

# REACTIVITY OF NO-CLEAN FLUX RESIDUES IN ELECTRONIC ASSEMBLIES: A SYSTEMATIC STUDY

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## ABSTRACT

The manufacturing process of electronic assemblies and semiconductor packages is considerably simplified by the adoption of no-clean fluxes. However, the transition from water soluble to no clean systems requires a thorough understanding of the reactivity of the unwashed flux residues in the final assembly. Case studies of in-field reliability failures are too application-specific in essence to shed some light on the complex physicochemical interactions at play. In this paper, we report a systematic study of various reliability failure modes associated with a chemically homogeneous series of fluxes tested in model conditions. Leveraging traditional reliability testing standards as well as in-house protocols using custom-designed boards, we demonstrated how the interplay between chemical packages, processing conditions and end-use environment is a far-more decisive parameter than the “Halogen-Free” label on a soldering flux. Electrochemical migration, corrosion and other chemically-driven failure modes were analyzed in terms of the chemical equilibria at play between the flux and its environment. From this perspective, progresses in the fundamental understanding of the reactivity of flux residues, combined with an end-user driven testing program of these processing by-products can significantly mitigate the risks associated with the use of no-clean fluxes.

Key words: Reliability, corrosion, electrochemical migration, dendrites, Bono test, liquid fluxes, activators

## INTRODUCTION

No-clean fluxes are widely used across the Electronic Assembly industry. A combination of no-clean product lines (pastes, liquid fluxes, cored wires) addresses the great majority of assembly processes. Achieving the right balance between soldering performance and post-process residues safety enable significant productivity gains while eliminating the concerns of removing chemically active residues. The latter is particularly important given the relentless integration trends characterizing the microelectronic industry. Miniaturization of semiconductor packages, coupled with a complexification of the component architectures and a general increase of their form factors make the assemblies ever harder to clean, as well as more susceptible to in-field failures.

The direct implication of using no-clean fluxes is the presence of a chemical residue from the soldering process in

the final assembly. In an industry where reliability concerns are paramount, the activity of this residue must be tightly controlled. Over the last decade, assembly material suppliers have been extremely successful at commercializing no-clean soldering products providing excellent performance to end-users while leaving safe residues on the board. However, the increasing complexity of microelectronic components paired with the integration of new assembly processes sets challenging targets on the assembly products roadmap. No-clean pastes need to be reengineered to meet ever increasing reliability constraints in complex end-use environments produced over wide assembly process windows.

Traditional formulation approaches to no-clean fluxes are also being challenged for various reasons. Rosin, while an extremely safe component, is a natural product subject to seasonal and geographical variations. Halogens, the most efficient activators, are progressively being phased out for regulatory reasons, but also for their propensity to yield unsafe residues on the board [1].

Facing these challenging trends, it is critical to generate a body of knowledge on the inter-relationships between materials chemistry, assembly processes and end-user performance (solderability and reliability). This paper follows this approach by testing a homogeneous series of liquid fluxes for their reliability under model conditions. Various design parameters were explored within a common and commercially-representative formulation structure. Given the large set of reliability tests (industry-standards or customer-specific) and the challenges in interpreting their output from a scientific perspective, we followed specific experimental procedures based on simple chemical fundamentals. These protocols discriminate the two primary chemical mechanisms causing reliability failures: corrosion and electrochemical migration. Two industry standards were employed to assess corrosion: the unbiased test method defined by the Joint Industry Standard IPC J-STD-004B was complemented with the Bono test [2] performed under a large voltage bias (167V/mm). The latter, recently adapted by Turbini and al. [3], utilizes a specifically designed testing pattern and a mathematical model to assess the intrinsic corrosivity of fluxes and solder pastes, regardless of other failure mechanisms.

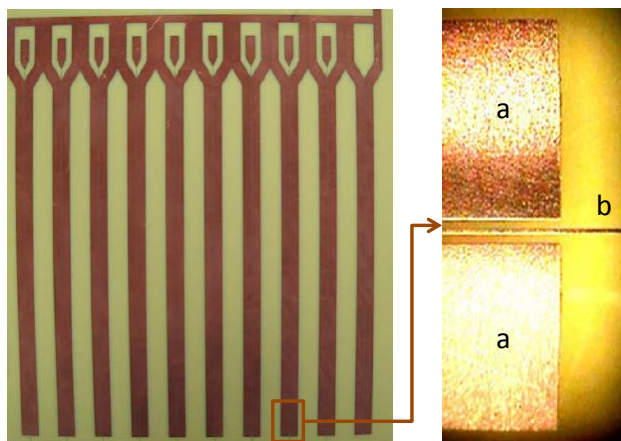
Because electrochemical migration (ECM) and surface insulation resistance (SIR) tests, as defined by IPC J-STD-004B, are both affected by multiple failure mechanisms, a customized experimental protocol was designed to grow

dendrites in a controlled environment. The testing conditions described in the experimental section show how the electrochemical activity of flux residues can be specifically monitored and quantified on printed circuit boards.

## EXPERIMENTAL

A homogeneous series of fluxes was created in order to screen various chemical contributions to reliability failures in a commercially representative formulation template. Various groups of active components were studied (weak organic acids, amines, corrosion inhibitors, rosins), while the solvent and cosolvents, additives and total solid contents were kept unchanged.

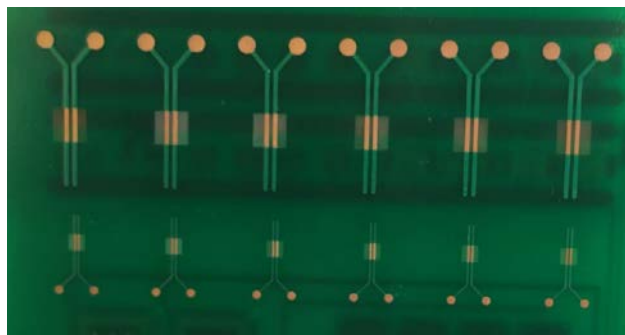
Two industry standards were applied to determine the corrosion properties of each flux: A first series of corrosion tests were executed according to the Joint Industry Standard IPC J-STD-004B, following test method IPC-TM-650 2.6.15 RevC where the flux residue produced from a 5s exposure at reflow temperature is aged 10d at 40C and 93% relative humidity. The corrosive properties of the fluxes were further assessed using the Bono protocol. The testing board (Figure 1) is made of an FR-4 epoxy substrate with a single copper layer patterned into 10 electrolytic cells composed of a thin anode (80 $\mu$ m) sandwiched between two thick cathodes (3mm). Fluxes were dried on the testing board for 24h at room temperature, prior to being subjected to a 20V bias (167V/mm) for 15days, under air and at 85C and 85% relative humidity. The testing theory and corrosion factor calculation details can be found in the published testing method [2].



**Figure 1.** Bono test board  
(a)Cathode (b)Anode

Electrochemical migration was assessed by means of the customized testing method mentioned earlier. Dendritic growth was monitored on custom-designed printed circuit boards (Fig. 2) consisting of six Y-shaped conductors. An opening in the solder mask allows the contacting of fluxes with Cu traces in a well-defined area. The fluxes are dried at room temperature. A drop of 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 $\mu$ A to prevent burn-out effects.

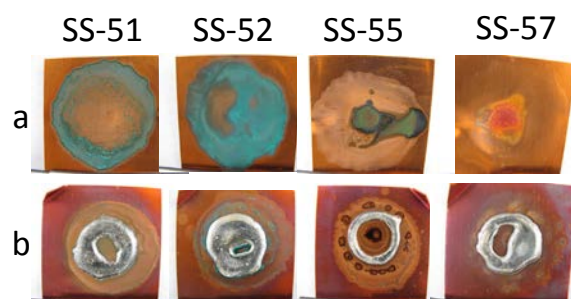


**Figure 2.** Customized ECM board design

## RESULTS AND DISCUSSION

### Corrosion Testing

The IPC standard for flux corrosion evaluation calls for a flux reflow cycle of 5s at 235C in presence of solder pellets, prior to exposing the residue to the moist environment. We also studied the corrosion properties of room-temperature dried flux residues, in order to simulate processing conditions where excess flux spatters on the board or spreads excessively and remains unheated. These extreme conditions can be encountered in selective soldering applications. Flux residues exposed to a reflow cycle should have different physicochemical characteristics than their unheated counterpart, potentially resulting in differences in their corrosion activity. We also wanted to operate the test in conditions similar as the ones adopted for the Bono test, where residues are unheated. Figure 3 reports a first set of results, where various activators were screened for their impact on corrosion in our standard formula.

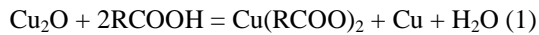


**Figure 3.** Corrosion test – Activator effect

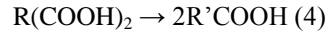
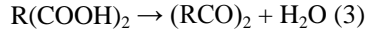
(a) Unheated residues

(b) Joint industry standard IPC J-STD-004B – Reflowed

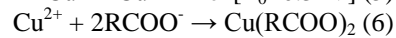
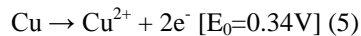
Varying corrosion levels and residue characteristics can be observed on the copper coupons. Some activators are also very sensitive to processing conditions, as can be observed with SS-51 and SS-55. Therefore, corrosion phenomena can be mediated by the formulation activators. Weak organic acids flux metal surfaces (i.e. remove the passivation layer) according to the following disproportionation and complexation reactions [4-6]:



The Cu(II) complexes thus generated are typical constituents of the soldering residue produced during reflow. Aside from the fluxing reaction products, these residues can also contain unconsumed activators, dehydration and decomposition products as exemplified in equations (3) and (4):



All these chemical equilibria are strongly affected by the reflow profile and its atmosphere. Therefore, the nature and physical characteristics of the residues depends on the assembly process conditions. The corrosion activity of the residues results from their ability to supply ligands to catalyze copper oxidation, according to reactions (5-6):

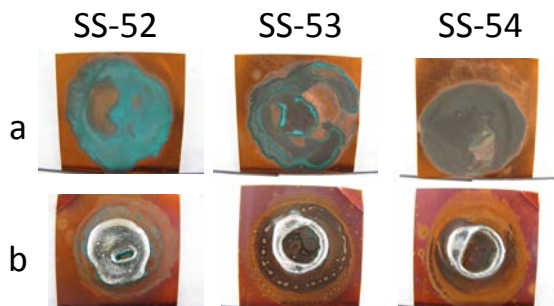


Strong complexation effects in equation (6), driven by a low solubility constant (pKs), displace the oxidation equilibrium (5) to the right, resulting in a lower apparent oxidation potential of copper:



As a consequence, the corrosion phenomena critically depend 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 carbonation. Based on the specificities of the activators employed in this study, the variations in corrosivity reported in Figure 3 result from their Cu complexation power coupled with the moisture sensitivity of the complexes. Differences in coloration simply result from differences in energy levels of the Cu complexes electronic states according to the ligand field theory.

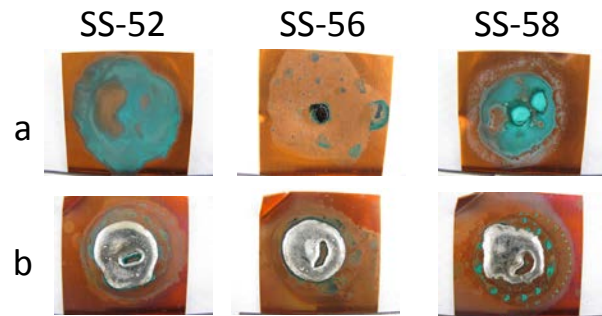
One common way to shut off this phenomenon is the use of corrosion inhibitors, which typically sursaturate copper solutions, even at extremely low copper levels, thus interfering with the catalytic effect from the activators described in (5) and (6).



**Figure 4.** Corrosion test – Corrosion inhibitor effect  
(a) Unheated residues  
(b) Joint industry standard IPC J-STD-004B – Reflowed

Figure 4 shows such an effect, where increasing amounts of a specific inhibitor identified in a preliminary screening experiment are extremely effective at mitigating corrosion. One has to be particularly cautious with these formulation approaches: this class of additives can also negatively influence other performance attributes as they strongly interfere with the metal fluxing equilibria. As always, a proper experimental design taking into account all the response factors of importance should be the rule for these complex formulations where multiple second-order interactions occur between components.

Organic amines are another class of additives found very effective at affecting the corrosion activity of flux residues (Figure 5). This didn't come as a surprise since amines are well known for their ability to generate a large variety of stable copper complexes [7], which greatly affects the electrochemical equilibria of copper metal [8]. Organic amines are a key class of components involved in the design of high-performance fluxing systems [9]. It is therefore of paramount importance to understand their impact on reliability properties.



**Figure 5.** Corrosion test – Organic Amines effect  
(a) Unheated residues  
(b) Joint industry standard IPC J-STD-004B – Reflowed

By contrast, the Bono protocol didn't detect significant differences between fluxes in term of corrosion properties. The testing results reported in Table 1 show that the strong impact of the corrosion inhibitor level observed with the other testing method (Figure 4) was not replicated.

**Table 1.** Bono Test Results – Corrosion inhibitor effect

	SS-52	SS-53	SS-54
Corrosion Factor Fc (%)	1.3	1.1	1.5

**Table 2.** Bono Test Results – Activator effect

	SS-51	SS-52	SS-55	SS-57
Corrosion Factor (%)	0.9	1.3	0.1	1.1

**Table 3.** Bono Test Results – Organic Amines effect

	SS-52	SS-56	SS-58
Corrosion Factor Fc (%)	1.3	1.2	1.1

Similar results were found with the Activators and Organic Amines screening tests (Table 2, 3): each formula presents acceptable corrosion factors, in stark contrast with prior corrosion testing.

We had modified the preparation method of the Joint industry standard for corrosion testing (condition (a) in figures 3-5), in order to match the Bono protocol and thus eliminate the residue characteristics as a variable. Dramatic differences in the testing output show that the testing method environment (voltage bias, temperature, humidity) strongly impacts the flux corrosion properties. This is another example of the criticality of the end-user application conditions. No single test is able to predict the reliability of assembly materials in general. Understanding the operating conditions of the final device is of utmost importance to set up the right reliability testing procedure. No holistic model is applicable to specific end-use conditions: the assembly process, the interactions between assembly components (e.g. fluxes, metal finishes, underfills, conformal coatings, die-edge coats, adhesives), and the end-user environmental conditions (temperature cycling, humidity, voltage bias, vibrations, shocks, atmosphere, etc.) are all key factors.

### Electrochemical Migration Testing

Electrochemical phenomena are preponderant in electronic assemblies [10]. Dendritic growth results from electrochemical migration (ECM), where metal ions move between adjacent metal conductors under the influence of a voltage bias. The customized testing method described in the experimental section has been applied to our series of fluxes to study the influence of chemical parameters on ECM.

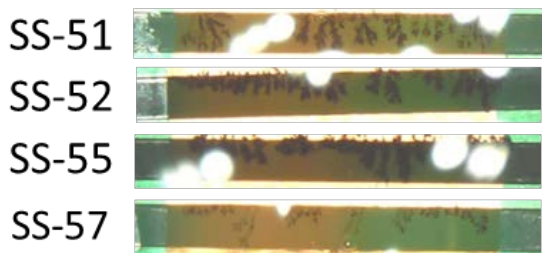


Figure 6. Customized ECM test – Activator effect

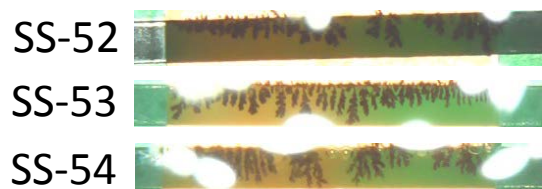


Figure 7. Customized ECM test – Corrosion inhibitor

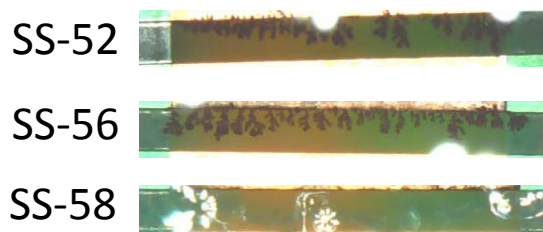


Figure 8. Customized ECM test – Organic Amines

The general shape of the dendrites grown in presence of our fluxes is reported in Figures 6-8. The activators (Figure 6) are found to have a strong impact on the shape of the dendrites. This demonstrates that these species have a key role in the dendritic growth mechanism. In contrast, the influence of corrosion inhibitors (Figure 7) and organic amines (Figure 8) is less apparent.

The growth kinetics of dendrites was subsequently analyzed from the in-situ monitoring of dendritic growth enabled by our experimental setup. Induction times and growth rates were extracted from the digital records of the growth process and are reported in the tables below.

Table 4. Dendritic Growth – Activator effect

	SS-51	SS-52	SS-55	SS-57
Growth Rate ( $\mu\text{m/s}$ )	22.6	11.3	11.7	17.9
Induction time (s)	9.5	4.0	20.5	10.5

Table 5. Dendritic Growth – Corrosion Inhibitor effect

	SS-52	SS-53	SS-54
Growth Rate (mm/s)	11.3	11.4	8.9
Induction time (s)	4.0	8.5	12.0

Table 6. Dendritic Growth – Organic Amine effect

	SS-52	SS-56	SS-58
Growth Rate (mm/s)	11.3	4.5	0
Induction time (s)	4.0	18.5	Inf

All experiments were repeated, and standard deviations were such that the variations in growth rates observed with the activators (Table 4) or the corrosion inhibitors (Table 5) were not statistically significant. The impact of activators is more apparent on the morphology of the dendrites (Figure 6). On the other hand, organic amines strongly impact dendrite growth kinetics, while they marginally affect their shape. One of the organic amines even shut off the dendritic growth mechanism altogether.

The dramatic impact of organic amines on dendrite growth kinetics can be interpreted from a mechanistic perspective. Electrochemical Migration proceeds through 5 sequential mechanisms:

1. Formation of an electrolytic path 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 details by Anderson [11]. We eliminated this variable by supplying a large excess of water for the test.

2. Metal corrosion  
The electro-dissolution of metallic compound is mediated by the flux additives as shown in the first section of this paper.

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 electro-dissolved 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 dendrite growth kinetics. As mentioned earlier, amines are the source of a large array of stable copper complexes. The results reported in Table 6 illustrate how these complexes interfere with the dendritic growth mechanism.

4. Electrodeposition  
In a similar fashion, the characteristics of the metal complex will impact the reduction of the metal at the negatively charged cathode.

5. Dendritic growth  
We believe the fractal geometry of dendrites results from electrostatic interactions between building blocks, as this structure presents the optimum configuration to minimize the repulsion between similarly charged species. The growth is then diffusion-driven by the concentration gradient of soluble copper complexes established between the anode and the cathode through the electro-dissolution of copper at the anode.

## CONCLUSIONS

Reliability of no-clean fluxes 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, and temperature and humidity conditions. We conducted a systematic study of the influence of various formulation design parameters on reliability by testing a homogeneous series of liquid fluxes under model conditions. The two primary chemical mechanisms causing reliability failures, Corrosion and Electrochemical Migration, were discriminated through the application of customized protocols involving basic scientific principles. Our experiments show how three major classes of formulation components are able to turn on or off both corrosion and electrochemical migration.

The characteristics of the weak organic acids used as activators in these fluxes have a strong influence on both

corrosion and dendritic growth. From this perspective, we showed that a “Zero-Halogen” flux is not a guarantee for reliability. A careful experimental design is necessary to balance the activity of all formulation components to find the right balance between solderability and reliability. A striking example was the use of corrosion inhibitors, which can effectively shut-off corrosion effects but were marginally effective on electrochemical migration. Conversely, we identified 2 organic amines which were extremely effective at mitigating dendritic growth while leaving corrosion residues. A proper experimental design taking into account all the response factors of importance should be the rule for these complex formulations where multiple second-order interactions occur between components. We recommend innovative ‘Zero-halogen’ products introduced on the market follow these development principles.

We also observed dramatic differences from various reliability testing protocols, where the application environment (voltage bias, temperature, humidity) was the critical experimental variable. This is another example of the criticality of the end-user application conditions. Understanding the operating conditions of the final device is of utmost importance to set up the right reliability testing procedure. From this perspective, progresses in the fundamental understanding of the reactivity of flux residues, combined with an end-user driven testing program of these processing by-products can significantly mitigate the risks associated with the use of no-clean fluxes.

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