

# Chemical Influences on the Reliability of Complex Assemblies

Bruno Tolla, Yanrong Shi, Xiang Wei, Hemal Bhasvar  
 Kester Inc.  
 Itasca, IL, USA  
[btolla@kester.com](mailto:btolla@kester.com)

## ABSTRACT

Reliability is one of the key performance drivers of the microelectronics industry today. Miniaturization trends, coupled with a dramatic increase in assembly complexity, increase the risks of in-field failures. Even more concerning to the end-users of electronic components is the difficulty to predict the failure rate of complex assemblies using accelerated tests. Therefore, it is of paramount importance for the end user to develop an in-depth understanding of the failure mechanisms at play, as well as an awareness of the potential contribution of each assembly material to these phenomena. In this paper, we leverage our body of knowledge on flux systems and fluxing mechanisms to bring a chemist’s perspective over reliability failures. After describing the chemical contributions to various failure modes (electrochemical migration, shorts, corrosion, deposits, etc.), we demonstrate how these mechanisms are influenced by the end-usage conditions. We then show how sound formulation principles, paired with a thorough understanding of the application environment, allow the chemists to design robust and reliable chemical systems able to sustain harsh operating conditions. From this perspective, this paper highlights the benefits of a thorough technical partnership between the flux formulator and the end-user to mitigate the risks associated with specific application environments.

Keywords: Reliability, Electrochemical Migration, Fluxing chemistry, Halogen-free activators, SIR

## INTRODUCTION

Following the semiconductor roadmap calling for a 50% scaling every second generation, the electronic packaging industry has been constantly evolving to satisfy the ever-increasing need for computing power and versatility. From conventional electronic assembly to high-end semiconductor packaging applications, interconnect densities are constantly

increasing (e.g. small pitches and thicknesses, low standoff heights). A whole array of complex architecture is appearing (2.5D/3D architectures, Systems in a Package), involving challenging form factors and a large variety of components and assembly materials. This growing complexity greatly increases the sensitivity of modern electronic assemblies to in-field failures. It also prevents the end-user from assessing the long term reliability of their assemblies. No holistic model is applicable to the specific usage conditions of one-of-a-kind assemblies subjected to particular environmental conditions (temperature cycling, humidity, voltage bias, vibrations, shocks, atmosphere, etc.), and involving peculiar interactions between assembly components (e.g. fluxes, underfills, conformal coatings, die-edge coats, adhesives).

This article analyzes the chemical mechanisms at play during the operating life of electronic components in an effort to contribute to the fundamental understanding of the in-field failures of complex assemblies and semiconductor packages. Chemically driven reliability failure modes are numerous: corrosion, dendrites, deposits, conductive anodic filaments (CAF), creep corrosion, etc. We will focus our discussion on the 3 former modes, whose occurrence is tentatively predicted through a large set of standard tests recognized by the electronics industry, as shown in Table 1.

Standard	Method	Temp C	H <sub>2</sub> O %RH	Bias V	Bias V/mm	Time h	Test Brd Spacing
IPC J-STD-004B	IPC-TM-650 2.6.3.3 (SIR)	85	85	50	100.0	168	IPC B24 0.5 mm
	IPC-TM-650 2.6.3.7 (SIR)	40	90	12.5	25.0	72	IPC B24 0.5mm
	IPC-TM-650 2.6.14.1 (ECM)	65	88.5	10	31.4	596	IPC B25A 0.318mm
Bellcore GR-78-Core	SIR 13.1.3	35	85	45-50	157.2	96	IPC B25A 0.3185mm
	ECM 13.1.4	65	85	10	31.4	596	IPC B25A 0.318mm
JIS Z 3197	SIR 8.5.3	40	90	0	0	168	IPC B25A 0.318mm
		85	85				

	ECM 8.5.4	40 85	90 85	45- 50	157	1000	IPC B25A 0.318mm
<b>BONO</b>	Inventec MO.SB.10029	85	85	20	166.7	360	BONO 0.120mm

**Table 1.** Industry Reliability Standards

These methods assess the resistance of standardized electronic assemblies to specific environments characterized by their temperature, relative humidity and voltage bias. As far as bias, the voltage gradient is the key factor governed by the test board geometry and conductor spacing. The chemical packages can be tested under various forms: chemical flux, paste, cored wire, preforms. Multiple criteria are usually taken into consideration to qualify a product, and the root causes for failure are frequently confounded. Therefore it is usually difficult to relate these tests to a fundamental assessment of the chemical activity of the products in the final assembly. For instance, the Electrochemical Migration (ECM) and Surface Insulation Resistance (SIR) tests as defined by IPC J-STD-004B are both based on a drop of the resistance at the surface of the epoxy laminate. Numerous root causes can affect these values as we will see later. To further complicate the matter, both of these tests can fail when corrosion or dendritic growth are evidenced. A notable exception is brought by the Bono test [1], later modified by Turbini and al. [2], leveraging a specific testing pattern and a mathematical model to assess the intrinsic corrosion ability of a flux, regardless of other failure mechanisms. In the following section, we report a series of customized reliability tests supporting our mechanistic analysis of the chemical causes of failure in electronic assemblies.

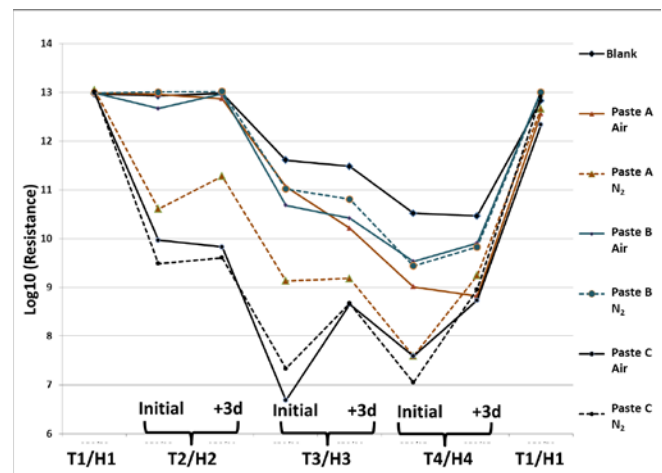
## EXPERIMENTAL

Two experimental No-Clean Halogen-free Lead-free solder Pastes (A and C) and one commercial No-Clean Zero-Halogen Lead-Free Paste (B) were included in this study. The customized SIR test method was carried out on standard IPC B24 testing boards (bare copper on FR-4) consisting of four comb patterns made of 0.4mm lines and 0.5mm spaces. The boards were cleaned using the standard protocol defined in IPC-TM-650 test method 2.6.3.7. The pastes were screen printed on the boards using a 5mil stencil and reflowed in a 7-zone reflow oven in air or nitrogen using a conventional profile. The boards were then exposed to increasing temperature (30 to 85C) and humidity (50 to 90% RH) conditions under a constant voltage bias (50V). SIR readings were collected every 72h under a testing voltage of 100V. The corrosion tests were executed according to the standard test method IPC-TM-650 test method 2.6.15 RevC. The customized Electrochemical Migration tests were conducted on standard IPC B25A-Pattern D testing boards, consisting of 1 comb pattern made of Cu traces on FR-4

with 0.318mm spacing. A 12V bias was applied immediately after the samples were deposited on the boards.

## RESULTS

Reliability is governed by the interaction between chemical residues from the assembly process and the board components under environmental stress, described by atmospheric composition, voltage gradient, temperature and humidity conditions. We will narrow down the chemical sources to the flux systems, although as denoted earlier, multiple board components and processing conditions can induce some chemical contamination. We investigated the failure mechanisms through the following test: the variation of the Surface Insulation Resistance (SIR) of a series of assemblies submitted to a constant bias (50V) was monitored through a succession of environmental conditions. Results are summarized in Figure 1.



**Figure 1.** Surface Insulation Resistance test under 50V bias through varying Temperature/Humidity conditions

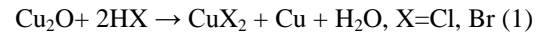
This test demonstrates how Temperature, humidity and exposure time play a major role in the results. One can observe that each tested paste respond differently to these 3 parameters. In other terms, their chemical package react differently to these environmental conditions. The reflow atmosphere (Air vs. Nitrogen) is a critical factor for one of the pastes as well. T1/H1 correspond to ambient conditions, while T2/H2, T3/H4 and T4/H4 represent increasing temperature ranges, the humidity remaining high (>85% RH) throughout the sequence. Obviously, one wants to design a robust paste which presents a good resistance to all these conditions and beyond. Paste C induces resistance losses at low temperature (T2/H2), while Paste B remains remarkably stable in all conditions with SIR values

remaining at least 1 decade above the standard lower limits. It is also interesting to note that SIR values for paste C tend to improve with exposure time in each T/RH condition. This demonstrates that the residue is active under these conditions and constantly evolves through a less electrically conductive mixture. Paste A presents an intermediate behavior, and contrary to the 2 others, its SIR values are strongly affected by the reflow conditions (e.g. 1 to 2 decades). The chemical residue left from this paste will evidently be of a different nature when the assembly process is conducted under air or nitrogen.

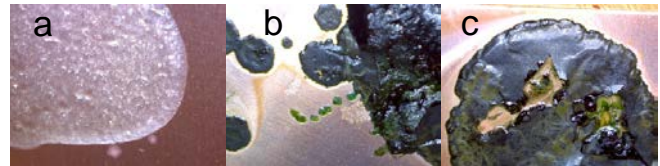
The temperature sensitivity of these tests has important consequences on industry standards. For instance, Paste A passes the new SIR test prescribed by IPC [3], but it fails the previous revision [4]. Wei and al. [5] have demonstrated that these differences were due to the higher ageing temperature required by the older standards, which softens the rosin system and let activators and reaction by-products leach out. This loss of encapsulation properties from rosin is further aggravated when the product has been reflowed under air, as rosin develops microcracks where dendrites can grow freely. The new IPC standard revision [3] was originally designed to maximize the activator impact on reliability: lowering the exposure temperature from 85C to 40C preserves the chemical residues, while increasing the relative humidity from 85 to 90% enhances their reactivity. A lower voltage gradient was also adopted to minimize the dendrite burn-off effects. While this new testing protocol discriminates chemical fluxes more thoroughly, it loses its selectivity on traditional high-rosin no clean packages. This example illustrates the limitations of the current reliability standards: they are only applicable to a specific set of environmental conditions, which can not be extrapolated to an end-user specific application. The industry is currently working at creating new standards involving multiple exposure conditions, in the same manner as the test reported in Figure 1.

While rosin natural chemistry can be engineered up to a certain point to optimize its thermal properties, its protective effects will be lost past a relatively low temperature, 130C at best. Also, improperly cleaned water soluble systems, typically under low stand-off components, will not benefit from rosin encapsulation. For all these reasons, the chemical activity of the flux activator packages is of paramount importance. We are now going to discuss the interaction between this specific group of compounds and the board components under various stresses. Halogenated activators will be used as the activator of choice to model this interaction, as this class of chemicals is commonly used by flux manufacturers across a broad range of applications.

Halogens are indeed praised for their strong fluxing properties according to reaction (1):

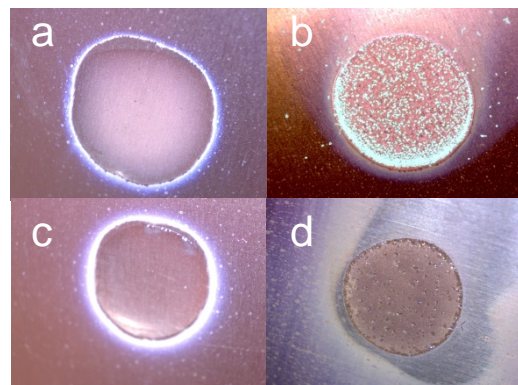


Given their well documented corrosion properties, formulators use chlorides or bromides in a combined form, either as salts or covalently bonded species, which are going to decompose at an intermediate temperature (e.g. soak) and release mineral acids (HCl and HBr). Following reaction (1), the residues from the fluxing reaction of the board metallic components (Cu, Ag, Sn, Au, Pb, Ni, Pd ...) will be a mixture of metal halides (CuCl<sub>2</sub>, SnBr<sub>2</sub>, CuBr<sub>2</sub>,...) with organic decomposition by-products. We performed a corrosion test on the residue created by the fluxing reaction of a conventional brominated organic compound on copper coupons (Figure 2).



**Figure 2.** Corrosion test under air of a Brominated organic compound  
 (a) After reflow  
 (b) and (c) After 6h/40C/93%RH exposure

Green compounds appear at the interface between the activator and the flux in 6h under a moist environment. These were not initially present as observed in Figure 2.a. This reaction matches the IPC J-STD-004B definition of corrosion: “a chemical reaction between the copper, the solder, and the flux residues, which occurs after soldering and during exposure to specific environmental conditions (40C/90%RH)” [6]. These species present a similarity with the ones obtained in the same conditions with the direct reaction of the mineral acids (HCl, HBr) on Cu (Figure 3).



**Figure 3.** Corrosion test under air

- (a) HCl, After deposition (b) HCl, After 2.5h/40C/93%RH  
 (c) HBr, After deposition (d) HBr, After 2.5h/40C/93%RH

The analogy between these experiments results from the common fluxing reaction products: The Cu(II) halogenated salts produced by Reaction (1) are very moisture sensitive, contrary to the Cu(I) salts. CuCl<sub>2</sub> is light brown while CuBr<sub>2</sub> is black. Under a moist environment, these compounds are going to evolve into their green hydrated forms (CuCl<sub>2</sub>·2H<sub>2</sub>O, CuBr<sub>2</sub>·4H<sub>2</sub>O) and ultimately hydrolyse into a green hydroxy precipitate (Cu(OH)<sub>2</sub>). We can formalize the corrosion phenomenon in electronic assemblies by two concurrent mechanisms (reactions are given as an example):

- Residue reaction under environmental stress
  - Moisture absorption:  $\text{CuBr}_2 + 4\text{H}_2\text{O} \rightarrow \text{CuBr}_2 \cdot 4\text{H}_2\text{O}$  (2)
  - Hydrolysis:  $\text{SnCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Sn(OH)}_2 + 2\text{HCl}$  (3)
  - Carbonation:  $\text{PbCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{PbCO}_3 + 2\text{HCl}$  (4)

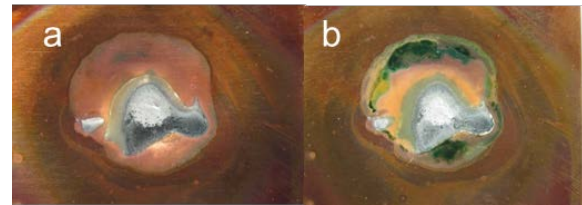
The high ionicity and moisture sensitivity of the metal halides makes them very reactive. Under the presence of moisture, these residues will evolve according to reaction 2-4 and release corrosive mineral acids.

- Corrosion of metallic compounds
  - Oxidation:  $\text{Cu} \rightarrow \text{Cu}^+ + \text{e}^-$  [ $E_0=0.52\text{V}$ ] (5)
  - Complexation:  $\text{Cu}^+ + \text{Cl}^- \rightarrow \text{CuCl}$  [ $\text{pK}_s=6.7$ ] (6)

Strong complexes drive the oxidation reaction (5) to the right [7]. For instance, the apparent oxidation potential of copper in hydrochloric environment becomes:

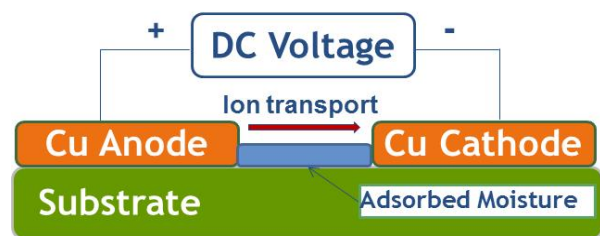
$$\text{Cu} + \text{Cl}^- \rightarrow \text{CuCl} + \text{e}^-$$
 [ $E_0=0.14\text{V}$ ] (7)

As a consequence, processing residues supplying strong metal complexing agents can promote corrosion. These residues need to be hygroscopic to enable some ionic mobility in the conductor's environment for these reactions to happen. Halides, as a byproduct of halogenated fluxes, are particularly corrosive. In addition to binding Cu ions, they will produce hygroscopic species from their initial fluxing reaction on metal oxides and induce acidic conditions as shown in reactions (2-4), thus placing copper in the corrosion domain of the potential-pH diagrams [8]. However, it should be noted that these mechanisms are not specific to halides and can be applied to any other class of activator presenting the same characteristics. As an example, we report in Figure 4 the corrosion observed with a halogen-free paste



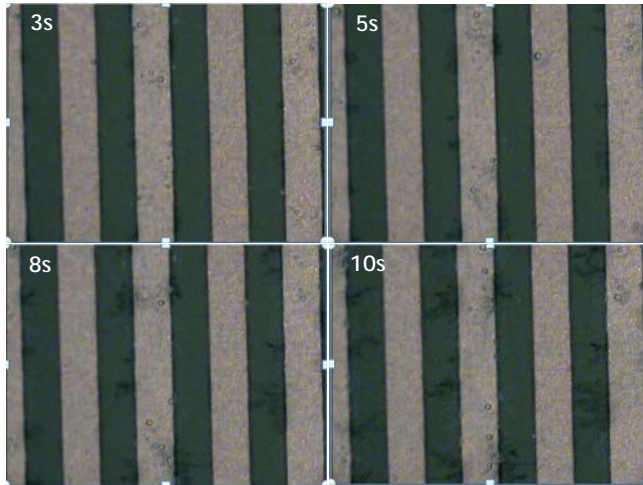
**Figure 4.** Corrosion test under air of a halogen-free paste  
 (a) After Reflow (b) After 10d /40C/93% RH

Cavallotti [9] has noted that electrochemical phenomena are preponderant in electronic assemblies. Electrochemical migration (ECM), not to be confused with Electromigration (EM), is an electrochemical process where metal ions move between adjacent metal conductors through an electrolyte solution under an applied electric field, resulting in dendritic growth. It is commonly said to be fueled by three ingredients: Moisture, Ions and a voltage Bias, following the basic model represented in Figure 5.



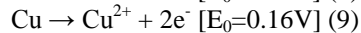
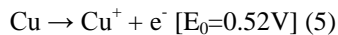
**Figure 5.** Basic Model for Electrochemical Migration

Moving beyond this basic description, we have applied a customized ECM test to demonstrate the critical influence of chemical residues on this specific phenomenon. As mentioned earlier, Surface Insulation Resistance measurements represent a combination of mechanisms. Also, the dendrites tend to burn-off during the standards tests as the typical voltage gradients tend to be high due to the small conductor spacing on testing patterns (Table 1). Therefore, we have designed a testing protocol allowing us to monitor dendritic growth in-situ. The standard IPC B25 coupons (Cu on Fr-4) modeling printed circuit boards conventionally used for circuit assembly were polarized with a relatively small voltage gradient (38V/mm) across the conductor spacing (0.318mm). Multiple chemicals have been tested in water solution to discriminate the already well-documented residue moisture sensitivity effects from the chemistry-driven behaviors. Executing this test with deionized water shows the impact of standard operating voltages on the small metal pitches used in electronic assemblies (Figure 6).

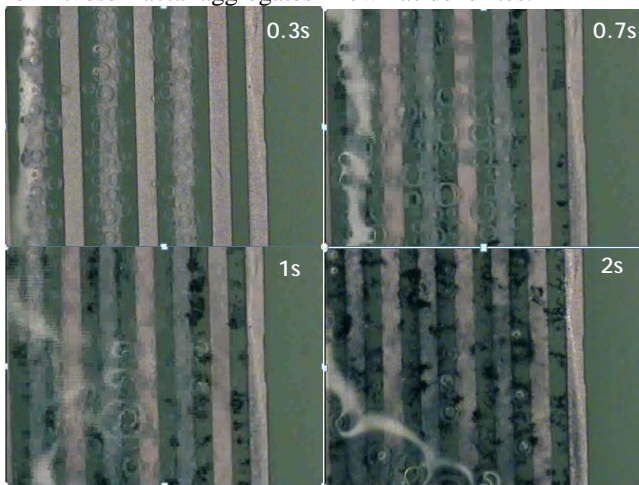


**Figure 6.** Customized ECM test on DI Water

While voltage gradients were on the low side compared to the standards tests reported in Table 1, they are sufficient to electrolyze water on the copper electrodes. The bubbles observed on every other trace correspond to water reduction at the cathode:  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$  [ $E_0=0.0\text{ V}$ ] (8) Copper plays the role of the sacrificial anode in this case, since its standard electrode potential is lower than water:



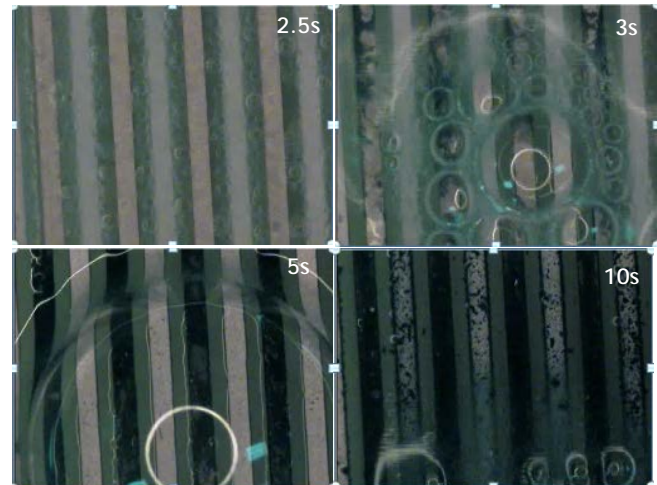
Soluble Aquo-complexes of  $\text{Cu}^{2+}$  are migrating to the negatively charged cathode where they are reduced and form these fractal aggregates known as dendrites.



**Figure 7.** Customized ECM test in 0.25M HCl

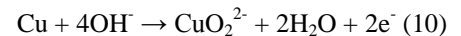
The accelerating effect of a hydrochloric environment is drastic as shown in Figure 7. Dendrites grow approximately 10 times faster in a 0.25M hydrochloric environment than in DI water, shorting the traces in 1 second. In order to discriminate the electrolytic effects, we conducted the

experiment in a sodium hydroxide solution of the same ionic strength. Results are radically different in this alkaline environment (Figure 8).



**Figure 8.** Customized ECM test in 0.25M NaOH

No dendritic growth is observed in this case, but severe corrosion is evidenced at the anode after 3s. Some corrosion residues also tend to deposit at the cathode after 10s. This phenomenon is a classic example of Cu corrosion in alkaline conditions referenced in Pourbaix diagrams [8]:



The previous test (Figure 7) was also carried-out in a corrosion domain of Copper (e.g. acidic conditions), but there is a key difference between the hydrochloric and alkaline environments: the chloride ion is a strong complexing agent of copper. The presence of chloride ligands is going to fundamentally affect the reactivity of copper, as discussed previously in the section on corrosion. Figure 7 evidences a significantly higher reaction rate in the hydrochloric environment. It is also going to change the nature of the dissolved species between the conductors. A large variety of charged complexes results from the interaction of copper with Chloride ions:



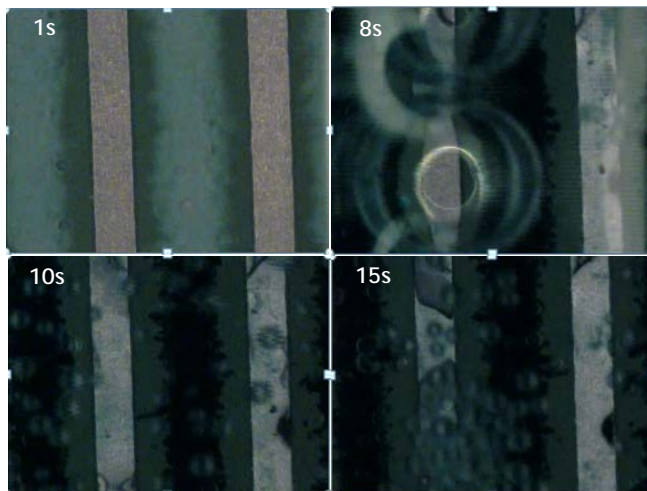
The following species are the most prevalent [7], their relative occurrence depending on pH and Chloride concentration:



One can notice that the majority of these soluble compounds are anionic. Therefore, a strongly repulsive electrostatic

barrier needs to be overcome for their migration to the negatively charged cathode. We believe this is the reason for the fractal geometry of the dendrites. This structure presents the optimum configuration to minimize the electrostatic repulsion between charged particles and the electrode. The growth is then diffusion driven, resulting from the concentration gradient of soluble copper species established between the anode and the cathode by the electro-dissolution of copper at the anode.

Similar to corrosion mechanisms, these phenomena are not specific to halogens. A strong copper complexing agent generating stable soluble species should be efficient at growing dendrites. As an example, we report in Figure 9 the result of the ECM experiment conducted with a halogen-free salt composed of sulfonate and amine groups, both showing a strong affinity for copper.



**Figure 9.** Customized ECM test with 0.5M halogen-free salt

While a very significant dendritic growth is observed at the cathode, the reaction rate is much smaller than in hydrochloric conditions (Figure 7). Either the Cu corrosion process or the migration of the charged species must be a rate limiting step.

In summary, three concurrent mechanisms need to occur for a dendrite to grow:

1. Formation of conductive water films at the surface of the epoxy laminate.  
 Ionic conduction at the surface of epoxy laminates is negligible unless ionic contaminants are present. The thickness and conductivity of the water film depend on hygroscopic contaminants. From this perspective, Anderson [10] has demonstrated that Surface Insulation Resistance

values decreased dramatically above the critical humidity level for water absorption of these moisture sensitive compounds.

## 2. Metal corrosion

The corrosion processes discussed earlier play a key role in the dendritic growth mechanisms as well. These 2 failure modes are therefore confounded and can be merged into a general discussion on Electrochemical migration.

## 3. Stabilization of charged metal complexes between the polarized electrodes

Only when this condition was met were we able to generate dendrites by means of a customized electrochemical migration test. Some ligands, like halogens, are able to generate a large spectrum of stable soluble complexes on the board. These results make perfect sense from a mechanistic perspective. They also resonate with an earlier study from Turbini [11], where the temperature effects on dendrite formation were associated with the solubilization of copper intermediates.

## CONCLUSIONS

Reliability is governed by the interaction between chemical residues from the assembly process and the board components under environmental stress, described by atmospheric composition, voltage gradient, temperature and humidity conditions.

A classical protection against any chemical influence is the encapsulation of the fluxing residues by rosin. We have demonstrated the impact of the thermal properties of Rosin on the reliability performances of no-clean formula. From this perspective, the standard reliability tests need to be adapted to this class of products, in order to be more representative of the end-use conditions. This also demonstrates the necessity to control the chemical influences from the activator system regardless of the use of Rosin. No-clean solutions don't protect the user from in-field failure in aggressive conditions.

We have shown that two basic chemical processes best model the interaction between the activators and their environment: Corrosion (in its broadest definition) and Electrochemical Migration. Our discussion on these two mechanisms demonstrates the profound influence of the residue chemistry on the reliability failures. It also highlights recurrent comments made by Cavallotti and others [9,12] about the corrosivity of the residues not being related to the total ionic level but only to certain ionic species.

Our mechanistic study also highlights the harmful effects of halogens in activator packages. With no possibility to

prevent the halogens to corrode, the industry has limited their use to 'acceptable' levels. The JEDEC IEC-61249 standard calls for a maximum of 1,500 ppm of combined halogens in fluxes, limiting the individual Cl and Br levels to 900ppm. However, the final halogen level present on the board will depend on the application conditions and general workmanship on the assembly line. While some halogenated fluxes do not create any visible defect when used properly, the simple presence of halogens in the residue will induce corrosion based on the mechanisms discussed in this paper. Clearly, Zero-halogen solutions (meaning with no intentionally added halogens) represent the future of Electronic Assembly. We have shown however, that the same mechanisms, hence the same effects, apply to halogen-free activators. Therefore a thorough understanding of the chemical influences on the reliability of complex assemblies is in order to develop these Zero-halogen solutions. We will present our work on these systems in a future publication.

#### ACKNOWLEDGEMENTS

The authors would like to acknowledge Kyle Loomis for the reflow profile development and application expertise. Paul Klimah has also brought significant insight on in-field failures by leading the analytical work on various electronic assemblies.

#### REFERENCES

[1] C. Puechagut, A.M. Laugt, E. Guene, R. Anisko, The IPC Printed Circuit Expo. APEX and Designer Summit Proceedings, 21336 (2010).

- [2] Y. Zhou, L. J. Turbini, R. Deepchand, C. Bev, M. Pritzker, J. Electronic Mat. (2013), 42(12), 3609-19
- [3] IPC J-STD-004B (Dec2008) / IPC-TM-650 test method 2.6.3.7
- [4] IPC J-STD-004A (Jan2004) / IPC-TM-650 test method 2.6.3.3
- [5] X. Wei, B. Tolla, SMTA International Conference Proceedings (2014)
- [6] IPC-TM-650, Test Method #2.6.15, (2004) Rev C
- [7] G. Charlot, Les reactions chimiques en solution aqueuse, 7 ed. (1983)
- [8] M. Pourbaix, Atlas of electrochemical equilibria in aqueous solutions. 2d English ed. 1974, Houston, Texas
- [9] P.L Cavallotti, G.Zangari, V. Sirtori, J. Electronic Mat. (1995), 24(4), 365-70
- [10] Anderson J.E., IEEE Trans. Comp., Hybrids, Manuf. Technol., 11, 1, 152-8, 1988
- [11] B. A. Smith, L. J. Turbini, J. Electronic Mat. (1999), 28(11), 1299-1306
- [12] L.J. Turbini, G.B. Freeman, D. Cauffiel, MRS Symposium Proceedings (1994), 323, 147-52