

IMPACT OF REFLOW AND CLEANING CONDITIONS ON THE ELECTROCHEMICAL ACTIVITY OF FLUX RESIDUES UNDER SURFACE MOUNT COMPONENTS

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ABSTRACT

Managing the electrochemical activity of flux residues is a key aspect of the design of robust processes enabling complex and highly-reliable electronic assemblies. This paper leverages our fundamental knowledge of flux systems and soldering mechanisms, and complements it with a series of customized tests for corrosion and electrochemical migration under various SMT components, to establish the impact of reflow and cleaning conditions on the electrochemical activity of flux residues confined in tight spaces and partially shielded from a convective heat transfer or a thorough cleaning process. Various chemical packages are investigated, and the failure modes are analyzed in terms of the chemical equilibria at play between the flux and its environment. The demonstration of the interplay between assembly architecture, processing conditions and flux formulation illustrates how sound chemical principles paired with a holistic understanding of the application environment can enable the design of robust and reliable chemical packages mitigating the risks of in-field failures for the final assemblies. This study also forms the background for the proposal of new reliability testing standards for the electronic assembly industry.

Keywords: Electrochemical migration, Surface Mount Components, Solder Paste, Flux, Reflow, Cleaning

INTRODUCTION

While the Semiconductor industry has matured into a single-digit growth environment and Moore's law is called into question, disruptive trends are, once again, profoundly changing the business landscape. The Internet of Things (IoT) movement can justifiably be considered as the next revolution, following PC and Mobile. It is bringing tremendous opportunities to the Microelectronics Packaging segment, as well as new challenges. Heterogeneous integration, paired with a growing complexity of the package architectures, larger component form factors and higher interconnection densities increase the risk of in-field failures. The usual requirement for sensors to be operating in challenging environmental solutions compounds the risk: Large temperature swings, thermal shock, moist environments, vibrations, corrosive atmospheres are examples of environmental factors altering the life cycle of an electronic assembly. Due to the almost infinite number of assemblies, processes, and environments at play, modelling

the life cycle of assembly materials from application testing is a challenging task. It cannot be simply accomplished in isolation, through mathematical analysis, but also requires a deep understanding of the mechanisms at play. From this perspective, this article intends to analyze the failure modes of custom-made reliability testing boards from a mechanistic perspective. While numerous failure modes and contamination routes are possible, the experimental setup and discussion are focused on the chemically-driven reliability failures induced by assembly materials and their associated reflow and cleaning processes. For this purpose, a homogeneous series of flux components was screened for their contribution to electrochemical migration in a commercially representative formulation template. A tailor-made electrochemical migration protocol was devised, and various groups of active components were studied (weak organic acids, amines, rosins, corrosion inhibitors) while the solvent system, additives and total solid content were left unchanged. In a second series of experiments, an advanced custom-made testing board was designed to study the interactions between chemical factors, components and process parameters.

EXPERIMENTAL

A tailor-made electrochemical migration protocol was devised to grow dendrites in a controlled environment. Dendritic growth was monitored on custom-designed boards consisting of six Y-shaped copper traces (Figure 1).

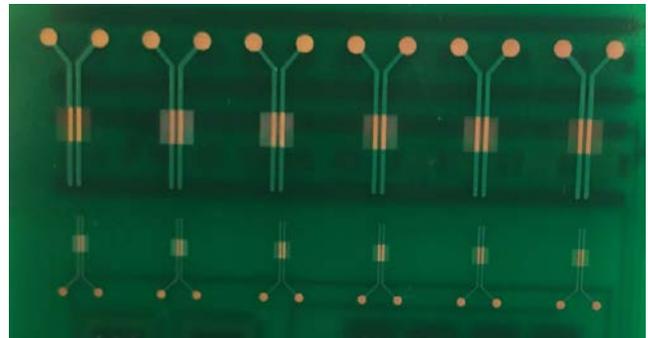


Figure 1. Customized ECM board design

An opening in the solder mask (brown square on top of each Y pattern) allows the contacting of fluxes with Cu traces in a well-defined area. The fluxes are dried at room

temperature. Water is added to the residues, prior to biasing the assembly with a 12V/mm gradient across the conductor spacing (0.62mm). The amount of water and the voltage gradients were optimized to yield acceptable dendritic growth rates for the experimental timeline. The dendrites are protected by the relatively low voltage gradient, as well as a current limiting device set at 295 μ A to prevent burn-out effects. Dendritic growth is monitored visually, and by means of recording the current evolution in function of time. This simple test allowed us to screen a comprehensive series of flux components for their ability to induce electrochemical migration. A commercially representative flux formulation template was designed and all chemicals were tested in isolation.

A more complex test board was designed to model the influence of flux residues on the reliability of electronic assemblies in function of the assembly materials chemistry, components and process parameters. This 62mils thick board features multiple components (BGA100, Resistors 2512, 1210 and 0805, QFN44 and QFN100) under which sensor traces were placed to collect the local surface insulation resistance values. The surface finish is Cu OSP. Figure 2 shows an example of the electrical setup, where two sensor loops located between the perimeter I/O's and the center pad collect the SIR signal under a QFN100 component.

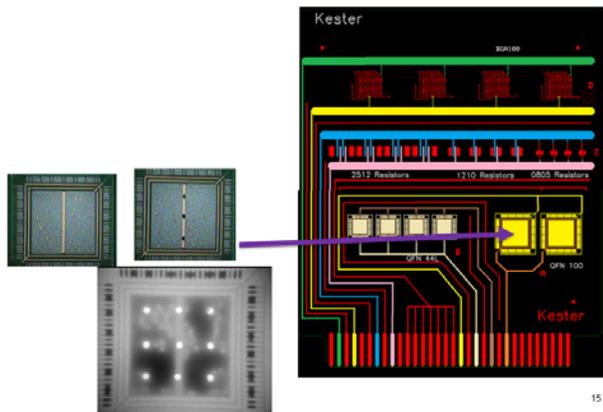


Figure 2: Custom-designed SIR testing board under components - QFN 100 Sensor Traces

The specific chemical makeup under investigation is formulated as a no-clean solder paste, and tested in combination with various reflow and cleaning processes. The pastes are screen-printed on the pads and sensor traces by a Speedline MPM Momentum printer equipped with a laser-cut stainless steel stencil (4mils). The board is then populated with components using a Juki KE-1080LN pick and place system, and subsequently reflowed in a Speedline Electrovert OmniExcel 7-zone reflow oven in air. The reflow profiles differ in duration and peak temperatures: the first one involved a direct ramp-to-spike, while the second had a more pronounced soak and a longer time above liquidus (Table 1).

	PEAK (C)	TAL (s)	Soak (s)	Ramp Rate (C/s)	Cooling Rate (C/s)
Profile1	233.0	48.3	70.8	1.2	-1.3
Profile2	250.0	84.1	113.0	2.1	-1.9

Table 1: Reflow Profile Characteristics

Soak = 150-217C range, Ramp Rate = 40-90C range

The assemblies are then cleaned at 65C in a customized in-line cleaner, using an aqueous wash chemistry from Kyzen designed for no-clean fluxes and injected at a 15% concentration. Variations of the cleaner belt-speed yields partially cleaned (2 fpm) and fully cleaned (0.5 fpm) assemblies.

The uncleaned and cleaned boards are then exposed to a moist environment (85C/85%RH) under a constant voltage bias of 8V, for a duration of 7 days. The IPC SIR Test method for open format B24 test boards (IPC-TM-650 §2.6.3.7) directs the user to apply an electrical bias of 25 V/mm (DC) between adjacent parallel traces. Using an 8V board bias yields a field strength of 28V/mm underneath the QFN100 components, while covering a broad range (16 to 45 V/mm) of voltage bias underneath the resistors to study their impact in a simple configuration. SIR data are collected at 20 minute intervals, under a testing voltage of 8V.

RESULTS AND DISCUSSION

Electrochemical phenomena are preponderant in electronic assemblies as reported by Cavallotti [1]. 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 3.

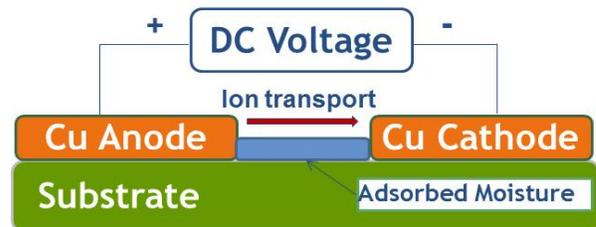


Figure 3: Basic Model for Electrochemical Migration

Moving beyond this basic description, our electrochemical migration protocol tested the influence of the flux chemistry on dendritic growth. Induction times and growth rates were extracted from the digital recording of the growth process and are reported in the tables below.

	Rosin	Act 1	Act 2	Act 3	Act 4
Growth Rate (mm/s)	32.1	22.6	11.3	11.7	17.9

Induction time (s)	83.5	9.5	4.0	20.5	10.5
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Table 2: Dendritic Growth – Activator effect

	No inhibitor	Inhibitor L1	Inhibitor L2
Growth Rate (mm/s)	11.3	11.4	8.9
Induction time (s)	4.0	8.5	12.0

Table 3: Dendritic Growth – Corrosion Inhibitor effect

	No Amine	Organic Amine 1	Organic Amine 2
Growth Rate (mm/s)	11.3	4.5	0
Induction time (s)	4.0	18.5	Infinite

Table 4: Dendritic Growth – Organic Amine effect

The activators were shown to have a strong impact on the shape of the dendrites. However, the variations in growth rates observed with the activators (Table 2) or the corrosion inhibitors (Table 3) were not statistically significant. On the other hand, Rosin presented a dramatic impact on induction times by preventing the nucleation of dendrites at the cathode. Furthermore, organic amines were found to strongly impact the dendritic growth kinetics (Table 4), while marginally affecting their shape. One of the organic amines even shut off the dendritic growth mechanism altogether. These effects can be visualized with the current curves reported in Figure 4, where the current amplitude quantifies the electrochemical activity while the abrupt cut-off identifies the time when dendrites short the polarized traces.

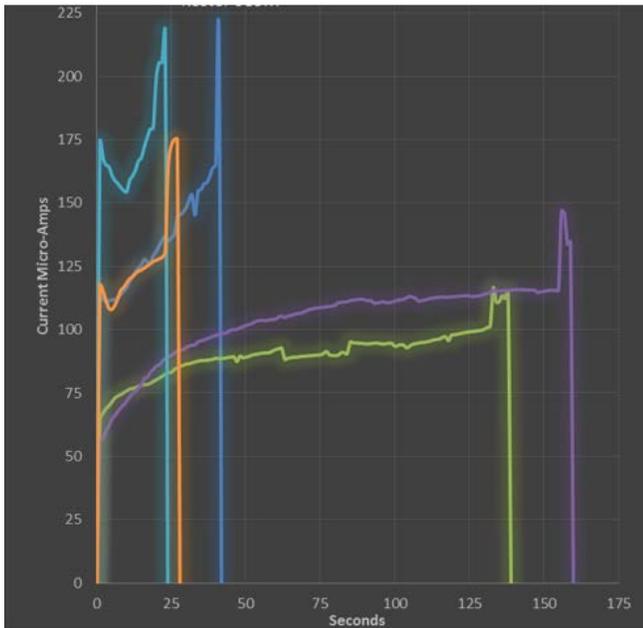


Figure 4: Current curves for various activator systems tested with the custom-designed ECM protocol

The dramatic impact of chemical compounds on dendrite morphology or growth kinetics can be interpreted from a

mechanistic perspective. Electrochemical migration proceeds through 5 sequential mechanisms, summarized in Figure 5.

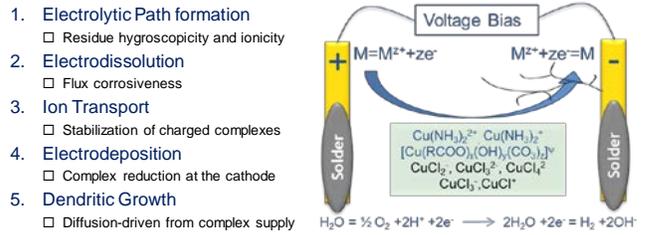
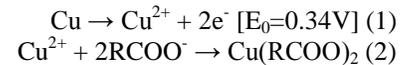


Figure 5: Electrochemical migration - Chemical mechanisms

1. Electrolytic path formation between conductors
The critical influence of chemical impurities on ionic conduction at the surface of epoxy laminates, and the impact of their moisture sensitivity on the characteristics of the conductive films were studied in detail by Anderson [2]. From this perspective, the flux residue moisture sensitivity and ionicity will have a strong influence.

2. Electrodissoolution
The oxidation and dissolution of conductive traces can be mediated by the fluxes. The corrosiveness of the flux residues result from their ability to supply ligands to catalyze copper oxidation, according to reactions (1-2):



Strong complexation effects in equation (2), driven by a low solubility constant (pKs), displace the oxidation equilibrium (1) to the right, resulting in a lower apparent oxidation potential for copper:



Therefore, this mechanism depends on the strength of the complexes formed between copper and the reflow residue constituents. It will also be governed by the propensity of the residue to release these ligands under environmental stress, typically through moisture absorption, hydrolysis and carbonatation.

3. Ion transport
Stabilization of charged metal complexes between the polarized electrodes is essential to grow a dendrite. From this perspective, the flux is a source of ligands for the electrodissoolved metal ions. The charged complexes originating from these metal-ligand interactions are the building blocks for the dendrites. Therefore, the stability and mobility of these species will drive the dendritic growth kinetics. As mentioned earlier, amines are the source of a large array of stable copper complexes. The results reported in Table 4 illustrate how these complexes interfere with the dendritic growth mechanism.

4. Electrodeposition

Figure 6: SIR Values from the brominated activator, for various reflow and cleaning conditions

The electrochemical activity of the residue is lower, and partial cleaning doesn't seem to be detrimental. However, the reflow process shows some contribution to the reliability of the assembly. The fact that brominated organic compounds tend to generate safer residues can be interpreted in various ways: first, the bromine ion is less polar, and therefore yields less ionic residues. Also, bromine is initially trapped in a covalent bond (as opposed to a salt for the chloride species). Therefore, unreacted species are much safer than chloride containing fluxes. Finally, brominated compounds are more volatile, such that a significant fraction is lost during reflow. A longer reflow profile will produce a residue with lower bromine levels, thus a lower potential for electrochemical migration.

Another interesting trend was found with one of the non-halogenated pastes (Figure 7). Although this paste doesn't contain any intentionally added halogens, it featured the worst reliability results under QFN's of any of the tested pastes.

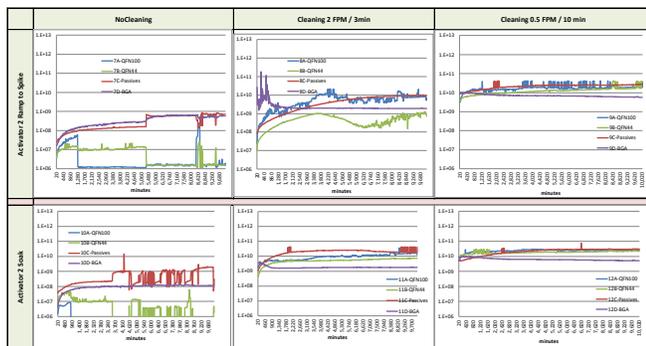


Figure 7: SIR Values from one of the non-halogenated paste, for various reflow and cleaning conditions

In these products, halogens are replaced by a blend or weak organic acids, organic amines and other organic additives to flux the metals, while the formulation backbone remains the same. These active components can undergo similar redox reactions as the one described for halogens, as illustrated by reactions (1-3) in the previous section. Therefore, it does not come as a surprise that these non-halogenated organic activators can induce electrochemical migration. This demonstrates that “Halogen-free” or “Zero-Halogen” characteristics are not a guarantee of reliability. From this perspective, the second non-halogenated paste tested in this study comprised a balance of chemical components (weak organic acids, organic amines, chelating agents and various additives) optimized for reliability (Figure 8). This paste could yield reliable assemblies populated with a large spectrum of components including low stand-off devices, even when produced under degraded cleaning conditions. However, the optimization of the reflow process is key to achieve that level of performance, otherwise a thorough cleaning process is mandated. Both non-halogenated pastes

required such a careful design of the reflow conditions, due to the heat sensitivity of these organic activators.

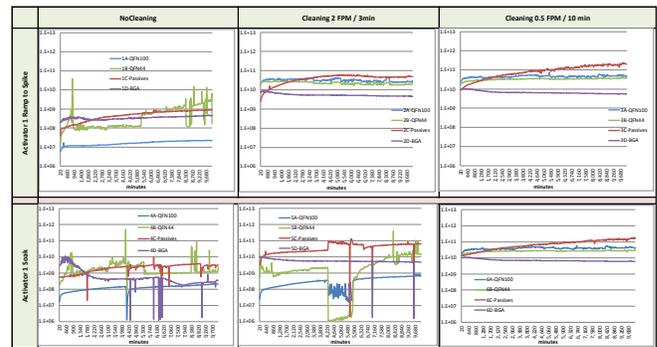


Figure 8: SIR Values from the second non-halogenated paste, for various reflow and cleaning conditions

CONCLUSIONS

We have investigated the interactions between flux formulations, board components and assembly processes by means of custom-designed boards quantifying electrochemical reactions. The analysis of the resulting reliability data from a mechanistic perspective brings interesting conclusions:

Flux activator packages, while designed to react with metallic oxides, can also induce corrosion and electrochemical migration after they are converted to solid residues during the assembly process. A safe residue requires the right balance of physicochemical properties, including a low moisture sensitivity, an adequate thermal stability and a carefully selected set of chemicals mitigating the risk of electro-dissolution. From this perspective, a non-halogenated flux is not a guarantee of reliability.

Out of the four component types tested, BGA's and passives showed the highest reliability when residues were presents. In contrast, complex leadless devices induced significant reliability issues due to their greater thermal mass, low stand-off, and the tortuosity of their outgassing channels, resulting in more active residues. This was compounded by the fact that these QFN's were much harder to clean: BGA's and passives could accept aggressive chemical packages combined with a mild cleaning process, while fluxes have to be specifically designed for reliability under QFN's in case residues are left from an incomplete cleaning process.

There is a widespread belief that a hotter profile is preferable to decompose the flux and yield inert residues. Our data indicate that this is not the case, at least when fluxes are tested under components (as opposed to opened conditions). Our tests show that the optimum reflow profile depend on the flux chemistry, for both solderability and reliability performance. Overall, we found the non-halogenated activator systems to be much more sensitive to reflow conditions compared to halogens. Brominated activators tend to volatilize and outgas early-on, while chlorinated activators show a strong electrochemical activity

regardless of the reflow profile due to their inherent heat stability.

Partial cleaning of the assembly (generally under low stand-off components) will not bring significant improvements. For some moisture-sensitive activators, it will increase the reliability risk factor. On the other hand, quantitative cleaning with the right process and wash chemicals will yield a perfectly reliable assembly regardless of the activator system, reflow process or components.

This discussion highlights the benefits of a strong technical partnership between flux suppliers and end-users to mitigate the risks of in-field failures of electronic assemblies and to prepare for their operation in ever more challenging environments following the IoT revolution. This study also forms the background for the proposal of new reliability testing standards for the electronic assembly industry.

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