of Clorox in a 100 ml beaker as per the standard iNEMI FOS test. Figure 5 shows typical optical micrographs of the resulting creep corrosion. No creep corrosion occurred on the OSP finished boards; there was very slight creep corrosion on the ImAg finished boards; and there was substantial creep corrosion on the ENIG finished boards, with better defined banding of the creep corrosion product as is often seen on boards that suffer creep corrosion in the field.

OSP

ENIG

ImAg

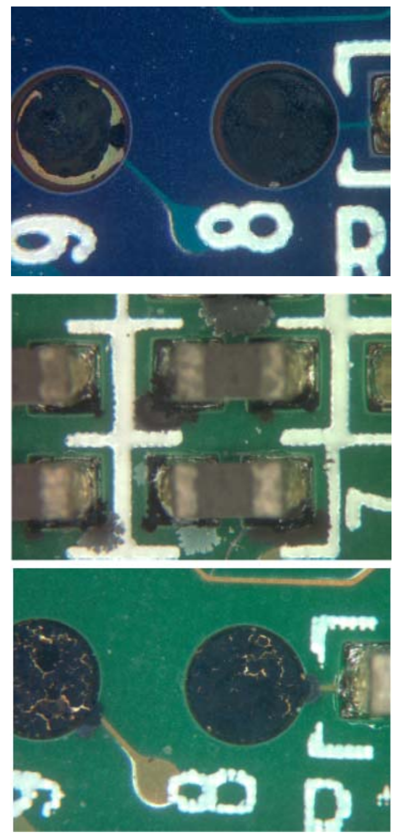


Figure 5: Results of exposure of the PCBAs with the three finishes exposed to 5 days of MFG environment followed by exposure to FOS environment without Clorox™ for 10 days and then to FOS environment with Clorox™ for 12 days. The OSP finished boards experienced no creep corrosion; the ImAg finished boards experienced minor creep corrosion and the ENIG finished boards experienced substantial creep corrosion with banded morphology similar to that seen on field returned failed hardware.

DISCUSSION

Creep corrosion testing of PCBs using MFG chambers is a well-researched topic with many recommended corrosive environments. The more recent test environment championed by iNEMI was employed for this work. The iNEMI MFG test results of Figures 3-4 and Tables 3-5 are in agreement with the generally expected trend that the creep corrosion propensity, amongst the PCBs with OSP, ImAg and ENIG finishes, is the highest in ENIG and lowest in OSP PCBs. The use of rosin flux is also key in reducing the likelihood of creep corrosion. While MFG testing is an indispensable research tool for atmospheric corrosion studies, there is clearly a need for a lower-cost qualification test that can be conveniently and unambiguously run by the PCB assembly suppliers to satisfy their customers that their products will have low probability of suffering creep corrosion in the field. Recent work by iNEMI has led to a standardized FOS test that has been proven in multiple case studies to successfully reproduce the creep corrosion banded morphology often seen on PCBAs that suffered creep corrosion in the field. Here we conducted one more study to verify the validity of the iNEMI FOS test. The FOS test results of Figure 5 are in general agreement with the MFG test results of Figures 3-4, with the exception that no creep corrosion occurred on the OSP finished boards and only limited creep corrosion occurred on the ImAg finished boards. The creep corrosion banded morphology on the ENIG finished PCBAs was better defined in the FOS test compared to the MFG test. This consistency of results is a validation of the comparison studies that have been conducted by the iNEMI corrosion team.

CONCLUSIONS

The iNEMI MFG test results were in agreement with the generally accepted position that creep corrosion occurs in the following order of decreasing propensity: ENIG, ImAg and OSP. The standardized iNEMI FOS test, a much lower-cost test that can be conveniently and reproducibly run by PCB assembly suppliers, produced similar results with somewhat better defined creep corrosion banded morphology found on boards that suffered creep corrosion in the field.

The planned use of OSP PCB surface finish and no clean rosin flux in the lead-free soldering paste is supported by the results of this study. Based on the testing completed and the level of corrosion observed in both MFG and FOS testing, there is high confidence that SSD drives will be adequately corrosion resistant in the data center environments expected for high end servers, even in growth market data centers.

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