Effect of Flux Systems on Electrochemical Migration of Lead-Free Assembly

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ABSTRACT
The reliability concerns regarding surface insulation resistance (SIR) and electrochemical migration (ECM) have been significantly raised in the printed circuit board (PCB) assembly with wide adoption of lead-free assembly materials and process. Moreover, the miniaturization trend of the electronic industry also increases the sensitivity of the functional assemblies to surface contamination and flux residues. There are numerous SIR reliability testing methods and standards, such as IPC, JIS, Bellcore, and Bono, whose predictive power will depend on the field of application including temperature, relative humidity and electric field. Each standard is limited in essence, because the failure mechanism is strongly affected by the chemistry of the assembly materials, e.g. soldering flux, paste, and substrate materials, which will perform differently under various conditions. This paper presents a summary and comparison of the major SIR reliability standards currently in use in the industry and discusses the impact of the different flux systems on the failure mechanisms.

Key Words: Reliability, SIR, ECM, Flux Residue, Solder Paste, Chemical Flux, Lead-Free, Root Cause Analysis

INTRODUCTION
Electrochemical migration (ECM) is an electrochemical process where metal ions move between adjacent metal conductors through an electrolyte solution subjected to an applied electric field. ECM is also characterized by the dendrites growth on printed circuit boards (PCBs), as a result of metal ions dissolving at the anode and plating out at the cathode, growing in needle-or spike like crystals. The other failure mechanism is the formation of conductive anodic filament (CAF) on printed wiring boards (PWBs) in general.

The ECM process consists of five sequential steps: path formation, electrodissolution, ion transport, electrodeposition, and dendrite growth [1]. The preferential path, an electrolyte layer, comprises dissolved ions and the solvent which can be either condensed water or non-condensed moisture absorbed onto the substrate. This step significantly depends on the PCB material composition, the board surface roughness, the concentration and distribution of contaminants, and the relevant environmental conditions (temperature and humidity). The board contaminants include the residues from the board plating and laminating process, the flux soldering process, as well as airborne contaminants from board handling and storage processes. Hygroscopic process and service-related contaminations increase the risk of forming a water layer on the PCB surface along with being a source of ions for solution conductivity For example, the flux residue after soldering can still contain hygroscopic ionic activators and their decomposition fractions, as well as reaction intermediates and by-products, which enhance the adsorption of moisture from

the environmental humidity and provide conductive ions.

Electrodissolution is the step where the metals loose electrons to form cations, typically through oxidation at the anode (positive electrode). Another route for metal cations formation is by chemical reaction between the flux and metal oxide during the soldering process. In traditional flux chemistry, the halides react with metal and metal oxides to leave water-soluble ionic residues on the PCBs. These metal cations tend to migrate to the cathode under a DC bias voltage, get reduced into neutral metal, and then deposit onto the cathode (negative electrode) in the form of needles or spikes. Once these nuclei have formed, the higher current density at their tips will greatly increase the probability of further deposition. As more and more metal deposits on the cathode, branching occurs at the preferred crystal orientation, and then a characteristic dendritic structure grows from the cathode toward the anode.

Once the dendrites have spanned the distance between adjacent conductors, the surface insulation resistance (SIR) will reduce, and the leakage current will increase. Under different current densities, the dendrites can either grow and short adjacent conductors, or blow out, which result in permanent or intermittent circuit failures.

There are few mathematical model established to describe the phenomenon of ECM. The Arrhenius equation is commonly used to calculate the acceleration factor that applies to the time-to-failure distributions. It is defined as

$$t(T) = A exp\left(\frac{\Delta H}{kT}\right)$$

Where t is the time to failure, A is a scaling constant, ΔH is the activation energy (eV0, k is Boltzmann's constant (8.61710^{-5} eV/K), and T is the temperature (K). However, the acceleration factors can be a function of multiple basic stresses, which is more complex than the basic Arrhenius model. The Eyring model published in IPC Surface Insulation Resistance Handbook expands Arrhenius equation and includes other stresses as necessary [2].

$$t = AT^{\alpha}\left\{\frac{\Delta H}{kT} + \left(B + \frac{C}{T}\right)S_1 + \left(D + \frac{E}{T}\right)S_2\right\}$$

Where A is a scaling constant, ΔH is the activation energy (eV), k is Boltzmann's constant, T is the temperature (K), α, B, C, D, E are constants determined by the stress interaction, and S_1 and S_2 are stresses, such as humidity or voltage. Other acceleration factors can be calculated for electrical, mechanical, environmental, and other stresses that can affect the reliability of a device. These can be classified into two categories:

- Physical factors: a potential voltage gradient (V/cm); temperature (˚C), and relative humidity (%RH)
- Chemical factors: solder alloy, flux residues, PCB solder mask and laminate materials, plating materials, and other surface contamination.

The potential bias on the PCB at adjacent points or heterogeneous material combinations serves as a thermodynamic driving force for the corrosion cell. Many studies have shown that the higher the polarizing DC voltage (or "bias"), the greater will be the rate and severity of the electromigration. In addition, the migration rate and the width of the interconductor spacing have an inverse relationship. These observations indicate that the critical voltage is not the absolute value of the applied voltage, but rather the voltage gradient across the width of the spacing between conductors. Over the last decade, the size of electronic assemblies has been reduced by over 70%, and about 90% for flip-chip ICs. The miniaturization and higher density integration are more vulnerable to insulation failure due to the higher voltage gradient between the finer pitch leads and easier formation of corrosion cell. Under humid conditions, a nanoscale water layer is condensed locally on the PCB components, giving rise to a conductive path for current flow and thereby establishment of electrochemical corrosion cell between two points on PCBs. Shown in both models, the temperature is another key stress. For many common chemical reactions at room temperature, the ion mobility increases, and the reaction rate doubles for a 10˚C temperature increment. The lead-free and halogen-free requirements in the electronic assembly industry also increase ECM failure risk due to the significant changes in the chemistry of assembly materials. For example, the flux

formula consists of higher concentration of active ingredients to survive multiple higher temperature reflow cycles for the lead-free assembly. The flux residue may contain the unconsumed activator package or the ionic species created during reflow to induce ECM failure. In particularly, those residue trapped under the low standoff device never undergoes high temperature exposure and may result in sever ECM failure.

Many SIR and ECM test methods were established based on these acceleration factors. Table 1 presents the method and criteria details of some industrial standards along with three customized ones. The users generally choose the applicable method under consideration of their product nature and application requirements, but it is always a hot topic about which is the "Harsher" or "Righter" test method to reveal the "true" product level performance. In this study, both solder paste and chemical flux products were evaluated with different SIR and ECM testing methods for comparison. The flux chemistry contribution to ECM failure is discussed in details, which hopefully could provide a reference for the process engineer to choose or establish the right reliability test protocol for assembly materials qualification.

EXPERIMENTS
Two paste (**A** & **B**) and two chemical flux (**C** & **D**) products are included in this study. Paste A and B are both no-clean, halogen-free lead-free solder paste. Chemical flux C is no-clean halogen-free alcohol-based and D is no-clean VOC-free products.

For the residue moisture sensitivity study, the solder paste were reflowed under a typical lead-free profile and the chemical flux were dried under 80˚C to obtain the solids, in order to mimic the top side board conditions with over sprayed flux. The residue obtained from these two processes were placed in a chamber under 40 ˚C and 90%RH. The sample weights were monitored over exposure time to estimate the moisture sensitivity level of the flux residue. The conductivity of activators used in A-D formula was measured in a specific solvent by using YSI MODEL 32 Conductance Meter with YSI 3402 cell. The paste flux (**A** & **B**) conductivity was

also measured during reflow with the special equipment setup.

The standard IPC, SIR, ECM and two customized test methods listed in Table 1 were applied to products A-D. Optical microscopy with backscattered mode was used for corrosion and dendrites observation on the test boards. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) was used to analyze the residue composition found on the test boards.

Table 1. Reliability Test Standards Summary including three Customized Methods

Standard	Test Method	Temp. (°C)	Humi. (%RH)	Test Volt. (V)	Bias Volt. (V)	Test Dura.(hrs) /Frequency	Board Characters	Pass Criteria
IPC J-STD-004B	TM650 2.6.3.3	85	85	-100	50	168 / 24h, 96h, 168h	IPC B24 1.4 mm lines, 1.5 mm spacing	IR >10^8 after 96h
	TM650 2.6.3.7	40	90	25V/mm	25V/mm	>72 / 20min	IPC B24 1.4 mm lines, 1.5 mm spacing	IR >10^8
	TM650 2.6.14.1	40 65 85	93 88.5 88.5	45-100	10	596/ 96h & 596h	IPC B25A 0.318mm line & Spacing	IR_{ini}/IR_{fin} <10x
Bellcore GR-78-Core	SIR 13.1.3	35	85	100	45-50	96 / 24h, 96h	IPC B25A 0.318mm line & Spacing	IR >$2x10^{11}$
	ECM 13.1.4	65	85	45-100	10	596 / 96h & 596h	IPC B25A 0.318mm line & Spacing	IR_{ini}/IR_{fin} <10x
JIS Z 3197	SIR	40 85	90 85	100	0	168	IPC B25A 0.318mm line & Spacing	IR >$1x10^{11}$
	ECM	40 85	90 85	100	45-50	10000	IPC B25A 0.318mm line & Spacing	
Bono[3]	SIR	85	85	12	20	360	Bono board	Refer to reference
Cus.#1	SIR	30→85	50→90	100	50	240 / every 72h	IPC B24 1.4 mm lines, 1.5 mm spacing	IR >$5x10^8$
Cus.#2	SIR	55↔25/24h cycle	95↔90/24h cycle	50	50	144 / 20min	0.325mm line & gap; 0.325mm line & 0.2mm gap	IR >10^8
Cus.#3	ECM	50	90	5	5	672/ <10min	IPC B25A 0.318mm line & Spacing	IR >10^8 & IR<10^2 below control

RESULTS AND DISCUSSION
Flux Basic Chemistry
The major components in the flux matrix are rosin (optional for chemical flux product), solvent, activator and rheology modifiers, in which the activator is not only the key ingredient for fluxing mechanism, but also impact the final assembly reliability. Two chemistry factors have to be considered for reliability aspect. The first one is the original activator leftover in the reflow residue, and the second is the by-product from the reaction between activator and metal oxides. The conductivity study of the activator package in all four products is shown in Table 2. The activator has much higher conductivity in paste

B than paste A, indicating high possibility to cause ECM failure if any unconsumed activator is left in the reflow residue. A similar comparison can be established between fluxes C and D.

Table 2. Activator Conductivity Data

	Paste A	Paste B	Flux C	Flux D
Activator Conductivity (milliS/m)	8.28	797	6.58	18.9

During reflow, the metal passivation layer is removed by reaction with the activator. The typical activators are carboxylic acids and halides. They react with metal oxide to form metal salts as the general reaction products, as shown in the equation below:

$$Cu_2O+2RCOOH(or\ HX) = Cu(RCOO)_2(or\ CuX_2)+Cu+H_2O$$

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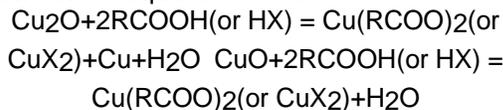
The solubility and conductivity of reaction by-product will depend on activators. The higher solubility and conductivity of metal salts will enhance the residue moisture absorption and form efficient conductive path to pass current. For example, the typical tin halide salts, $SnCl_2$ and $SnBr_2$, can dissolve in less than its own mass of water to create metal ions, which are hydrolyzed into an insoluble basic salt and precipitate out when the solution is diluted. $SnCl_2$ solution is also unstable toward oxidation under the air atmosphere, and form very soluble $SnCl_4$ as well as insoluble hydrolysis products. When mixed with a small amount of water, a semi-solid crystalline mass of the pentahydrate, $SnCl_4.5H_2O$ is formed [4]. These reactions are shown below:

$$SnCl_2(aq) + H_2O(l) \leftrightarrow Sn(OH)Cl(s) + HCl(aq)$$

$$6SnCl_2(aq) + O_2(g) + 2H_2O(l) \rightarrow 2SnCl_4(aq) + 4Sn(OH)Cl(s)$$
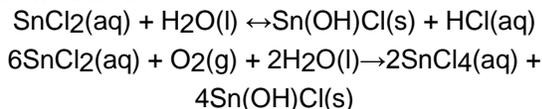
The ions are created in all these reactions have very strong conductivity and can cause current leakage or even result in ECM failure.
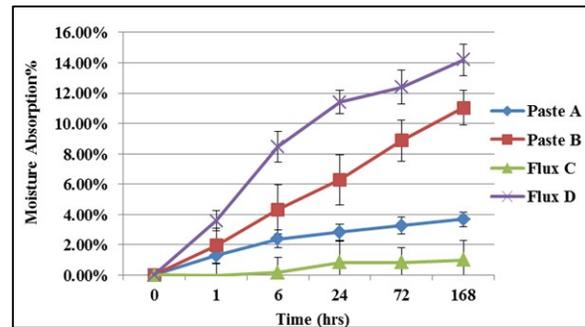
Figure 1. Flux Residue Moisture Sensitivity
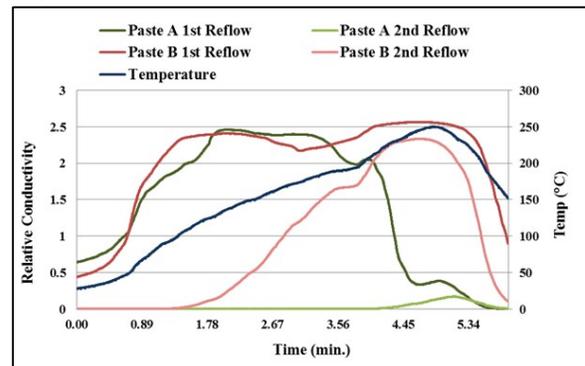
Figure 2. Paste Flux Conductivity during Reflow

Figure 1 shows the moisture sensitivity of the soldering residue for products A-D under the same temperature/humidity condition as OPC SIR 2.6.3.7 method. Paste B and Flux D apparently absorb much more moisture than A and C which implies that B & D residue contains more hygroscopic and/or ionic components. Figure 2 shows the flux conductivity change during the first and second reflow cycle of Paste A and B. Paste A clearly loses majority conductivity after the first reflow, but Paste B still maintains strong conductivity on the second reflow. Therefore, the flux residue from B and D is much easier to form the conductive path for current flow by moisture absorption and providing conductive ions.

Reliability Test Comparison
Two SIR test results from IPC 2.6.3.3 and 2.6.3.7 for Paste A and B are shown in Figure 3 and 4. SIR boards with Paste A & B were reflowed under a typical lead-free reflow profile in both air and nitrogen. The resistance of Paste A is close to the blank board in both tests, but the resistance of B is much lower in 2.6.3.7 and

barely passes $10^8 \Omega$ in 2.6.3.3 method. As explained previously, Past B presents higher ionic conductivity and more hygroscopic compounds than A, resulting in the low reliability performance. On 2.6.3.7 test boards, no corrosion or dendrites are observed and there is no significant difference between Paste A and B. However, a large amount of white crystals are observed on 2.6.3.3 test boards for Paste B. These crystals tend to primarily deposit on the positive charged traces (anode) on B24 SIR boards. SEM/EDS analysis in Figure 5 shows they are most likely Sn-based compound. In reference to $SnCl_2$ chemistry, Sn^{2+} in the paste B flux residue either forms a less soluble hydrate or oxidizes to Sn^{4+} and precipitates out. The higher anode polarization and temperature will accelerate these reactions; thereby the white crystals only appear in 2.6.3.3 method, but not in 2.6.3.7. There is still a remaining amount of soluble tin ions migrate from anode to cathode and cause the low resistance or current leakage during the test.
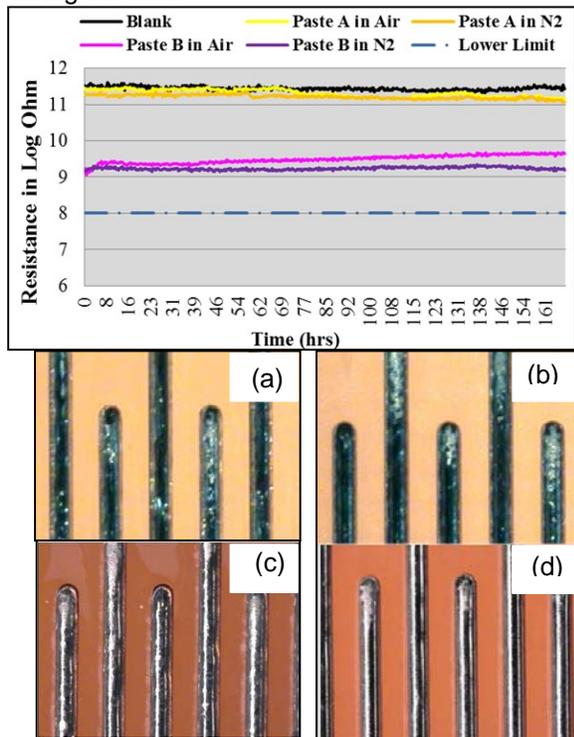
Figure 3. Paste A and B under IPC **2.6.3.7** SIR Test: (a) Paste A reflow in Air; (b) Paste A reflow in N_2; (c) Paste B reflow in Air; (d) Paste B reflow in N_2.
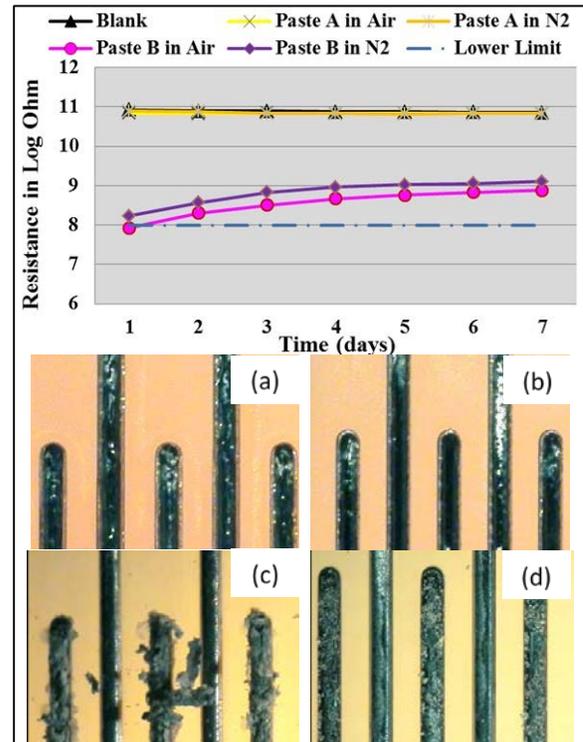
Figure 4. Paste A and B under IPC **2.6.3.3** SIR Test: (a) Paste A reflow in Air; (b) Paste A reflow in N_2; (c) Paste B reflow in Air; (d) Paste B reflow in N_2.

Besides the activator contribution, rosin is also an important ingredient in the paste flux matrix for the product reliability performance. After reflow, rosin forms a protective layer and freezes other active residue under in a water-impervious coating. The softening point of rosin used in the lead-free formula is generally in the range of 60°-130°C. When the operation temperature is consistently higher than the softening point, the flux residue will spread and the active components will be slowly released from the softened rosin. The set point of 85°C used in 2.6.3.3 method falls in the range of the rosin softening point, which can accelerate ECM failure, while 40°C used in 2.6.3.7 method is not sufficient to break this protective layer. Comparing the residue pictures reported in Figure 3 and 4, both A&B products form clear and hard residue without any cracks when reflowed in nitrogen, and this stronger protection layer may prevent any active residue release to the PCBs. However, the air-reflowed flux

displays a large amount of cracks, which enhance moisture absorption and expose the active components to the PCB surface. Figure 6 shows dendrites grow along the residue cracks between Cu traces. This could explain the slightly higher resistance and less white crystals occurrence when Paste B is reflowed under nitrogen in 2.6.3.3 method.

The reliability performance of Flux C and D was evaluated by two IPC SIR methods after wave soldering in both Pattern Up and Pattern Down configurations. The top board temperature is controlled at 100°C, and the dwell time is 3s with the solder pot temperature at 265°C for lead-free assembly. Flux C and D both pass 2.6.3.3 test without any corrosion or dendrites growth on the test boards, while Flux D has lower resistance than C shown in in Table 3. As explained earlier, Flux D contains activators with a higher tendency to dissociate, turning into more hygroscopic residues after soldering. These are prone to form an electrolyte path for electrochemical migration and result in low resistance readings. When subjected to 2.6.3.7 procedure (Figure 7), Flux C keeps high resistance on both patterns through the whole test period, but Flux D Pattern Up fails the test during the initial 64 hours and then slowly recovers above $10^8 \Omega$. Since the chemical flux matrix only contains negligible rosin amount, the unprotected ionic residue is depleted during the initial SIR test period under a consistent DC voltage, which explains this gradual increase of the SIR value over time. Similarly, the Pattern Up generally presents lower resistance values than the Pattern Down conditions. As the Pattern Up boards only underwent 100°C preheating stage without the high temperature exposure in the solder pot, there is more active flux residue left on the Pattern Up board than Pattern Down board. The Pattern Up boards coated with Flux D also show a bluish discoloration on copper traces and between conductors, indicating the presence of reactive ionic species with the ability to trigger copper corrosion in the right electric and environmental conditions. Comparing two IPC SIR methods, 2.6.3.7 is more challenging than 2.6.3.3 for chemical fluxes especially those in the VOC-free category. As discussed previously, the trend is opposite to the no-clean solder paste products,

whose reliability properties are primarily driven by the evolution of the rosin-based protective coating. The less reading frequency in 2.6.3.3 cannot catch the low resistance and the resistance recovery in the first 24 hours.
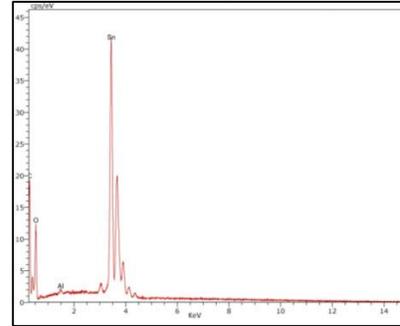
Figure 5. SEM/EDS Analysis of Crystals on SIR Boards
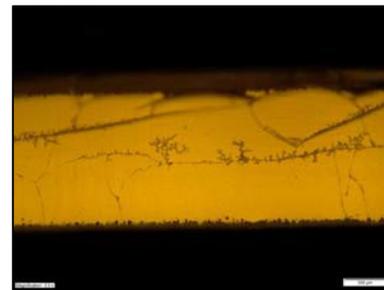
Figure 6. Dendrites Growth along Residue Crack

Table 3. IPC **2.6.3.3** SIR Test Result for Flux C & D

		Day 1	Day 4	Day 7
Blank		7.9×10^{10}	1.8×10^{11}	2.3×10^{11}
Flux C	**Up**	1.34×10^{11}	9.9×10^{10}	8.6×10^{10}
	Down	9.7×10^{10}	6.2×10^{10}	6.4×10^{10}
Flux D	**Up**	5.0×10^{9}	1.1×10^{10}	1.1×10^{10}
	Down	1.7×10^{9}	1.9×10^{9}	3.8×10^{9}
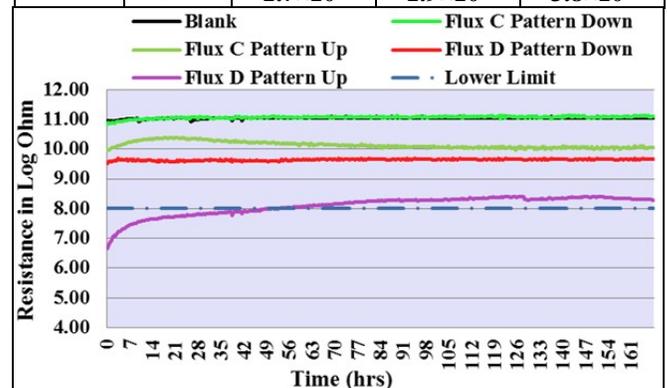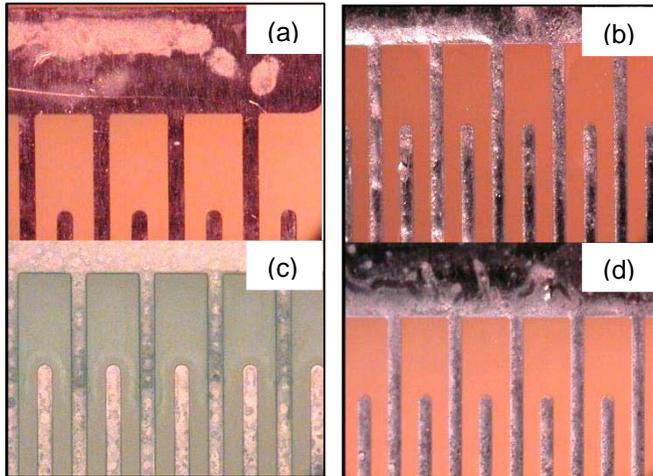
Figure 7. Flux C and D under IPC **2.6.3.7** SIR Test: (a) Flux C Pattern UP; (b) Flux C Pattern Down; (c) Flux D Pattern Up; (d) Flux D Pattern Down.

Since the moisture and temperature are two major stress factors for the ECM failure, the customized #1 and #2 methods listed in Table 1 are designed with various temperature/humidity levels and cycles aiming to force water condensation on the test boards and thus mimic the harsh environmental conditions that some applications experience. Figure 8 shows Paste A and Paste B reliability comparison under the customized #1 test method. In this method, temperature and humidity are varied over time, and each reading is acquired initially and after three days of stabilization. Paste B starts failing under the application of the third set of temperature/humidity combinations, where moisture saturation and rosin degradation reach a critical point for the assembly reliability. The white Sn-based crystals are also found on the boards assembled by Paste B after this test.

Figure 8. Paste A and B under Customized #1 SIR Test: (a) Paste A reflow in Air; (b) Paste A reflow in N_2.
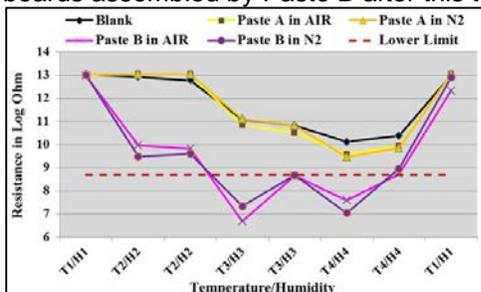
Table 4 shows IPC ECM and the customized ECM test results for both Paste A and B. The customized method details and performance criteria are listed in Table 1 (#3 method). For IPC ECM, 65°C/88.5%RH combination was used as the environmental condition, with the test voltage at 100V. Paste A passes both tests, while Paste B barely passes ICP ECM and fails the customized method with lower resistance and dendrites growth as shown in Figure 9. The key differences between two test methods are the voltage and the reading frequency. The lower voltage used in the customized method can preserve the dendrites, and the 10min reading frequency catches the minimal resistance when dendrites bridge the metallic traces.

Table 4. Paste A and B under IPC 2.6.14.1 ECM & Customized #3 ECM Test

Sample	IPC 2.6.14.1		Cus. #3
	IR initial (after 96h)	IR final (after 596h)	IR min
Blank	4.27E+10	6.04E+10	3.63E+9
Paste A in Air	2.61E+10	6.82E+10	1.41E+8
Paste A in N2	7.17E+09	1.82E+10	2.18E+8
Paste B in Air	5.16E+08	2.63E+08	2.34E+6
Paste B in N2	1.47E+09	1.76E+08	9.12E+6

Figure 9. Dendrites Growth on Paste B boards under Customized #3 ECM Test

Conclusion: Which Test Method is "Harsher"?

This study shows that both physical and chemical acceleration factors for ECM failure have to be considered when the engineer chooses or designs the SIR/ECM reliability test method. Each factor is not independent, but impacts each other and results in different test outcomes.

From four products A-D in this study, here is a summary and some recommendation for the reliability test:

- For no-clean solder paste, IPC SIR 2.6.3.3 is more challenging than 2.6.3.7 due to the higher temperature and voltage conditions. The higher temperature accelerates the chemical reaction and ion mobility, but also softens the rosin layer thus exposing the active ingredients. Even though the high bias voltage may blow out the dendrites, it significantly accelerates the ion migration in this short 7 day test. IPC 2.6.3.3 method can be improved by increasing the reading frequency to provide more detailed resistance data.
- For no-clean chemical flux especially those in the VOC-free category, IPC SIR 2.6.3.7 is more challenging than 2.6.3.3, contrary to the no-clean solder paste product because of the formulation chemistry differences explained above. The 40°C set point in this newer method preserves the residue activity, and the low voltage slows down the ion depletion and the resistance recovery rate.

- The dewing test can further stress assembly materials, as performed by the customized method #1 & #2. These procedures purposely create water condensation and alter the residue physical appearance, either cracks or softened rosin residue.
- For long term ECM tests, a lower voltage will favor dendrites growth without blowing them out. The higher reading frequency also helps catching any possible ECM failure. B25 board used in ECM test can provide higher voltage gradient with finer pitch size of copper traces.
- The product chemistry is critical. Paste A and Flux C consistently pass different SIR/ECM test, but B and D failed multiple tests.

In order to progress in our understanding of flux chemistry contribution to ECM failure and design the right reliability qualification test, further studies involving various product categories and test methods will be carried out in the near future.

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