Test Method Development for Detecting Pitting / Crevice Corrosion Formation on Electronic Assemblies

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Abstract

Pitting/Crevice corrosion on printed circuit boards has not been well studied in the industry. This mechanism has been seen at small solder mask openings near circuit traces on printed circuit boards when stored or shipped in a humid environment with no-clean soldering fluxes that passed all standard tests. Failure modes are theorized to be driven by openings or defects in solder masks and humidity levels that mobilized surface contamination. Harsh environments, that can bring in outside contaminates, can be one of the factors that causes pitting corrosion to initiate and grow.

In many of the applications employing high density assemblies processed with mixed technology, the quality of the laminate construction, the assembly process and quality of design are critical. Solder mask type (glossy or matte) curing and application process have been known to cause corrosion issues. Often the solder mask employed (manufacturer, chemical structure, Tg, filler type and thickness) can be factors that lead to pitting corrosion and should be understood. In some cases, the thickness, quality and roughness of the copper at the surface can contribute to corrosion.

The High Density Packaging User Group Consortium (HDP User Group) Electro-Chemical Migration (ECM) team is investigating pitting / crevice corrosion failure mechanism and the factors that cause the defect to occur. The purpose of the research is to report current findings and the experimental description for qualifying soldering materials and to determine conditions needed to mitigate this failure mechanism.

Introduction

Pitting and / or crevice corrosion has been detected on field failed boards that were soldered with a no-clean wave or selective soldering flux. The failure mode is suspected to be driven by openings or defects in solder mask. The failure is not an open surface type corrosion event. Pitting corrosion occurs between a soldermask defect and a copper trace on boards exposed to harsh environments with atmospheric pollutants and / or high humidity levels. A motivating factor driving this research is to understand the physics behind pitting corrosion such as seen when Cu corrosion propagates in the form of a ring around corrosion sites.

Pitting starts as an advanced form of uniform etch. It is believed that the combination of small active anodes to large passive cathodes initiates the corrosion (Figure 1). Residue on the surface of the board that is mobilized from humid environments can remove oxides from exposed copper. A small cell can form as mono-layers of moisture initiate small active anodes that are attracted to metal cathodes. As corrosion propagates, it can worsen into very severe corrosion that result in localized and relatively deep holes in the metal. The corrosion will eventually eat through the metal, which creates an open circuit (Figure 2).

Pitting usually initiates at breaks in protective coatings or film, scratches, and irregularities that are exposed to an aggressive electrolyte. Even though a pit is slow to initiate, once started, it will progress at an ever-increasing rate and will tend to undercut the surface as it grows. There is a close similarity "open pad" corrosion events that have access to oxygen in the atmosphere versus a pitting event that is isolated from the oxygen in the atmosphere by the solder mask. As the oxygen in the pit is depleted by the corrosion reaction, it becomes very acidic and drives the localized anode / cathode pitting cell. A ring of precipitation tends to migrate out of the pitting site in a circular ring. One corrosion expert consulted stated that "this might be a change in pH of the residue as it migrates away from the corrosion sites." As the pH of the ion migration increases, it has a tendency to migrate away from the corrosion site until it reaches an equilibrium point with equal distant circular formation around the pitting site (Figure 1).

Notice how the nucleus where the corrosion starts to propagate is on a copper trace protected with solder mask. If the copper under the solder mask is not fully sealed or if a scratch exposes the underlying copper, there is potential for pitting corrosion to occur. Boards waved and selectively soldered with no-clean flux materials can help propel the corrosion mechanism. When the right conditions are present, pitting corrosion can take place.

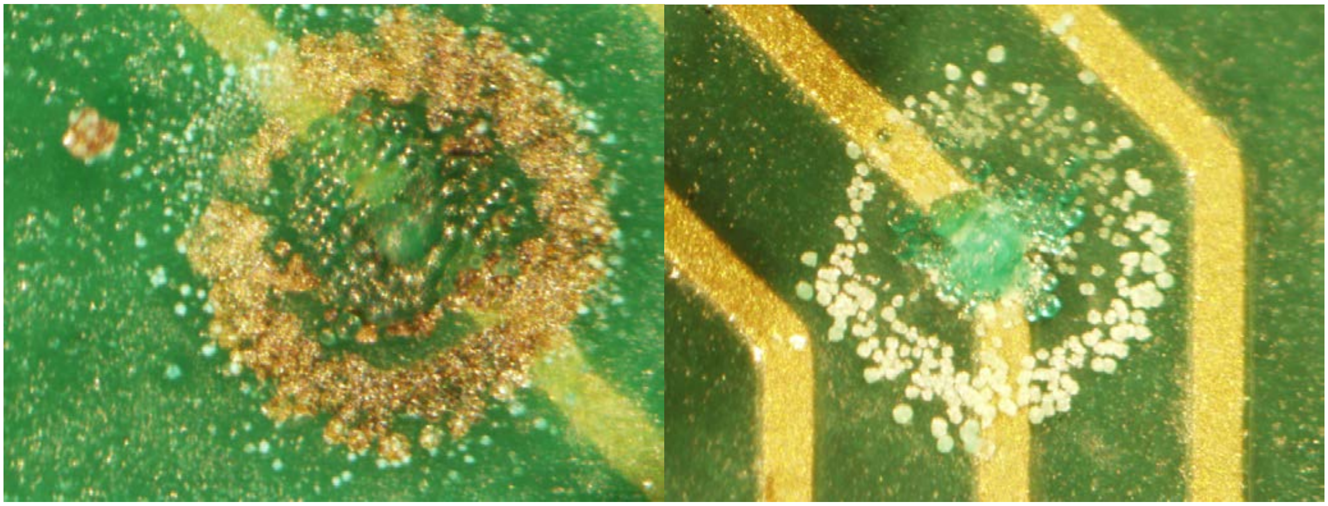


Figure 1 – Images illustrating Pitting Corrosion

Figure 2 is an X-ray image of a board that failed from pitting corrosion. Conditions were right for a scratch or defect on top of the power trace to create a site for pitting corrosion to occur. The corrosion eventually ate through the copper trace. This created an open circuit.

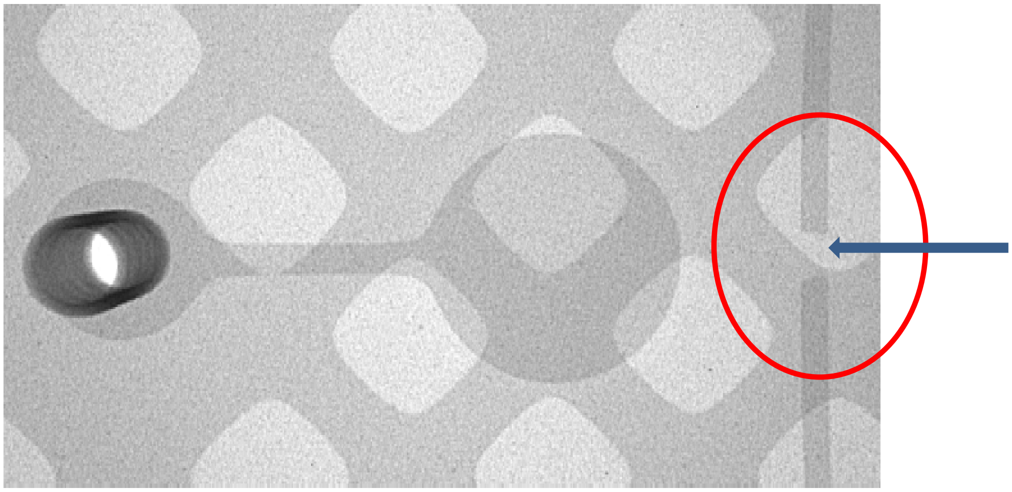


Figure 2: Open Power Trace that resulted from Pitting Corrosion

In contrast to pitting corrosion, many equate corrosion on a printed circuit board to electrochemical migration. Electrochemical migration (ECM) is the growth of conductive metal filaments on a printed circuit board (PCB) through an electrolyte solution under a DC voltage bias. These failures can be either intermittent or permanent, depending on the morphology of the resulting dendrites and the current density. The occurrence of ECM requires an electrolyte, a voltage bias, and migrating metal. The electrolyte comprises dissolved ions from condensed moisture absorbed on the surface. Figure 3 illustrates electrochemical migration from an open in the power trace next the ground pad.

Figure 3: Electrochemical Migration from a Power Trace not covered with Solder mask and the Ground Pad

To summarize, there are two forms of corrosion failures that can occur. When the anode and cathode are close enough to each other, then a dendrite forms (ECM) causing a short. If the gap between the anode and cathode is in the 5 mil or less range, a dendrite will form very quickly. Pitting corrosion occurs between a soldermask defect and a copper trace that is isolated from the oxygen in the atmosphere by the solder mask. When the oxygen in the pit is depleted by the corrosion reaction, the electrolyte becomes very acidic and drives the localized anode / cathode pitting cell. Active anodes start to migrate out of the pitting site. As corrosion migrates away from the nucleus, the pH of the ions increase until it reaches a point where anodes precipitate out at an equal distant circular to the pitting site.

Copper Conductivity

Electrical conductivity is a measure of how well a material transports an electric charge[1]. Printed Circuit Boards (PCBs) have been historically connected through the use of copper conductors. Copper has the highest electrical conductivity rating of all non-precious metals. Because of copper's superior conductivity, the industry standard conductor for PCBs is copper.

In a copper atom, from a Quantum theory perspective, the outermost 4s energy zone, or conduction band, contains one free electron. Copper imparts numerous electrons able to carry electrical current. When an electric field is applied to copper circuitry, the conduction of electrons accelerates toward the electropositive end, thereby creating a current.

FR-4 is the primary insulating backbone upon which the vast majority of rigid printed circuit boards are produced[2]. A thin layer of copper foil is laminated to the FR-4 glass epoxy panel and traces etched. Solder mask, a polymer, is applied over the copper traces for protection against oxidation and to prevent solder bridges from forming between closely spaced solder pads[3]. Solder mask curing and application processes have been known to cause corrosion issues.

Copper Corrosion

With exposure to atmosphere, copper oxidizes, causing bright copper pads and traces to tarnish. Copper corrodes at negligible rates in unpolluted air, water and non-oxidizing acids. Copper is susceptible to more rapid attack in oxidizing acids, oxidizing bases, sulfur, and ammonium compounds. Wave fluxes are formulated with activators that may have organic acid(s), chlorides and/or bromides as ionic impurities. These activators remain embedded in the no-clean flux. Following the wave or selective soldering process, other anions/cations that are not found in common wave fluxes such as fluoride, phosphates, nitrates, sulfides and sulphates are commonly present. Typical sources of these ionic contaminants include etching, plating, tinning or leveling residues, cleaning steps, solder masks, improperly cured permanent or temporary solder masks, dust, moisture, storage conditions, oil pollution from finger prints, component packaging materials, components and machine maintenance oils (from wave soldering conveyors), poor shipping handling or personal protection methods. Contaminants within the assembly process are a multi-variant issue that can be a contributing factor to corrosion.

One of the jobs of flux is to remove surface oxides. As the activity level of the flux increases, there is a greater chance of forming pitting corrosion.[1] The formation mechanism occurs when the copper gives up electrons (Figure 4). Thin pits within the copper form on the metal surface. Metal migration grows with the trace becoming more corroded over time. The oxidizing copper cation enables the formation of pitting even when there is no supply of oxygen to the copper trace.

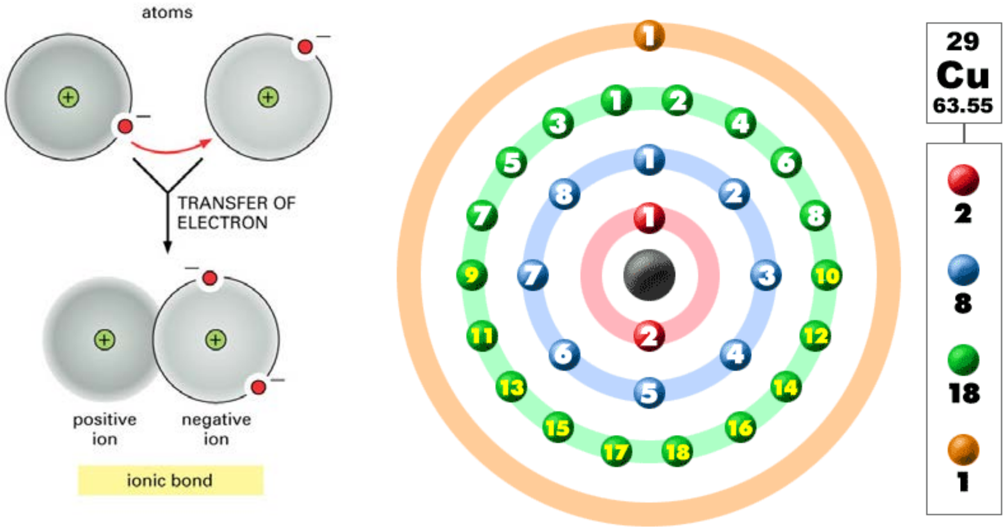


Figure 4 - Transfer of Electrons with a Metal and Ionic Residues in an Electrolytic Solution Initiates the Corrosion Process

Each of those colored balls shown in Figure 4 is an electron. In an atom, the electrons spin around the nucleus[5]. The electrons like to be in separate shells/orbitals even though these electrons do not stay in defined areas around the nucleus. They are found in clouds that have different shapes that include spheres and dumbbell like shapes. Copper is one of the transition elements that does not place the additional electrons in the outer shell, but in the one underneath. The electron in the outer shell makes copper a positive ion, commonly referred to as a cation.

Ion Mobility

Monolayers of moisture can form on the surface of a printed circuit board when exposed to environmentally humid conditions. Water forms an electrolyte by dissolving both cations and anions, which disperse uniformly (Figure 5) [6]. The corrosion process is initiated by an oxidation/reduction reaction of ions mobilized within the monolayers of moisture. The corrosion rate is surface mobility limited. Within a crevice, the ions dissolved in water can form a cell. Metallic fragments plate out until a dead short or an open circuit occurs. Higher temperature equals higher mobility. Additionally, higher percent relative humidity results in higher mobility.

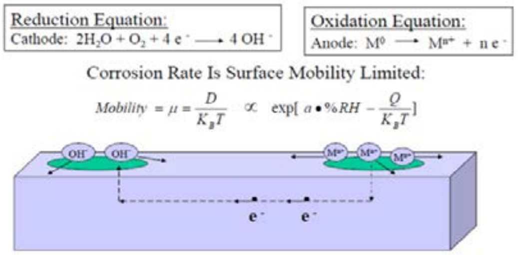
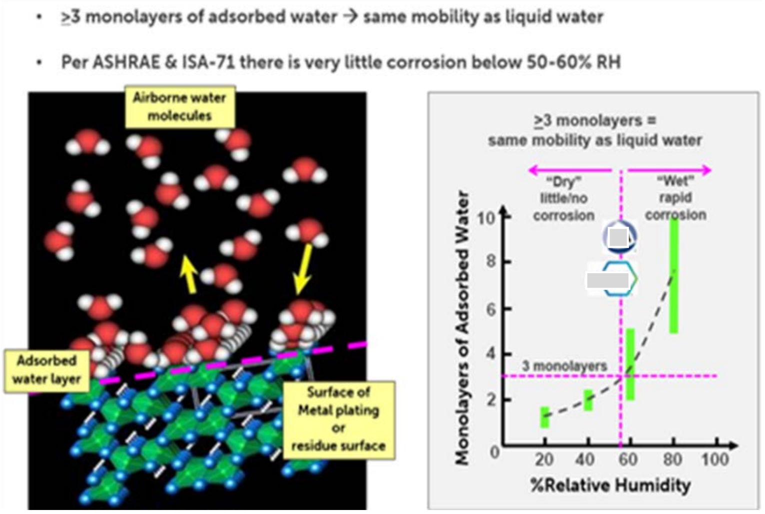


Figure 5: Corrosion Rate is a Function of Contamination, Ion Mobility, Time, Current, & Relative Humidity

Flux residues when mobilized with water can form a weak acidic or basic solution dependent on the flux activator chemistry. It takes roughly three monolayers of moisture to mobilize an ion (Figure 6) [6]. This weak electrolyte is attracted to copper cationic oxides. If an electrical potential (voltage) is present within the pit or crevice, the cations of the solution will be drawn to the electrode that has an abundance of electrons, while the anions will be drawn to the electrode that has a deficit of electrons. The movement of anions and cations in opposite directions within the solution creates current flow. Resistance drops as pitting corrosion grows and propagates.



- >3 monolayers of adsorbed water → same mobility as liquid water
- Per ASHRAE & ISA-71 there is very little corrosion below 50-60% RH

Figure 6 - Monolayers of Adsorbed Water Mobilize Ions

To summarize the corrosion mechanism, the residues mobilized in water, form an electrolytic solution. An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. The ionic residues from residual flux or other surface contamination dissolved within the electrolytic solution can be either acidic or basic. This electrolyte removes trace metal oxides, which are cations. The dissolved electrolyte separates into cations and anions, which disperse uniformly through the monolayers of moisture that serve as the solvent. When there is an electrical potential (voltage) present in the corrosion cell, the metal oxides within the solution are drawn to the electrode that has an abundance of electrons, while the anions are drawn to the electrode that has a deficit of electrons. The movement of anions and cations in opposite directions within the solution creates a current. The metal cations within the electrolytic solution start to form a circular morphology growth. This circular morphology growth can be seen where the pits develop (Figure 7). The corrosion grows outward with the potential nuclei remaining intact. Over time the corrosion grows and starts to move outward. Galvanic coupling in these areas where metal dissolution occurs initiates the formation of small anodes. These small anodes surrounding the nucleus form the negative side of the terminal of the primary corrosion cell.

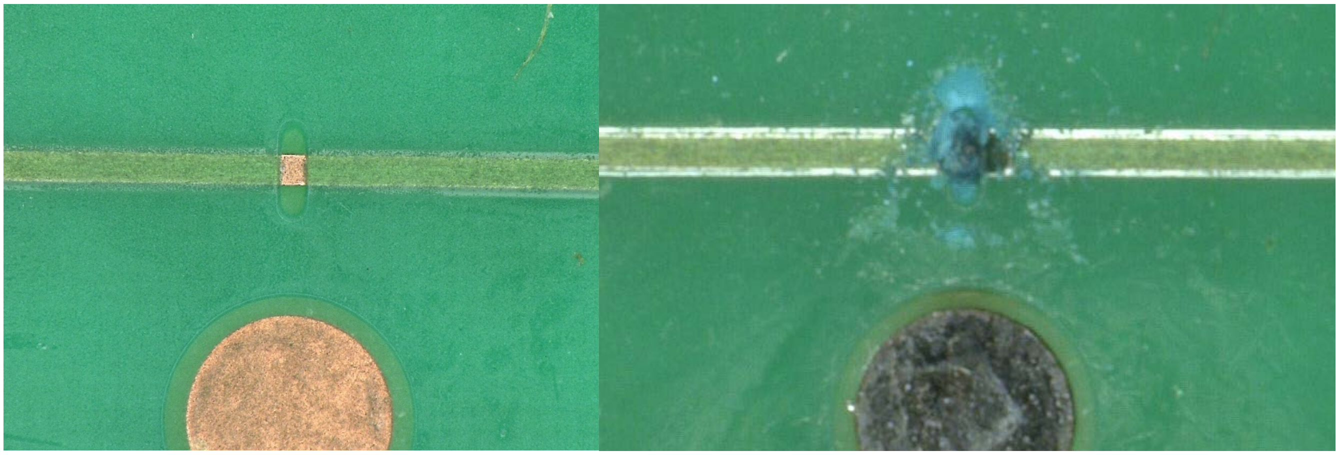


Figure 7 - Board with No-Clean Flux before and After Environmental Testing

No-Clean Soldering Flux

An important feature of no-clean solder fluxes is to leave a residue that is free of ionic, corrosive or conductive residues. Solder fluxes are formulated with activators, carrier vehicles, solvents and functional additives. The activity of the activator generally increases with temperature. As temperature rises, flux activators are designed to crosslink and outgas, eliminating the corrosive and conductive substances. Low residue no-clean fluxes are designed to consume all the activators during the solder reflow cycle.

Boards soldered with no-clean flux are expected to have only benign residues on the surface of the board and are commonly not cleaned following the soldering process. Temperature variations on the board and areas that entrap flux, such as low clearance parts or wave solder fixtures, can affect the ability to both react and drive off flux activators. These flux activators, some more problematic than others, can form harmful residues in the presence of moisture if left on the board. An additional problem is that no-clean flux can be wicked into openings and flaws within the solder mask. These flaws may shield proper flux activation. This can result in active flux residue that can cause corrosion of exposed metals.

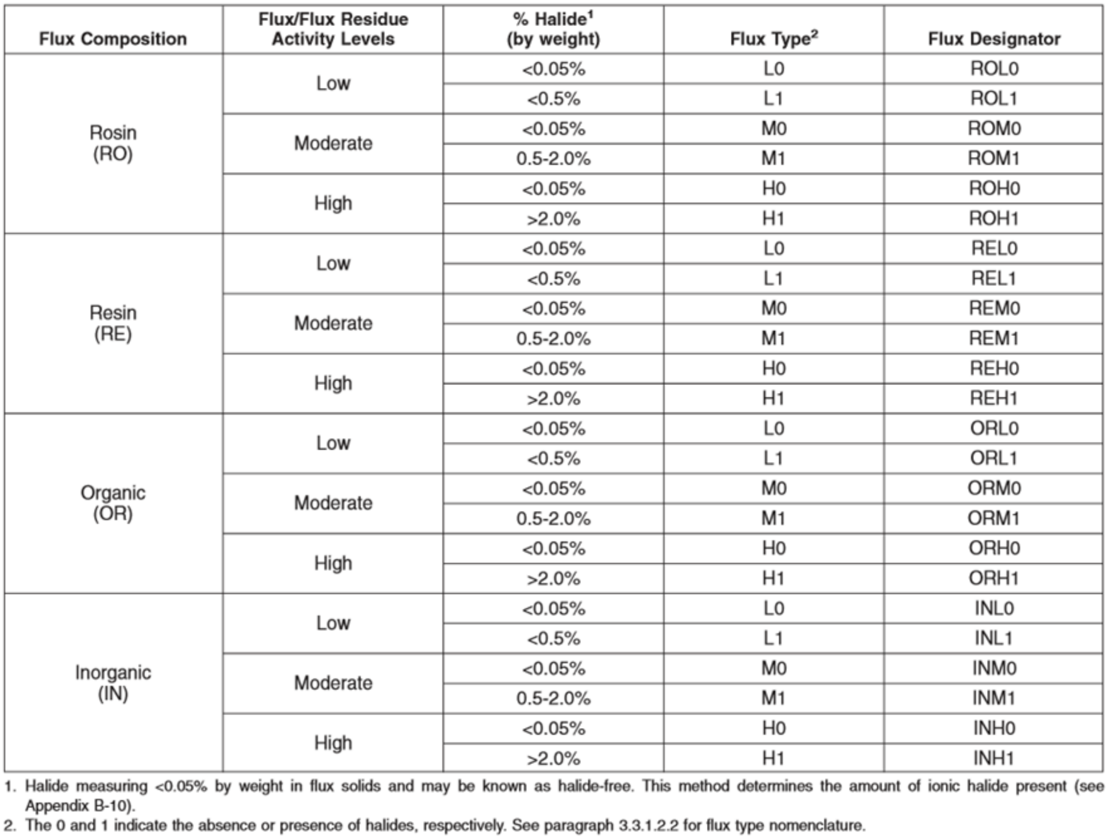
IPC J-STD-004 REV B is the Joint Industry Standard that defines the requirements for soldering fluxes[7]. Fluxes used in the process of soldering shall be classified according to the corrosive or conductive properties of the flux or flux residue. Soldering fluxes shall be classified according to the general chemical composition of the non-volatile portion. Based on a minimum 51% composition of the non-volatile portion, the flux shall be classified as either rosin, resin, organic or inorganic. The soldering fluxes listed in Table 1 are classified by test requirements relating to the activity of the flux and its residue. Soldering fluxes are classified according to one of the following three types:

1. L – Low or no flux/flux residue activity
2. M = Moderate flux/flux activity
3. H = High flux/flux activity

These classes are further characterized using 0 or 1 to indicate absence or presence of halide in the flux. The L, M, and H classifications are determined by test methods called out in the standard. Flux used for the soldering of electronic assemblies shall be assessed by the impact of flux residue on the assembly's performance. Conductive properties of the flux residue, to meet a no-clean condition shall pass the following test methods.

- Copper Mirror Test: IPC-TM-650, Test Method 2.3.32
- Corrosion Test: IPC-TM-650, Test Method 2.6.15
- Surface Insulation Resistance (SIR): IPC-TM-650, Test Methods 2.6.3.3 and 2.6.3.7
- Electro Chemical Migration (ECM), IPC-TM-650, Test Method 2.6.14.1

Table 1: Flux Classified by Test Requirements Relating to the Activity of the Flux and its Residue



Flux Composition	Flux/Flux Residue Activity Levels	% Halide[1] (by weight)	Flux Type[2]	Flux Designator
Rosin (RO)	Low	<0.05%	L0	ROL0
		<0.5%	L1	ROL1
	Moderate	<0.05%	M0	ROM0
		0.5-2.0%	M1	ROM1
	High	<0.05%	H0	ROH0
		>2.0%	H1	ROH1
Resin (RE)	Low	<0.05%	L0	REL0
		<0.5%	L1	REL1
	Moderate	<0.05%	M0	REM0
		0.5-2.0%	M1	REM1
	High	<0.05%	H0	REH0
		>2.0%	H1	REH1
Organic (OR)	Low	<0.05%	L0	ORL0
		<0.5%	L1	ORL1
	Moderate	<0.05%	M0	ORM0
		0.5-2.0%	M1	ORM1
	High	<0.05%	H0	ORH0
		>2.0%	H1	ORH1
Inorganic (IN)	Low	<0.05%	L0	INL0
		<0.5%	L1	INL1
	Moderate	<0.05%	M0	INM0
		0.5-2.0%	M1	INM1
	High	<0.05%	H0	INH0
		>2.0%	H1	INH1

1. Halide measuring <0.05% by weight in flux solids and may be known as halide-free. This method determines the amount of ionic halide present (see Appendix B-10).
2. The 0 and 1 indicate the absence or presence of halides, respectively. See paragraph 3.3.1.2.2 for flux type nomenclature.

Experiment Description

Flux Selection

Three industry-accepted wave soldering fluxes were used in this study. The flux classifications are as follows:

- High Rosin: ROL0 Alcohol based no-clean
- Low Activity: ORL0 Alcohol-based no-clean
- High Activity: ORL0 VOC-free, halide free no-clean

The test methods called out in J-STD-004 REV B were performed on these fluxes. The results from these test methods are reported in Table 2.

Table 2: Data Findings from Test Methods Performed on the Three Soldering Fluxes Selected for this Research Phase

Flux	**Copper Mirror**	**Corrosion**	**SIR**	**ECM**
Low Activity, Not Cleaned	Pass	Fail	Pass	Pass
High Activity, Not Cleaned	Pass	Fail	Pass	Pass
High Rosin, Not Cleaned	Pass	Fail	Pass	Pass

All test methods passed with the exception of the Corrosion Test method. All three fluxes were graded as "Major Corrosion" when exposed to highly accelerated life testing the procedures called out in the Corrosion Test method. The corrosion test method is designed to determine the corrosive properties of flux residues under extreme environmental conditions. After the exposure period, the test specimens removed from the humidity chamber are examined using 20X magnification. Corrosion is defined as a chemical reaction between the copper, the solder, and the constituents of the flux residues, which occurs after soldering and during exposure to defined environmental conditions. Minor corrosion is any initial change of color, which may develop when the test panel is heated during soldering. Major corrosion is any initial change of color which may develop when the test panel develops green-blue discoloration with observation of pitting of the copper panel or excrescences at the interfaces of the flux residue and copper boundary. For the three classified No-Clean fluxes tested, all three failed (Figure 8).

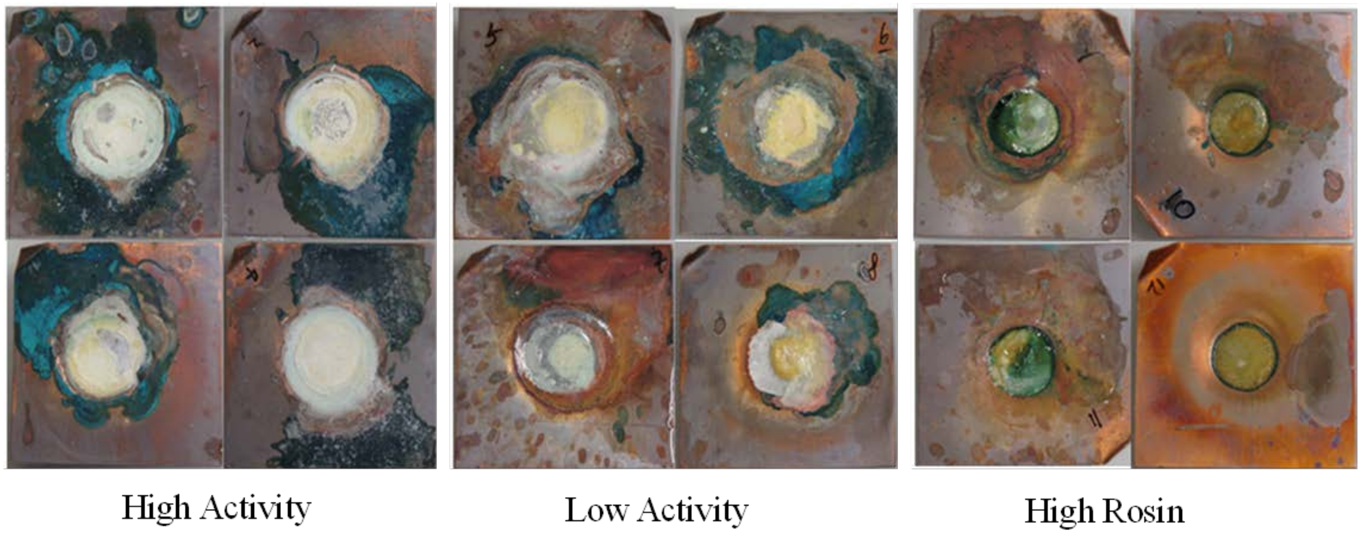


Figure 8 - Corrosion Data Findings on the Three Fluxes Selected for this Research Phase

Pitting / Crevice Corrosion Test Method

The ECM project team designed a test board for studying pitting and crevice corrosion. The test board, Figure 9, has exposed copper features designed to indicate which factors most contribute to corrosion. These corrosion sites were designed with variable openings in the solder mask and spacing to ground. The tests were done at 40°C and 85% relative humidity (RH) and for at least 4 weeks, at two voltages and with and without a selective wave fixture.

The test board is a standard 0.062 thick card with OSP finish over copper pads. A Liquid Photo Image solder mask was applied.

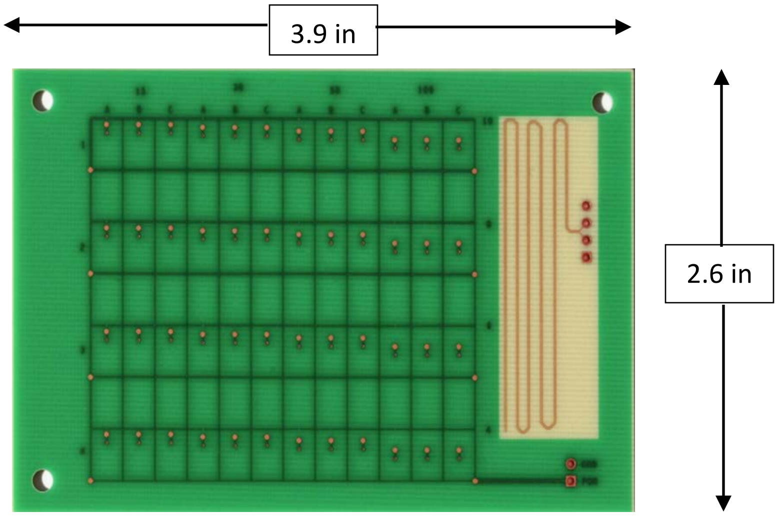


Figure 9 - Pitting/Crevice Corrosion Test Board

The topside circuit lines with the test corrosion sites are connected to the power supply. The back side of the board, Figure 10, is a ground plane with ground connections feeding to the top side through a via connected in a dog bone style.

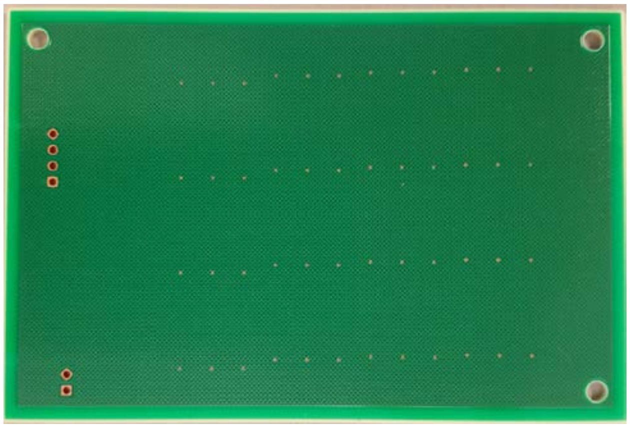


Figure 10 - Ground Plane on Back Side of Board

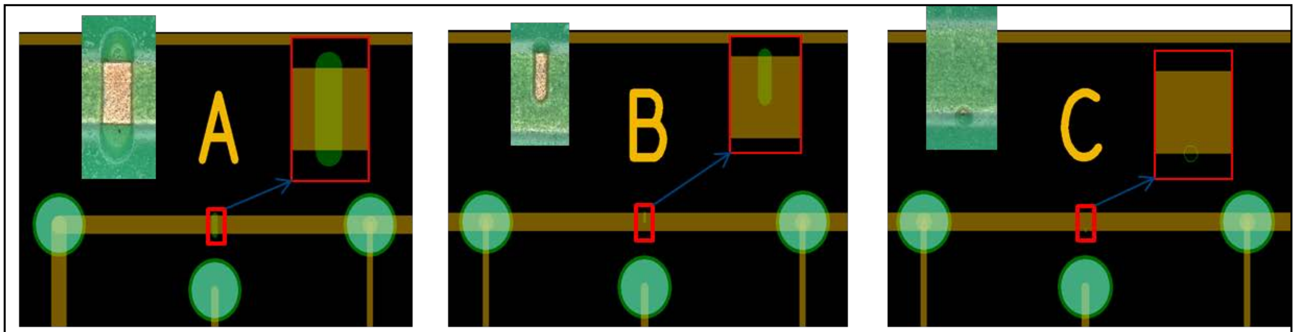
Test boards designed to have flaws in the soldermask were wave and selective soldered by depositing liquid flux over the surface area being soldered. Initially held at room temperature, the flux residue stayed on the cards at room temperature for 3 to 4 months with no sign of corrosion. When the coupons were put in the temperature and humidity chamber, the un-fluxed control samples were placed into the chamber at the same time the fluxed samples were tested. It is worth noting that all boards will have some degree of solder mask imperfections. There is also no known solder mask test that can be performed at the PCB vendors to determine the degree of inherent solder mask imperfections, so it is very difficult to remove this exposure from the product. The flux testing protocol evaluates exposure to the three test fluxes to determine how much risk the product will have from the flux residue in a humid environment.

Factors and Levels Researched

- Ground Pad to Corrosion Site Spacing
    - 15 mil
    - 30 mil
    - 50 mil
    - 100 mil
- Wave Solder Fixture
    - Selective Wave
    - Open
- Solder Mask Defect Simulation Sites
    - A, B, & C solder mask openings
- Three Fluxes Tested
    - Low Activity
    - High Activity
    - High Rosin

- Flux Levels Applied
    - Low/Normal
    - High
- Voltage Bias
    - +3 volts (positive and negative bias)
    - +10 volts

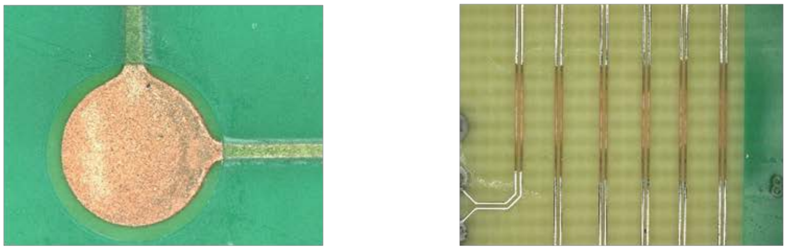
The test board has 56 corrosion sites as illustrated in Figure 11. There are 16 type "A" corrosion site solder mask openings, 16 type "B" corrosion site solder mask openings, 16 type "C" corrosion site solder mask openings, and 8 power pads (typical in circuit test probe pad configuration) on each test board.



16 Large SM test opening:
A, D, G, J

16 Medium SM opening:
B, E, H, K

16 Small SM opening:
C, F, I, L



8 Power / Ground pad
(Typical ICT test pad size)

Resistance comb to measure flux residue conductivity

Figure 11 - 56 Corrosion Sites designed into the Test Board

There is also a dog bone via ground plane connection adjacent to each of the 48 solder mask corrosion site openings as shown in Figure 12. These provide additional corrosion points at the copper plated via holes, copper ground pads, and the solder mask interfaces on each end of the trace connecting the via and pad. The 8 copper defined power pads also have solder mask interface corrosion sites at each power trace connection.

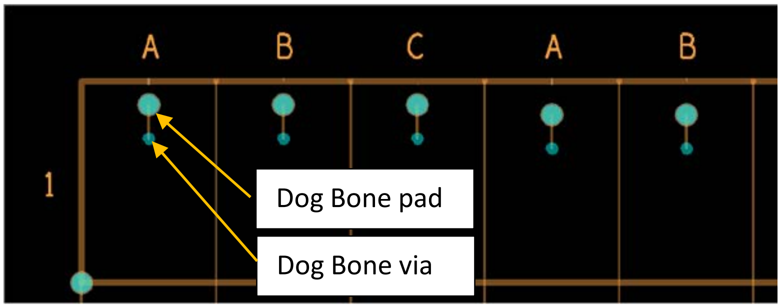
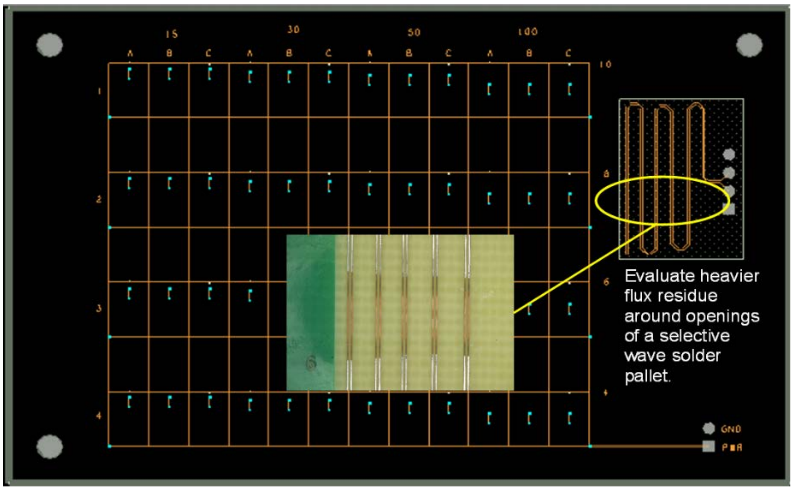


Figure 12 - Dog Bone Via Ground Plane Connection

In addition to the corrosion test sites and dog bone ground vias, a resistance comb was added to determine if the flux residue film has a measureable resistance level. See Figure 13. Some flux formulations leave a thicker or wetter flux residue than others, which can absorb and hold moisture, providing a conductive path on the surface of the board for ionic migration.



Evaluate heavier flux residue around openings of a selective wave solder pallet.

Figure 13 - Flux Residue Comb Pattern Test Site

Figure 14 illustrates the ground pad to trace spacing.

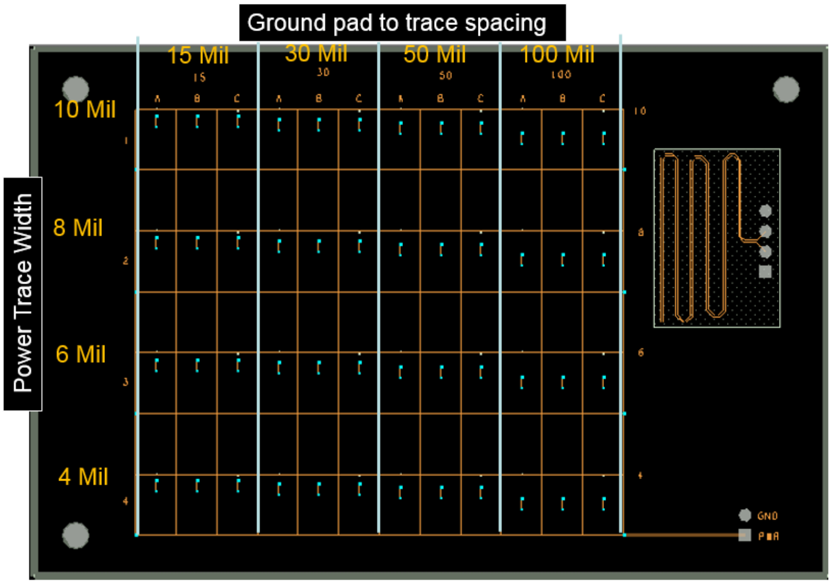


Figure 14 - Ground Pad to Trace Spacing

Test board corrosion features include:

- Ground pad to power trace spacing variation (15, 30, 50 & 100 mil)
- Corrosion site trace width variation (4, 6, 8 & 10 mil)
- Corrosion site solder mask opening variation (A, B, C)
- Ground pad. voltage pad, and via exposure
- Circuit line solder mask interface
- Flux residue resistance grid

Figure 15 illustrates the test board corrosion features.

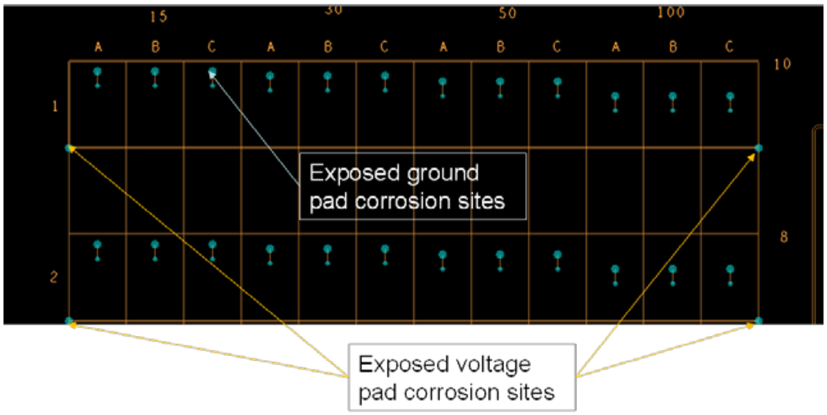
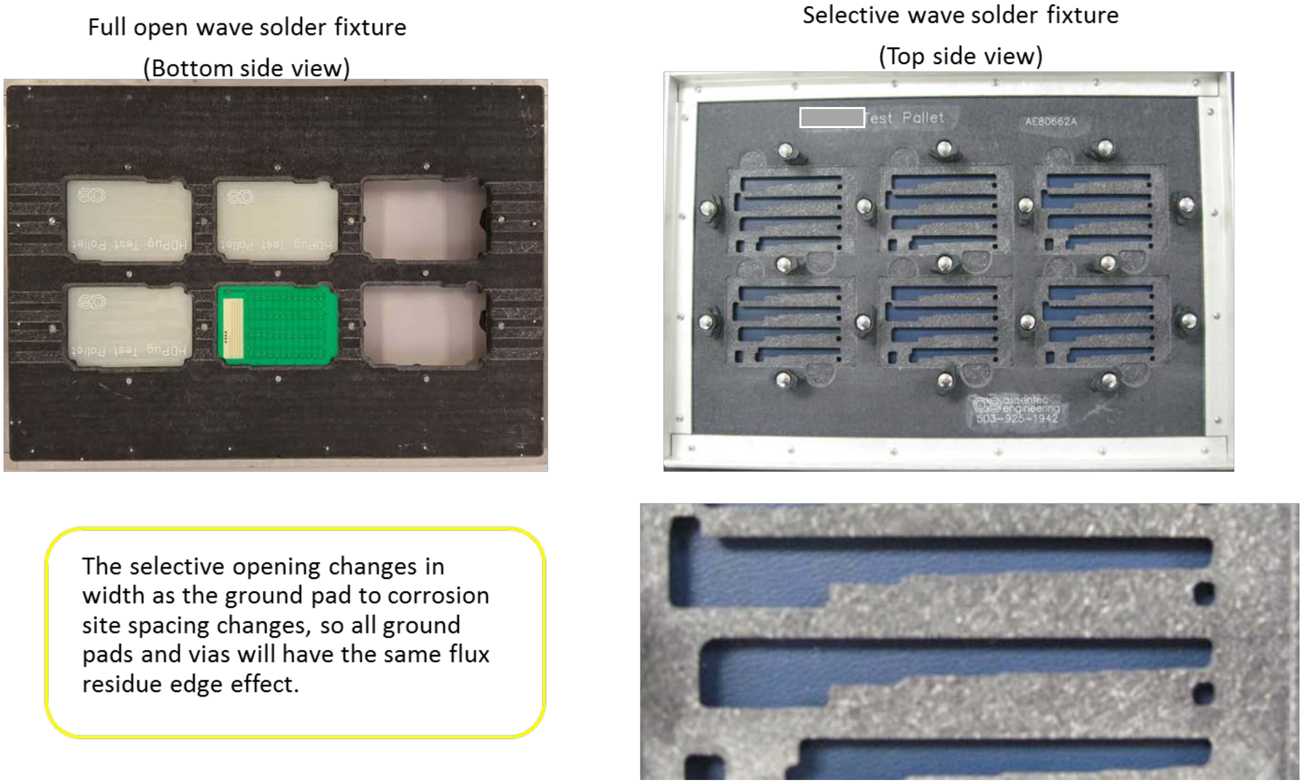


Figure 15 - Test Board Corrosion Features

Figure 16 illustrates the design of the Open and Selective solder pallets. The selective solder pallet is design to accumulate flux near the power and dog-bone ground pads.


Full open wave solder fixture (Bottom side view)

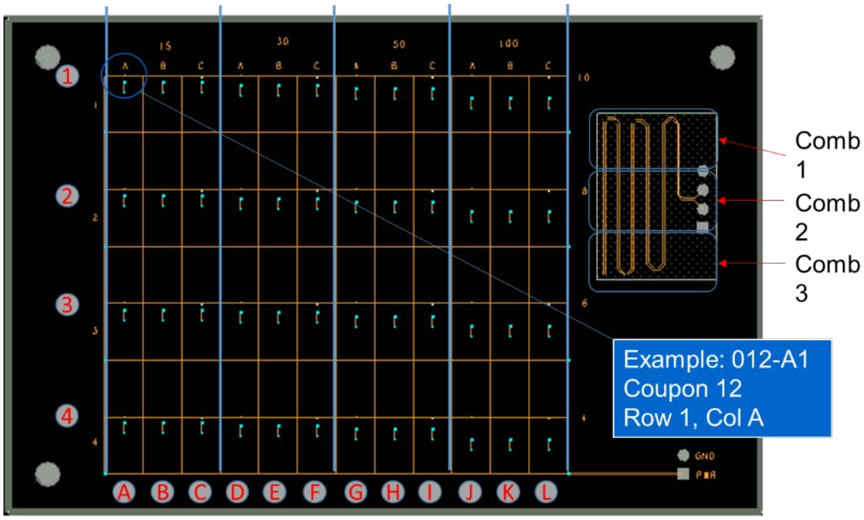
Selective wave solder fixture (Top side view)

The selective opening changes in width as the ground pad to corrosion site spacing changes, so all ground pads and vias will have the same flux residue edge effect.

Figure 16 – Open and Selective Wave Soldering Pallet Designs

Data Findings

For each board tested there are 48 solder mask opening test sites (Figure 17). Each site was imaged and scored using the grading scale (Figure 18). The total number of data points captured was 5,780.



Example: 012-A1
Coupon 12
Row 1, Col A

Figure 17 - Test Sites Nomenclature

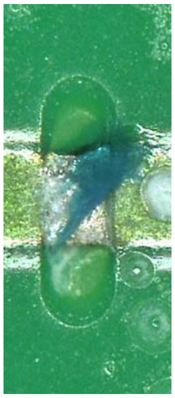
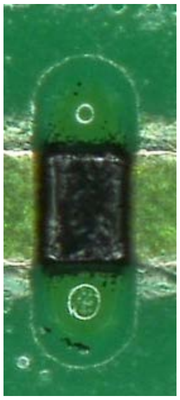
Score = 1 ~ No Corrosion	Score = 2 ~ Copper Oxidation	Score = 3 ~ Copper Migration Starting to Form	Score = 4 ~ Copper Migration Propagating over the Pad Area	Score 5 = Copper Migration Covering entire Pad Area	Score = 6 ~ Pitting / Crevice Corrosion Covering Pad Area	Score 7 = Massive Pitting / Crevice Corrosion that Leads to an Open
						

Figure 18 - Grading Scale Following Environmental Testing

The un-fluxed boards did not corrode at (40°C, 85% RH), while some of the fluxed samples corroded significantly when exposed to the moisture in the test chamber. Figure 19 provides a look at a subset of boards for the control and three fluxes tested.

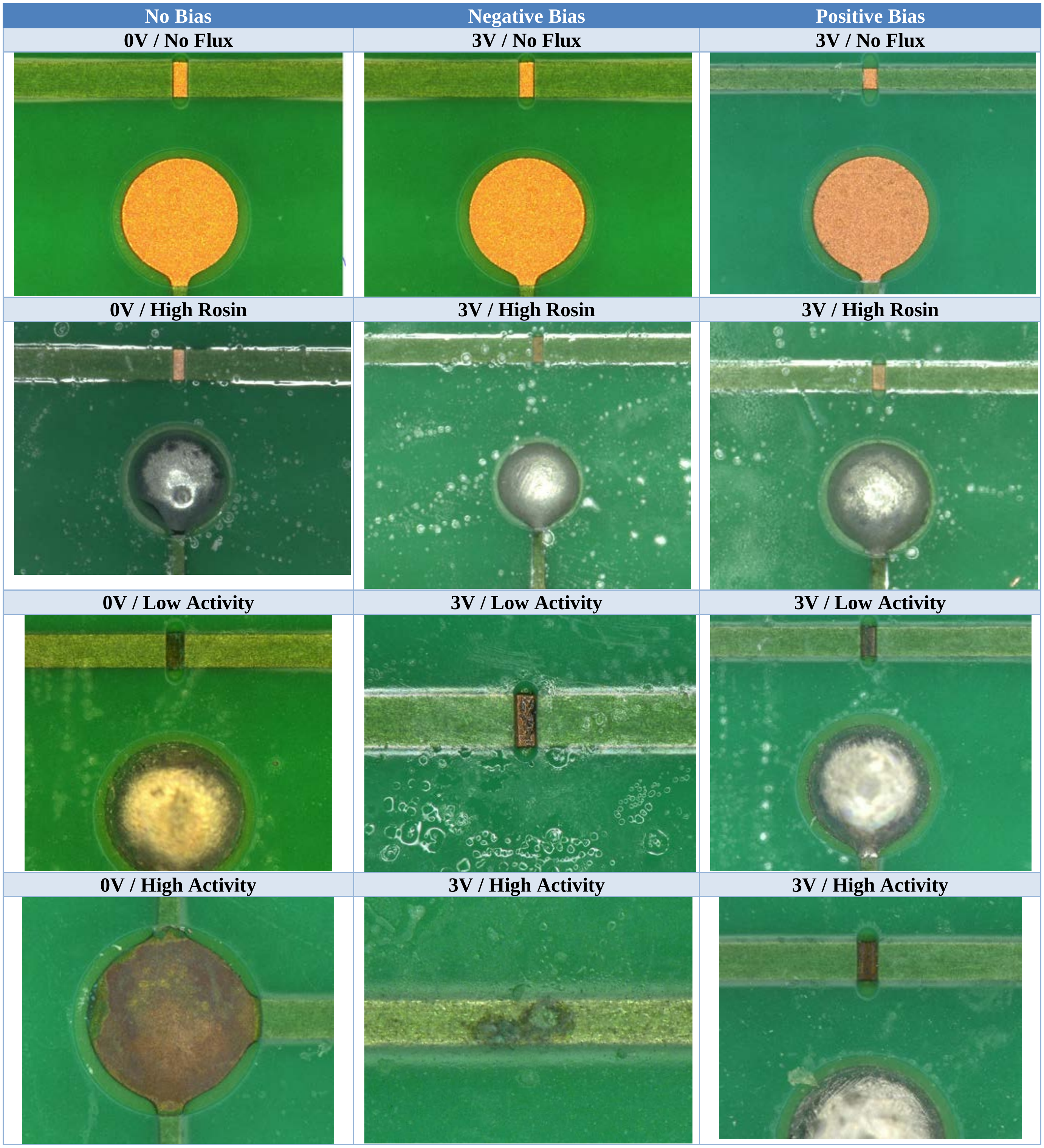


Figure 19 – Visual Images from a Subset of Conditions Tested

Low Activity: Alcohol-based no-clean flux that is both active and low solids. The soldering flux is designed with a wide thermal process window and may be used for tin-lead and lead-free alloys. The flux classification per J-STD-004 is ORL0. The flux may be applied using spray or foam fluxing and is compatible with pallets or selective soldering.

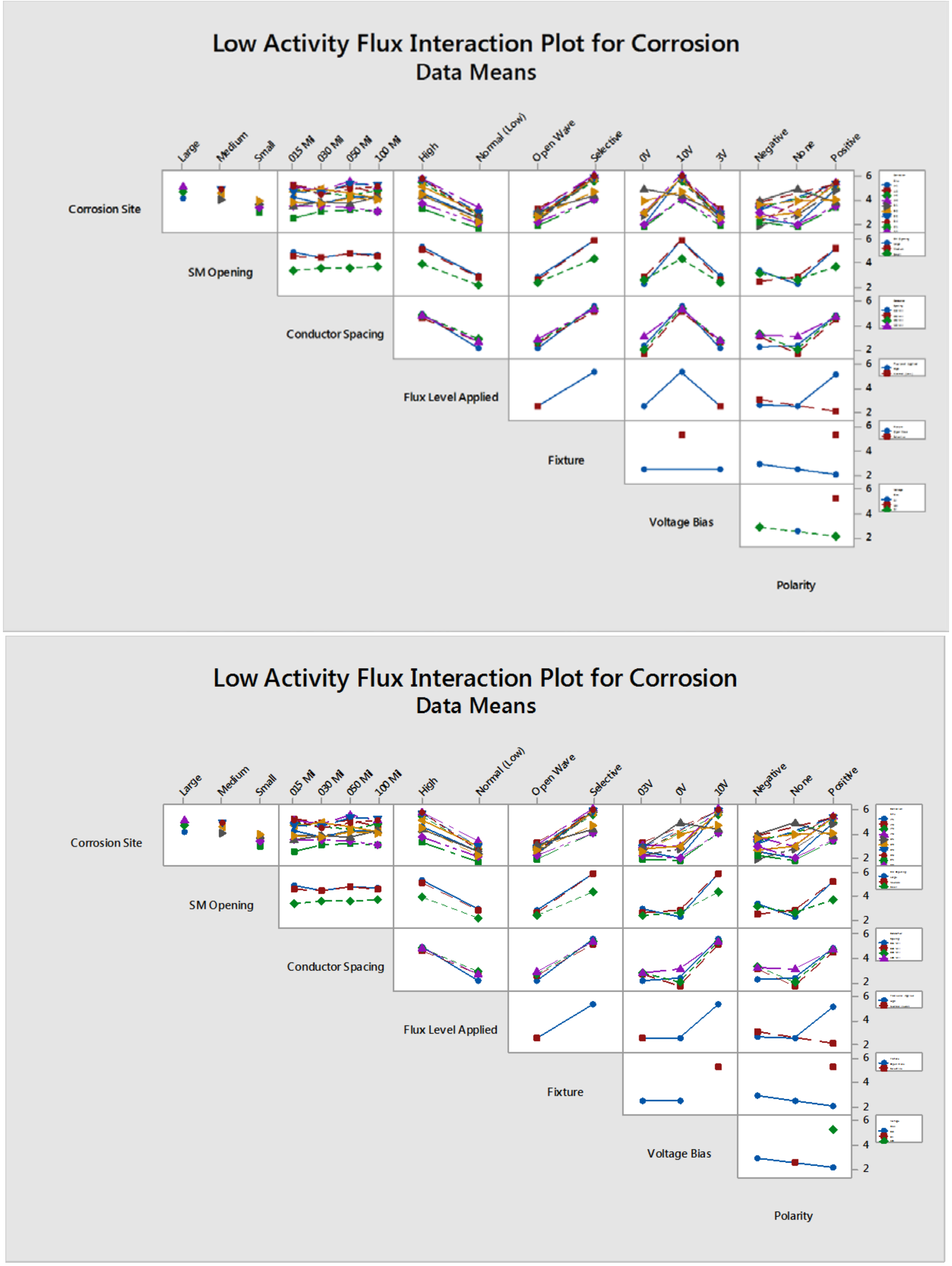


Figure 20 – Effect of Low Activity No-Clean Flux

For the Low Activity No-Clean Flux, the data findings in Figure 20 reveal key factors that accelerate corrosion. The samples using a selective solder fixture, which shields flux residues from activation temperature, showed higher corrosion than those soldered with an open solder fixture. On sites with larger exposed copper features, sizes A and B, corrosion was worse, particularly at 10V. Conductor spacing from power to ground was not material. Voltage bias is a significant factor with higher voltage increasing corrosion. The higher quantity of flux applied resulted in more corrosion.

High Activity: VOC-free, halide free, rosin/resin-free low solids no-clean flux designed to provide high activity on difficult to solder boards. The flux classification per J-STD-004 is ORL0. The flux may be applied using spray or foam fluxing and is compatible with pallets or selective soldering.

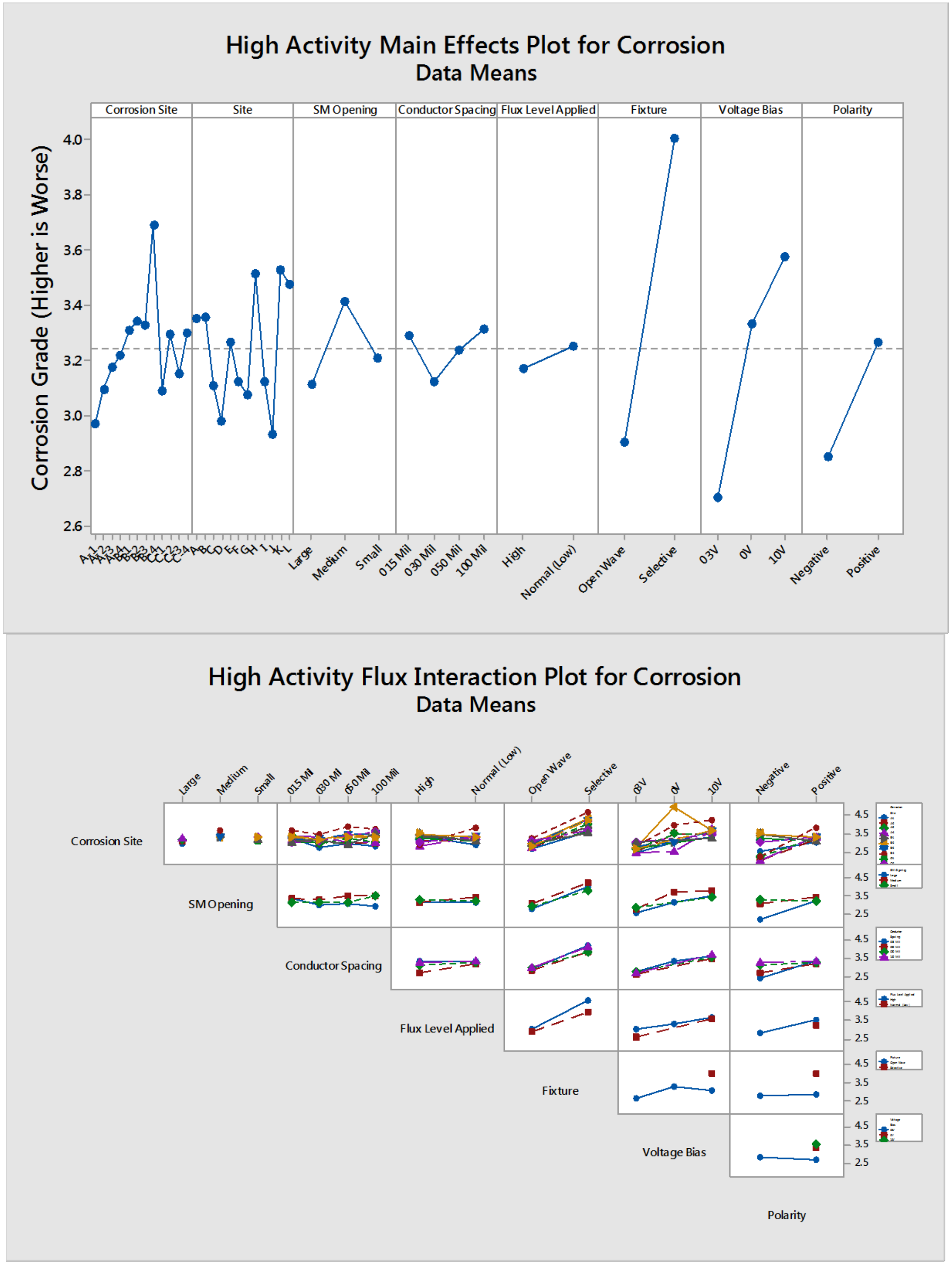


Figure 21 - Effect of High Activity No-Clean Flux

For the High Activity No-Clean Flux, Figure 21, the data finds the flux level applied was not statistically significant. The data did find that the boards processed with the Selective wave fixture corroded at higher levels than boards' process within the Open wave fixture. The data found the spacing between the ground and power was not materially significant. Voltage bias is a significant factor with higher voltage increasing corrosion.

High Rosin: Alcohol-based no-clean with rosin carrier designed for wave soldering. The flux classification per J-STD-004 is ROL0. The product works well on both tin-lead and lead-free alloys. May be applied using spray or foam fluxing. The flux is compatible with pallets or selective soldering.

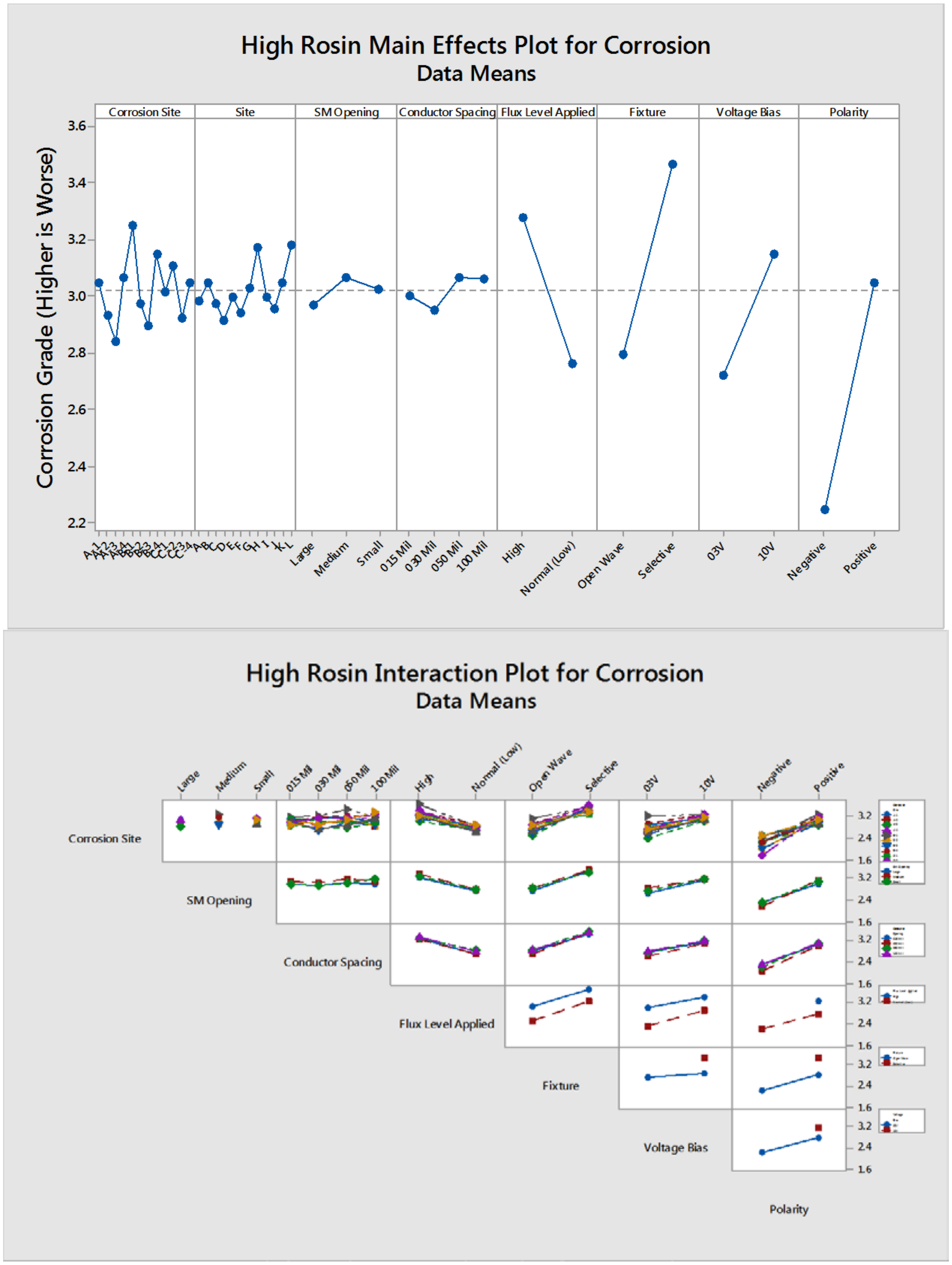


Figure 22 – Effect of High Rosin Flux

For the High Rosin Flux, Figure 22, the data finds the higher flux levels increased corrosion potential. The data did find that the boards processed with the Selective wave fixture corroded at higher levels than boards' process within the Open wave fixture. The data found the spacing between the ground and power was not materially significant. Voltage bias is a significant factor with higher voltage increasing corrosion. A positive bias showed more corrosion than boards applied with a negative bias.

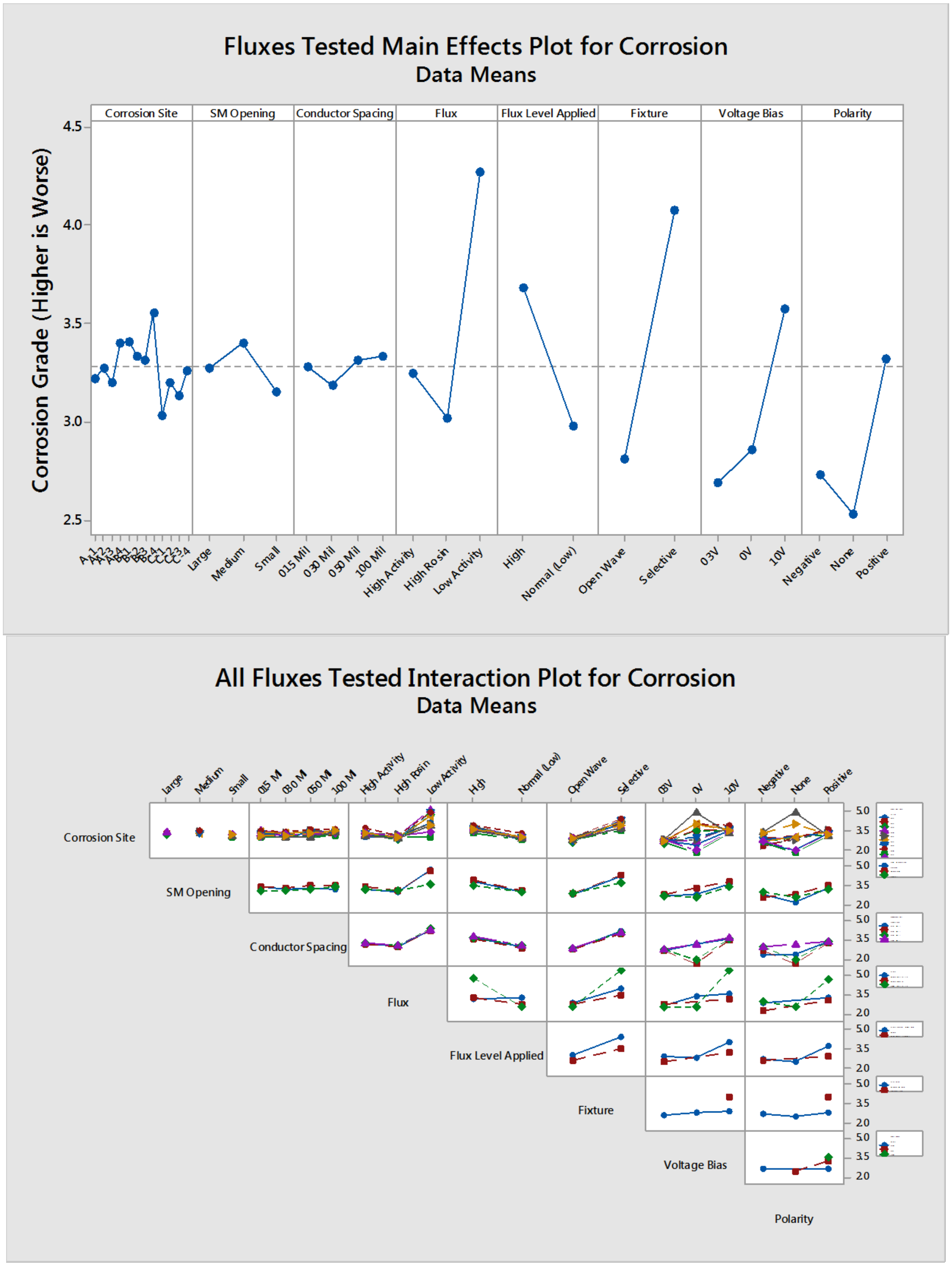


Figure 23 - Pitting / Crevice Corrosion Potential from Factors Tested

The Low Activity No-Clean flux showed the greatest levels of corrosion to copper. On boards using the selective soldering fixture, the corrosion levels were greater as compared to the open wave fixture. Even though the data can be misleading, the higher voltage applied correlated to greater the corrosion potential. The number of boards tested without bias was low but on the boards tested, the corrosion seen on copper was higher than expected.

Conclusions

All boards will have some degree of solder mask imperfections. There is also no known solder mask test that can be performed at the PCB vendors to determine the degree of inherent solder mask imperfections, so it is very difficult to remove this exposure from the product. The flux testing protocol should evaluate this exposure to determine how much risk the product will have from the neutralized flux residue in the hotter and more humid environments.

A flux can find its way into pits from solder mask, cracks, rough copper etching. Understanding these issues and having consistent process output of the laminate are important. Flux activators or other corrosive or conductive substances can remain on the board due to excessive quantity or flux entrapment, such as selective solder fixtures or wicking into solder mask gaps or flaws. If the environment subjects the device to high humidity, the ions can be mobilized and cause corrosion on exposed copper features.

The accelerated corrosion is always on the circuit lines and solder connections that are connected to an applied voltage. We assume the corrosion is happening everywhere on the board, but the rate of corrosion is accelerated on the traces with bias. In a corrosion cell, the voltage on the anode and cathode must be balanced. In a corrosion cell, there is a low voltage potential difference from the anode to the cathode. However, when a 3 volt bias is applied to one side of the corrosion cell, such as with a battery, the other side must be balanced, causing an accelerated rate of corrosion. That is our theory, and it seems to be holding up from our corrosion coupon testing. We were able to switch which part of the coupon corrodes (test sites versus the traces and vias) by reversing the polarity of the voltage applied to the coupon. This is reversing the anode / cathode relationship. Coupons with and without voltage will tarnish and corrode in a humid environment.

Selective soldering showed a strong correlation with corrosion. Fluxes can penetrate beneath the fixture, shielding them from the temperature required to render them benign, leaving unreacted residues on the surface of the board. Higher voltage levels result in more corrosion. The quantity of flux applied on the board was found to increase corrosion for the low activity and high rosin fluxes. The data finds that corrosion risk of no-clean flux when boards are exposed to harsh environments. When no-clean boards are exposed to harsh or humid environments, pitting and crevice corrosion will grow and propagate, leading to electrical opens. The test method under development by the ECM team will help identify fluxes with these risks.

Follow On Research

The Correlation Phase of this research pointed to key factors that cause pitting and crevice corrosion. The research also raised questions that will be considered as the team decides the direction for the next phase of this research. Areas for consideration are listed below.

- Are boards with OSP primary surface finish more susceptible to corrosion than say ENIG or Immersion Silver finished boards?
- Are some types of soldermask materials or chemistry more or less susceptible to pin-holes and/or allow more corrosion?
- Are there board design features that are more susceptible to corrosion (examples: soldermask-defined versus metal-defined SMD lands, acute trace angles on external layers, insufficient soldermask coverage beyond edges of traces, etc.)?
- What is the cause of the different forms of corrosion that occurred in the Correlation Phase of this research?
- What is the minimum voltage / polarity needed to propagate surface corrosion?
- Do larger copper surface defects take longer time to propagate surface corrosion?
- Why did all the no-clean fluxes tested fail IPC TM 2.6.15 Corrosion testing? Is this common for all no-clean fluxes?
- What are the physical properties that can create an electrolytic corrosion cell?
- Is it possible to correlate the conductivity of the no-clean residue on the surface with the corrosion potential?

References

1. Copper Wire and Cable (2015). Retrieved from https://en.wikipedia.org/wiki/Copper_wire_and_cable
2. FR-4 (2015). Retrieved from https://en.wikipedia.org/wiki/FR-4
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Test Method Development for Detecting Pitting / Crevice Corrosion Formation on Electronic Assemblies

HDP User Group Consortium

ECM Project

March 16, 2016

Mike Bixenman, Project Leader
Kyzen Corporation

Agenda

- Introduction
- Pitting / Crevice Corrosion
- Formation Mechanisms
- No Clean Solder Flux
- Experimental Description
- Data Findings
- Conclusions
- Follow-On Research

FORWARD THINKING
FOR TOMORROW'S TECHNOLOGY

INTRODUCTION

Pitting / Crevice Corrosion

- Pitting or crevice corrosion on printed circuit boards:
  - Has not been well studied in the electronics industry
  - Is seen at small solder mask openings over circuit traces
- Failure modes are theorized to be driven by:
  - Openings or defects in solder masks
  - Voltage bias
  - Flux activity
  - Humidity levels
  - Harsh Environments

Solder Mask

- The following qualities are critical
  - Solder mask construction
  - The assembly process
  - Quality of design
- Solder mask (glossy or matte), curing and application process have been known to cause corrosion issues
- Manufacturer, chemical structure, Tg, Filler type, and Level can lead to pitting corrosion and should be understood

Problem Statement

- Intermittent defects in soldermask provide potential failure locations
  - May expose a copper trace
- Wave and Selective Solder Processes
  - Deposit liquid flux over the surface being soldered
- No-Clean processes
  - Flux residue is not removed after soldering
  - Flux is formulated to have a non-ionic (benign) residue
- The problem
  1. Active flux can be wicked into openings or flaws in the soldermask
  2. Active flux can propagate corrosion onto exposed metals
  3. Ions from the flux residue can be mobilized with atmospheric moisture

Purpose of the Research

- Consortium
  - Electro-Chemical Migration team is investigating this issue
  - What factors must be present for pitting corrosion to occur?
- The status of this research:
  - Report current findings and experimental description
  - Inferences from data findings
  - Conclusions from the work done thus far
  - Follow on research

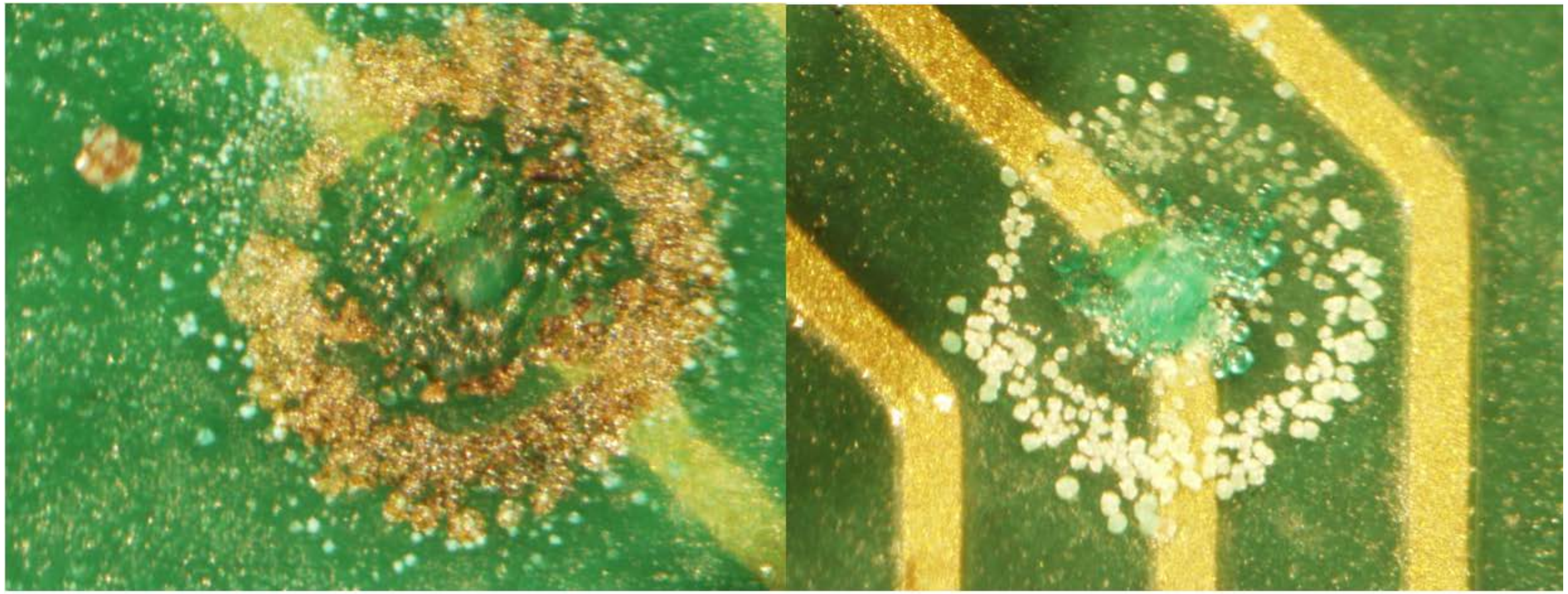
PITTING / CREVICE CORROSION

Pitting Corrosion

- Has been detected on field failure boards
  - Boards were soldered with a no-clean wave or selective soldering flux
  - The failure is **not** an open surface type corrosion event
  - Occurs on boards exposed to
    - Harsh environments
    - Atmosphere pollutants
    - High humidity levels

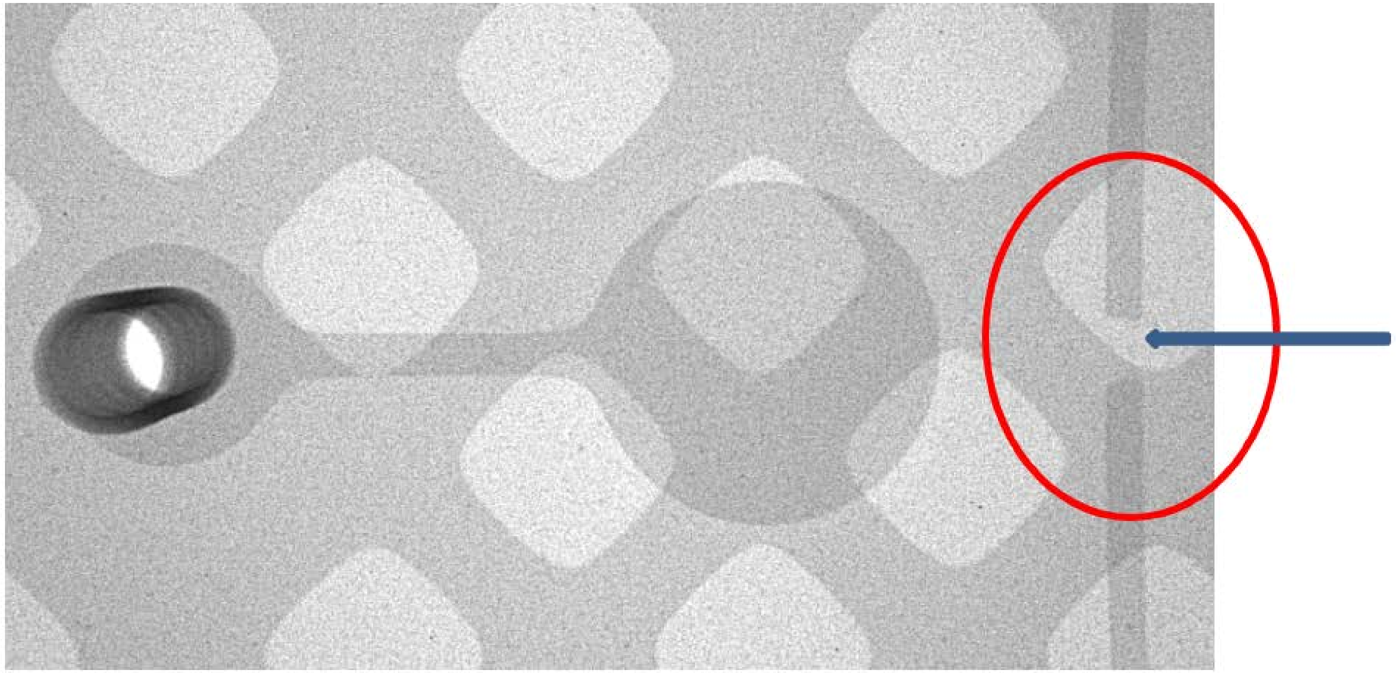
Pitting

- Starts as an advanced form of uniform etch
- The combination of small active anodes attracted to large passive cathodes initiates the corrosion



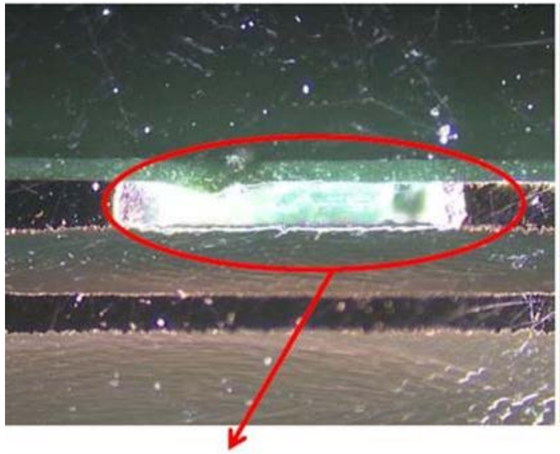
Failed Board

- X-Ray image of a board that failed from pitting corrosion
- Corrosion ate through the copper power trace

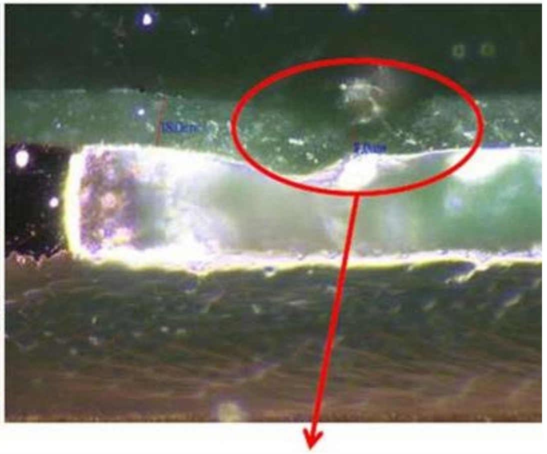


ECM vs. Pitting Corrosion

- ECM is the growth of conductive metal filaments on a PCB through an electrolyte solution under a DC bias
- Pitting corrosion occurs between the solder mask defect and a Cu trace.
- Factors driving the corrosion mechanisms are different



Open trace from pitting corrosion

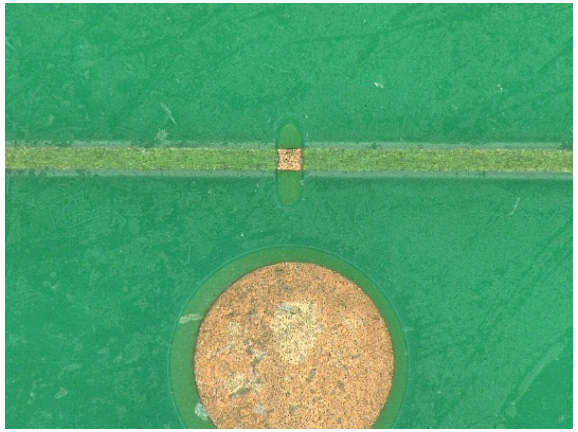


Solder mask defect that initiated pitting

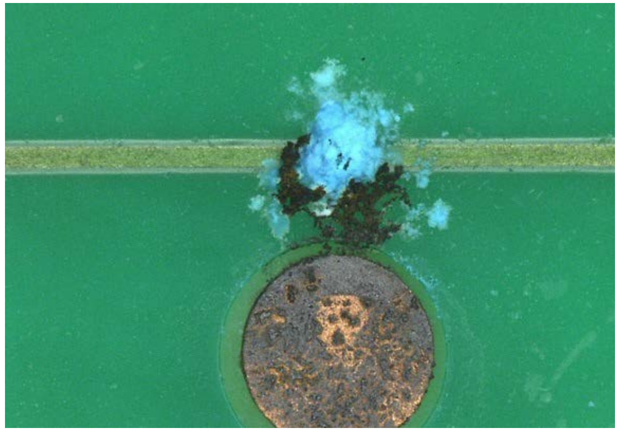
ECM corrosion

Typical Pitting / Open Trace Corrosion

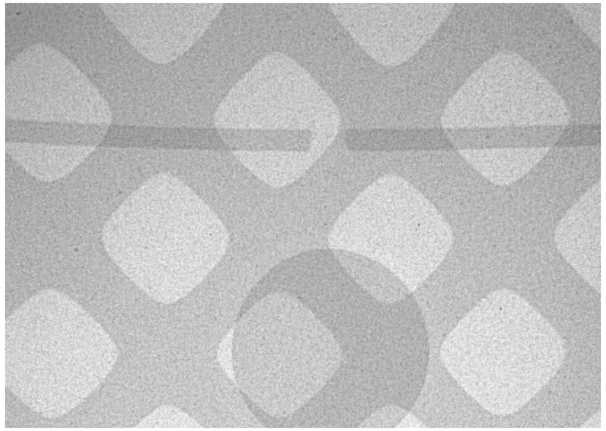
- Has been reproduced in the test environment, and key testing variables have produced significant differences in corrosion rates.



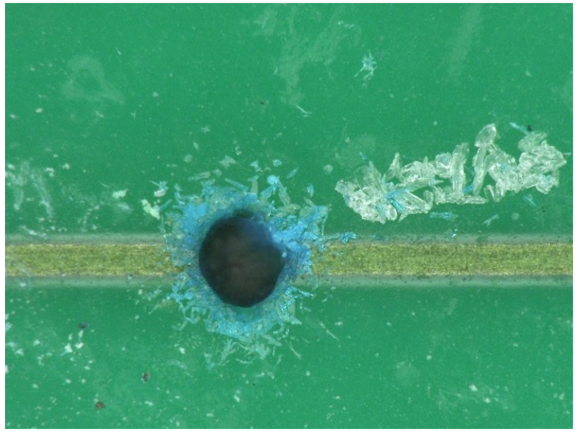
Time Zero Inspection



6 weeks in T&H chamber:
ECM and pitting



X Ray showing the open trace

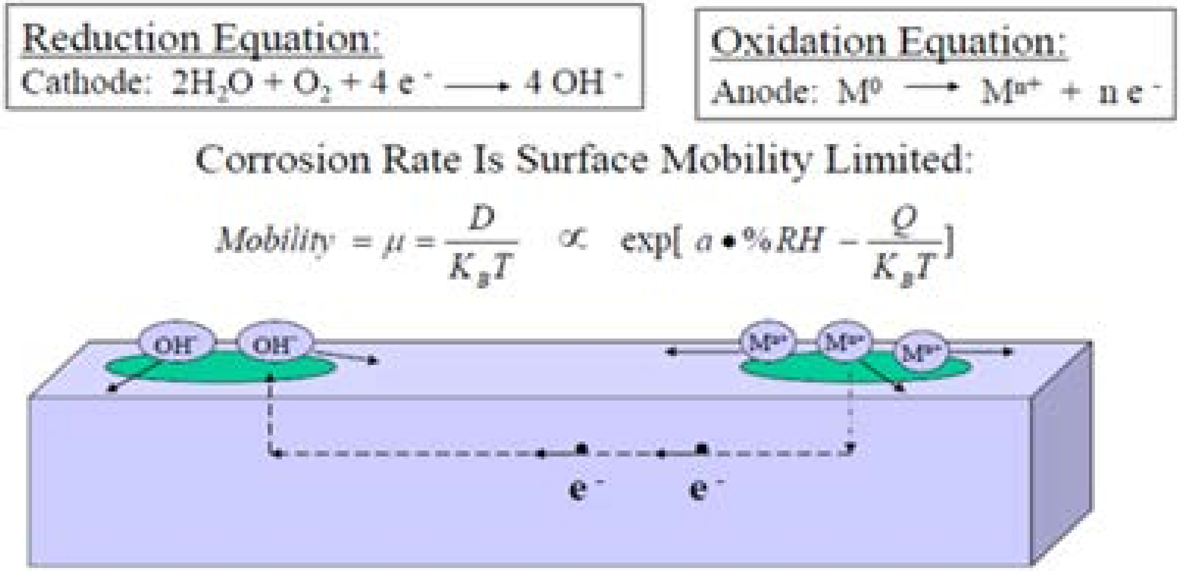


Pitting Corrosion example

FORMATION MECHANISMS

Corrosion Process

- Initiated by oxidation/reduction reaction
  - Ions mobilized by moisture
  - Surface mobility limited
  - Ions dissolved in water form a cell
  - Corrosion propagates and grows



Reduction Equation:

Cathode: $2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$

Oxidation Equation:

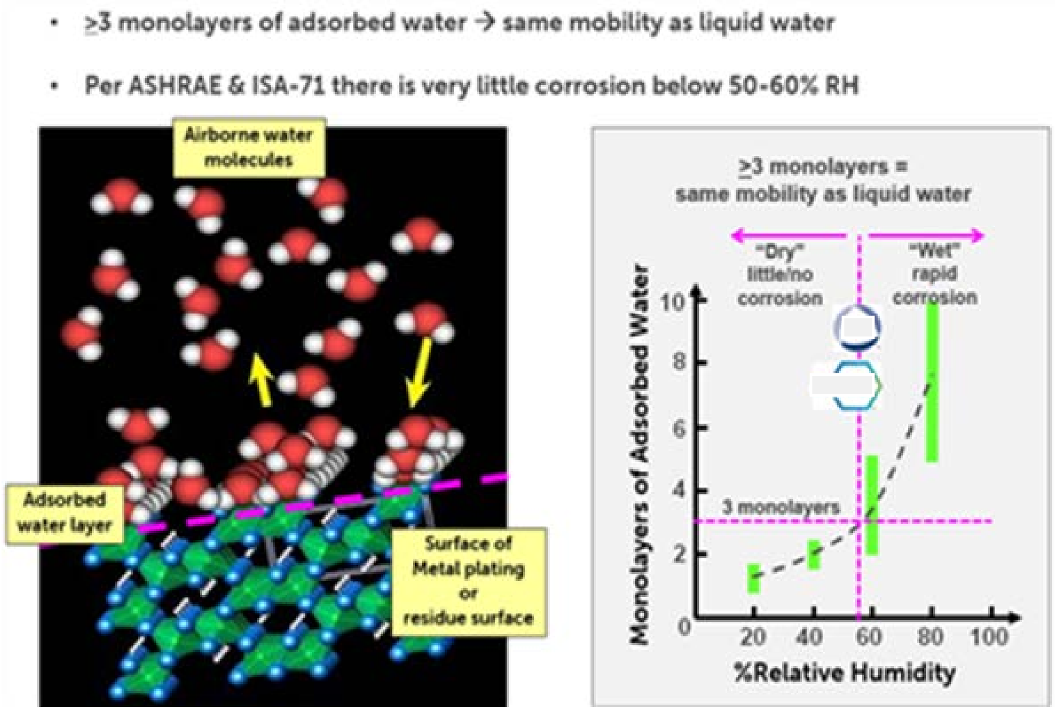
Anode: $M^0 \longrightarrow M^{n+} + ne^-$

Corrosion Rate Is Surface Mobility Limited:

$$Mobility = \mu = \frac{D}{K_B T} \propto \exp[a \bullet \%RH - \frac{Q}{K_B T}]$$

Ion Mobility

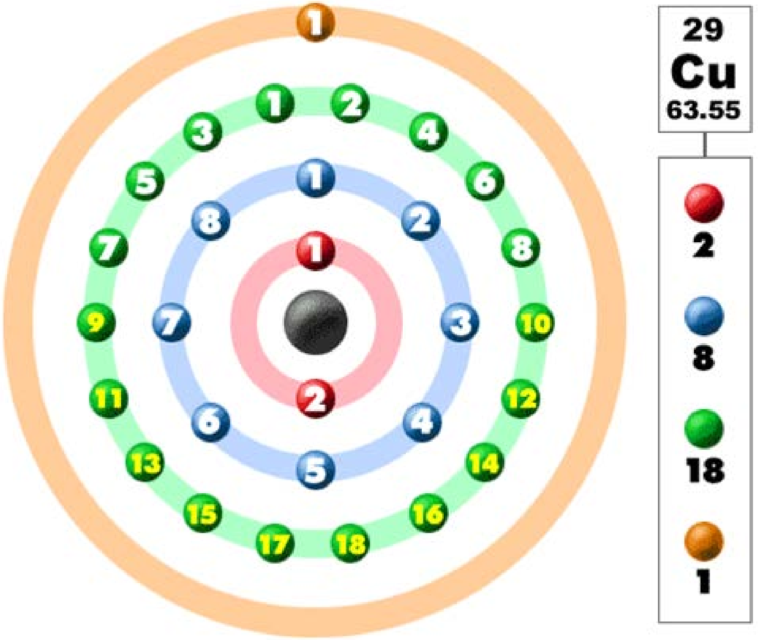
- Humid environments
  - Monolayers of moisture can form on the surface
- Water (moisture)
  - Dissolves cations and anions
  - Forms an electrolyte

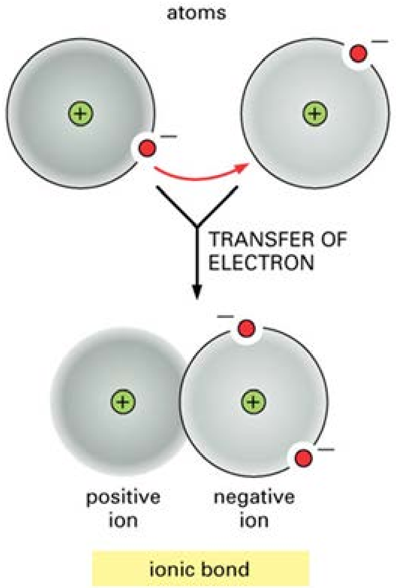


- ≥3 monolayers of adsorbed water → same mobility as liquid water
- Per ASHRAE & ISA-71 there is very little corrosion below 50-60% RH

Formation Mechanism

- Copper gives up electrons in outer shell
  - Thin pits within copper form on the metal surface
  - Metal migration propagates over time
  - Oxidizing copper cation enables pitting

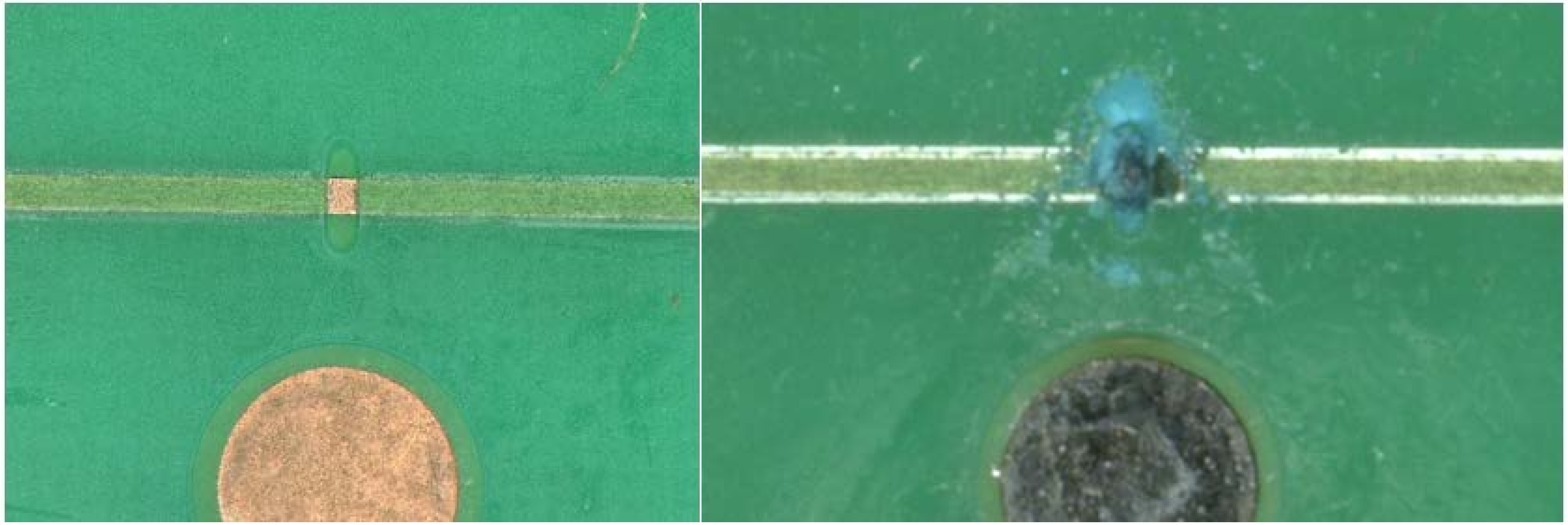




FORWARD THINKING
FOR TOMORROW'S TECHNOLOGY

Metal Cations form within the Electrolyte

- As corrosion progresses, the residue forms a circular morphology
- Corrosion grows outward
  - Galvanic coupling leads to the formation of small anodes
  - Anodes surround the nucleus



NO CLEAN SOLDERING FLUX

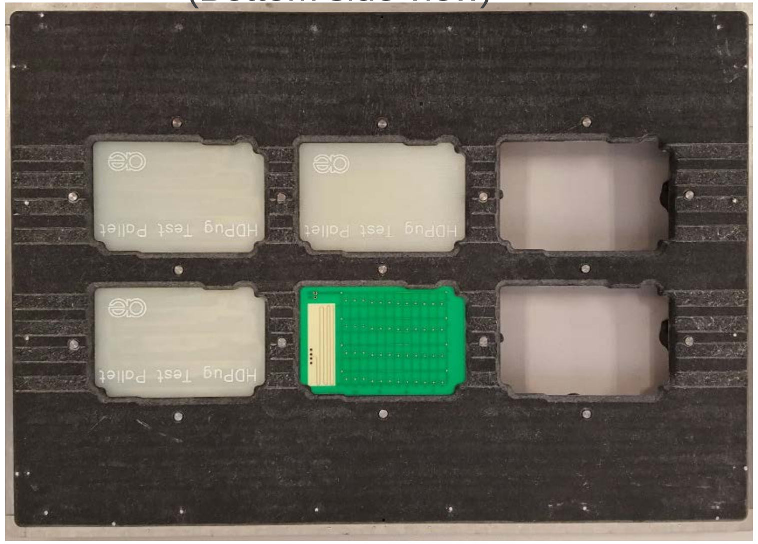
No Clean Solder Fluxes

- Important features of No-Clean fluxes
  - Residue free of ionic, corrosive or conductive properties
  - Usually not cleaned following the soldering process
- Flux activity of wave fluxes sold to industry are not created equal
  - Some more problematic than others
  - Residues can propagate corrosion when the right conditions are present
- Flux can be wicked into openings and flaws within solder mask
  - Can result in active flux residue that can cause corrosion to exposed metals

Wave Soldering / Selective Soldering

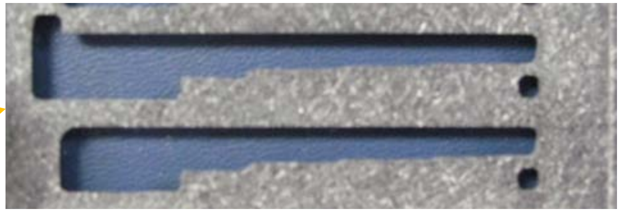
- Wave soldering process
  - Flux cleans components that are to be soldered
  - Flux removes oxide layers on metals to be joined
- Selective wave solder fixtures result in heavier flux residues around openings

Full open wave solder fixture
(Bottom side view)



Selective wave solder fixture
(Top side view)

Selective wave solder fixture
opening



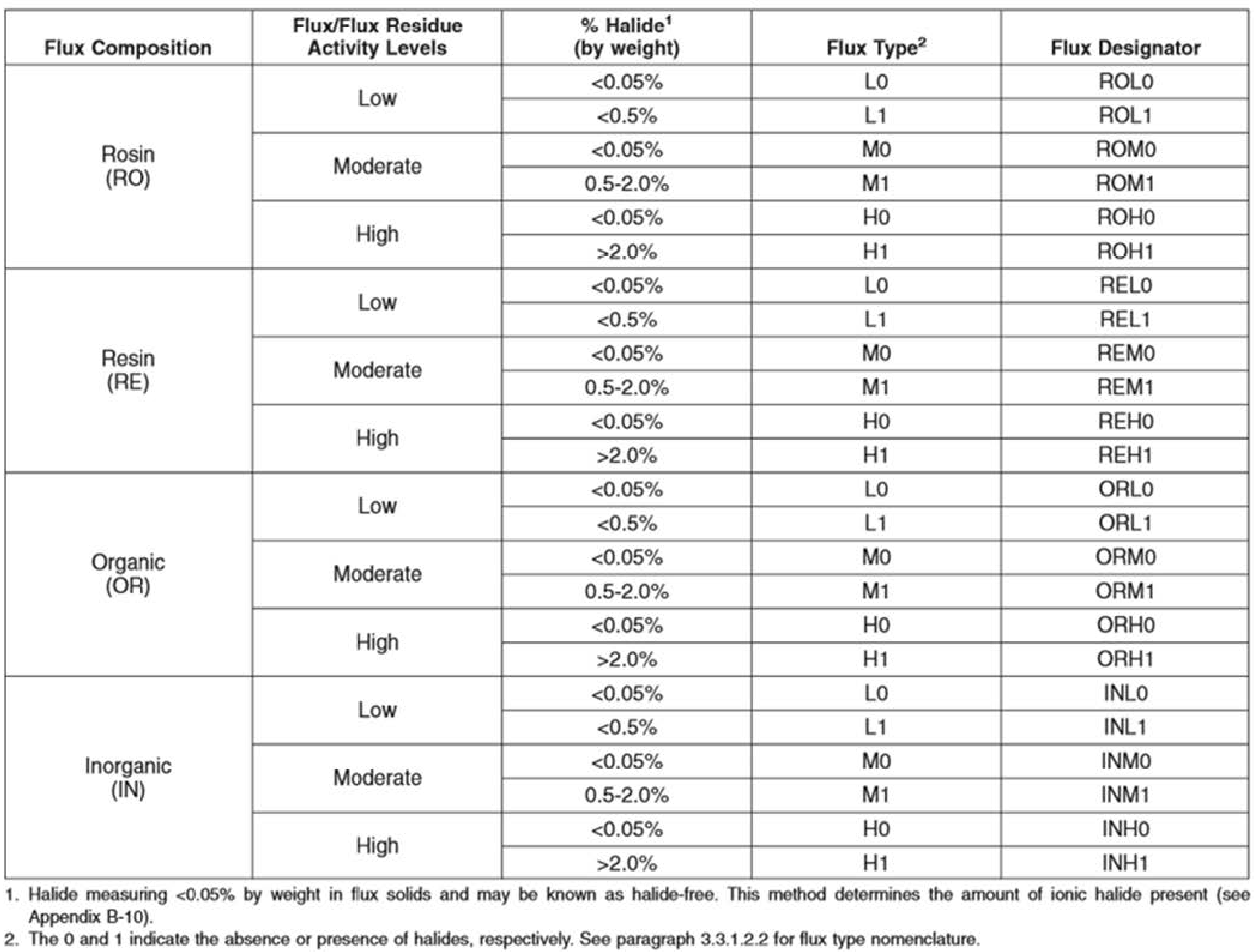
J-STD 004 REV B

- Defines the requirements for soldering fluxes
- Classified based on flux activation level
  - L = Low or no flux / flux residue activity
  - M = Moderate flux / flux activity
  - H = High flux / flux activity
- Classifications
  - Presence of halides (0 = NH; 1 = H)
  - Flux composition
  - Activity level

IPC Test Methods

- Designed to assess impact of flux on corrosion potential
  - Copper Mirror Test: IPC-TM-650, Test Method 2.3.32
  - Corrosion Test: IPC-TM-650, Test Method 2.6.15
  - Surface Insulation Resistance (SIR): IPC-TM-650, Test Methods 2.6.3.3 and 2.6.3.7
  - Electro Chemical Migration (ECM), IPC-TM-650, Test Method 2.6.14.1

Flux Classification



Flux Composition	Flux/Flux Residue Activity Levels	% Halide[1] (by weight)	Flux Type[2]	Flux Designator
Rosin (RO)	Low	<0.05%	L0	ROL0
		<0.5%	L1	ROL1
	Moderate	<0.05%	M0	ROM0
		0.5-2.0%	M1	ROM1
	High	<0.05%	H0	ROH0
		>2.0%	H1	ROH1
Resin (RE)	Low	<0.05%	L0	REL0
		<0.5%	L1	REL1
	Moderate	<0.05%	M0	REM0
		0.5-2.0%	M1	REM1
	High	<0.05%	H0	REH0
		>2.0%	H1	REH1
Organic (OR)	Low	<0.05%	L0	ORL0
		<0.5%	L1	ORL1
	Moderate	<0.05%	M0	ORM0
		0.5-2.0%	M1	ORM1
	High	<0.05%	H0	ORH0
		>2.0%	H1	ORH1
Inorganic (IN)	Low	<0.05%	L0	INL0
		<0.5%	L1	INL1
	Moderate	<0.05%	M0	INM0
		0.5-2.0%	M1	INM1
	High	<0.05%	H0	INH0
		>2.0%	H1	INH1

1. Halide measuring <0.05% by weight in flux solids and may be known as halide-free. This method determines the amount of ionic halide present (see Appendix B-10).
2. The 0 and 1 indicate the absence or presence of halides, respectively. See paragraph 3.3.1.2.2 for flux type nomenclature.

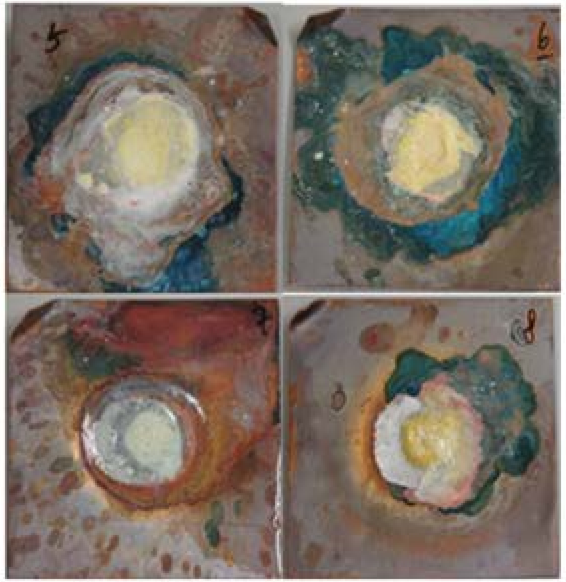
Flux Selection for this Study

- Three No-Clean fluxes
  - High Rosin
    - Alcohol based no-clean
    - Rosin carrier
    - ROL0
  - Low Activity
    - Alcohol based no-clean
    - ORL0
  - High Activity
    - Low solids no-clean
    - ORL0

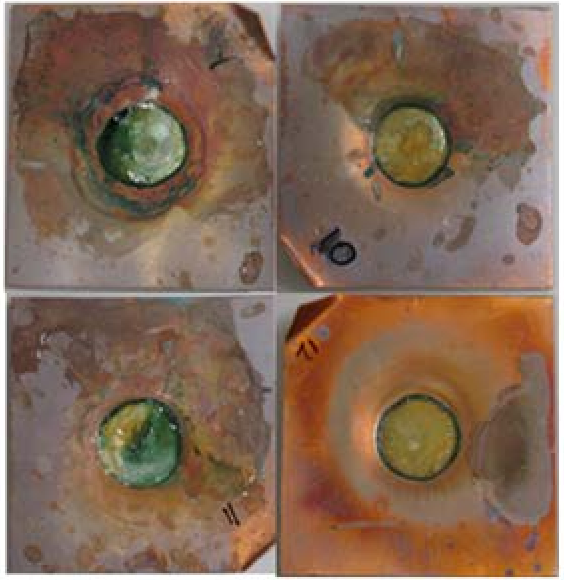
J-STD 004 Test Methods

Flux	Copper Mirror	Corrosion	SIR	ECM
Low Activity, Not Cleaned	Pass	Fail	Pass	Pass
High Activity, Not Cleaned	Pass	Fail	Pass	Pass
High Rosin, Not Cleaned	Pass	Fail	Pass	Pass

High Activity



Low Activity

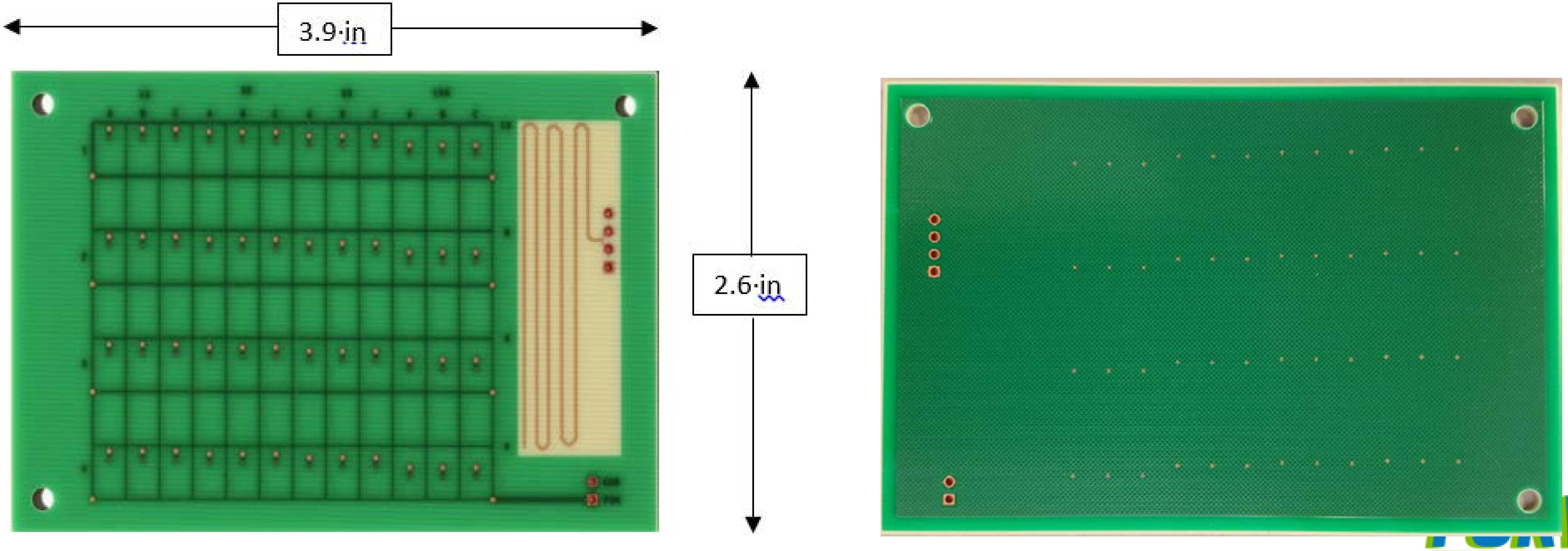


High Rosin

EXPERIMENTAL DESCRIPTION

Test Board

- Exposed copper features designed to study factors that contribute to corrosion
  - Corrosion sites have variable openings in solder mask

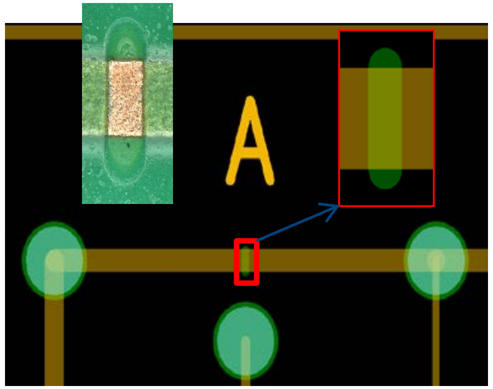


Factors and Levels Researched

- Ground Pad to Conductor Spacing
  - 15 mil
  - 30 mil
  - 50 mil
  - 100 mil
- Wave Solder Fixture
  - Selective Wave
  - Open Wave
- Solder Mask Defect Simulation Sites
  - A,B, & C solder mask openings
- Temperature / Humidity
  - 40°C
  - 85% RH
- Current
  - High
  - Low
- Three Fluxes Tested
  - Low Activity
  - High Activity
  - High Rosin
- Flux Levels Applied
  - Low/Normal
  - High
- Time
  - Approximately 4 weeks
- Voltage Bias
  - 0 volts
  - 3 volts
  - 10 volts
- Polarity
  - Positive
  - Negative

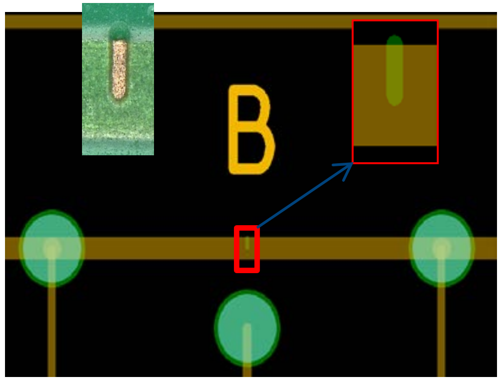
Test Board Corrosion Sites

- 56 Corrosion sites



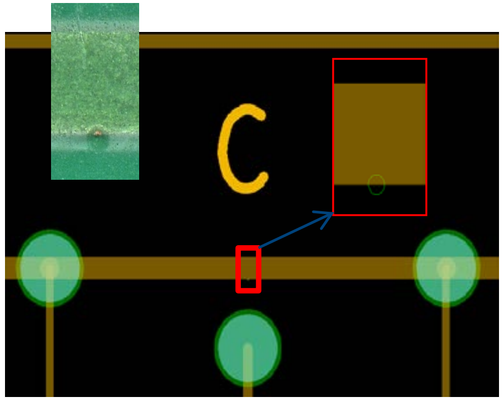
16 Large SM test opening:

A, D, G, J



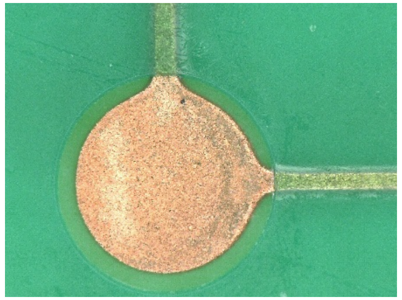
16 Medium SM opening:

B, E, H, K



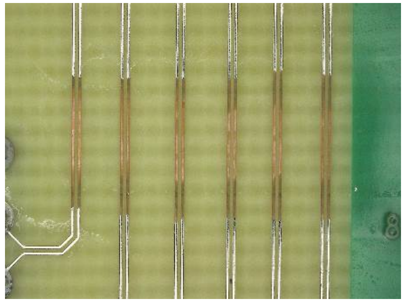
16 Small SM opening:

C, F, I, L



8 Power / Ground pad

(Typical ICT test pad size)

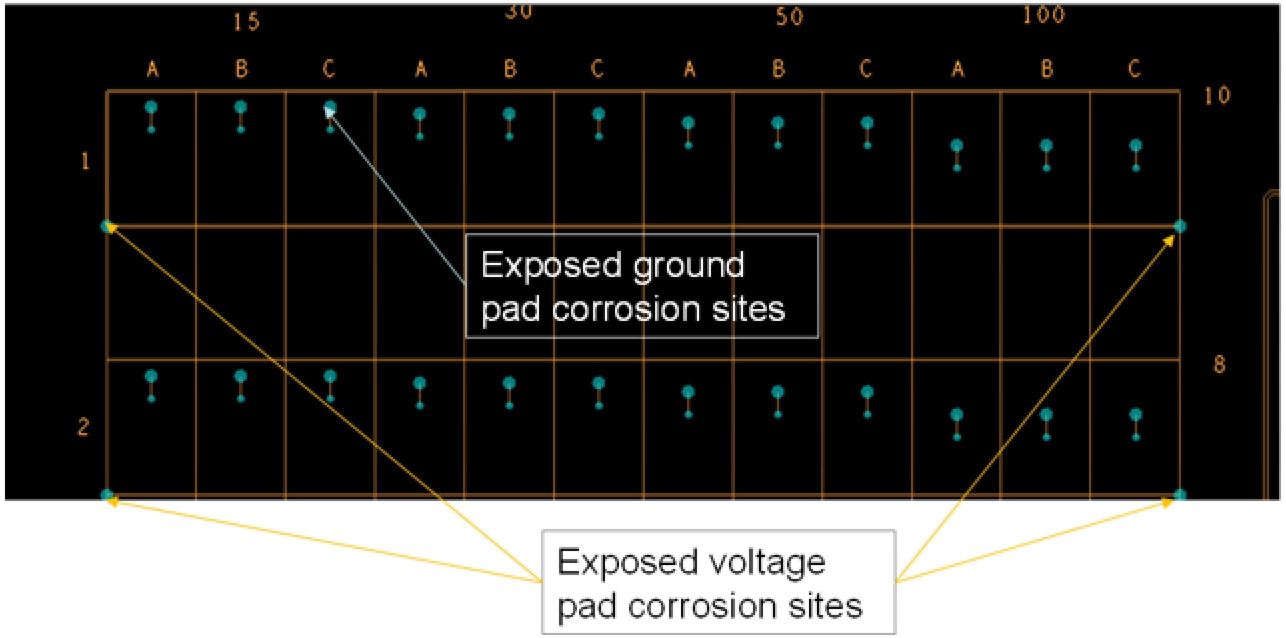


Resistance comb to measure flux residue conductivity

FORWARD THINKING
FOR TOMORROW'S TECHNOLOGY

Test Board Corrosion Features

- Ground pad to power trace spacing variation (15, 30, 50 & 100 mil)
- Corrosion site trace width variation (4, 6, 8 & 10 mil)
- Corrosion site solder mask opening variation (A, B, C)
- Ground pad. voltage pad, and via exposure
- Circuit line solder mask interface
- Flux residue resistance grid

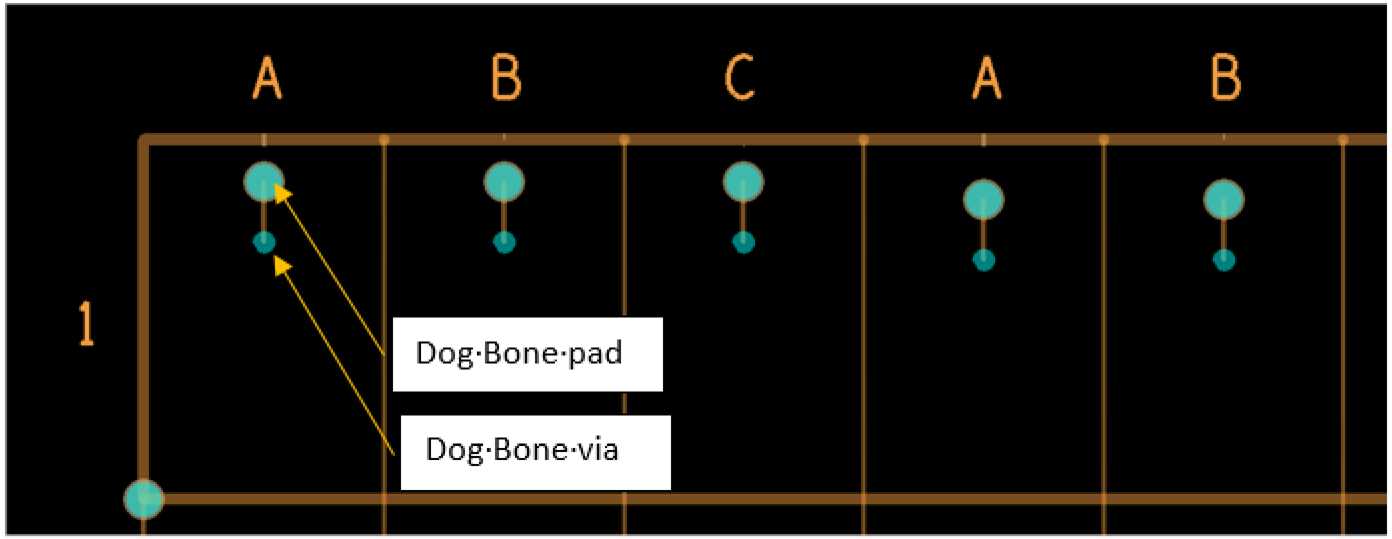


Exposed ground pad corrosion sites

Exposed voltage pad corrosion sites

Dog Bone via Ground Plane Connection

- Provide corrosion points at the
  - Copper plated via holes
  - Copper ground pads
  - Solder mask interfaces



Figure·11·-·Dog·Bone·Via·Ground·Plane·Connection

Ground Pad to Trace Spacing

- Designed to test corrosion as a function of
  - Power to ground pad distances

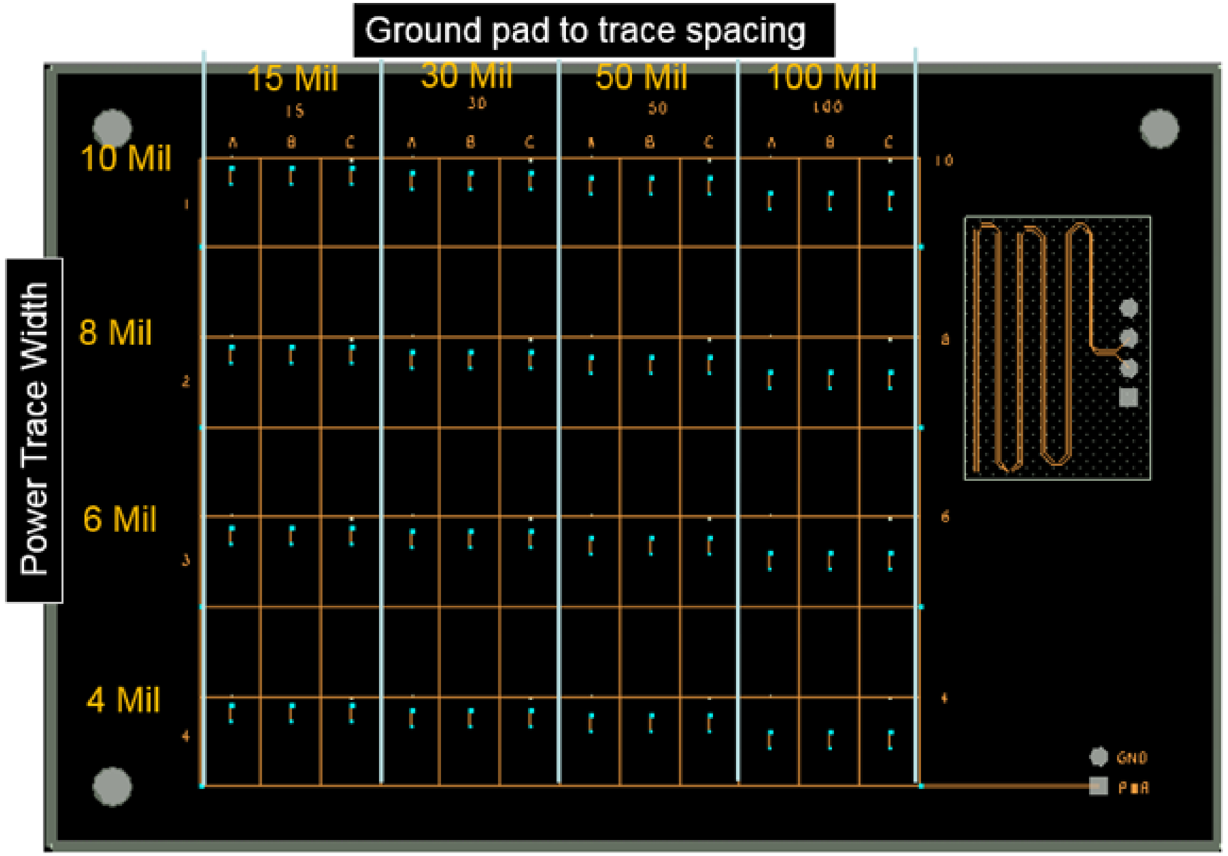
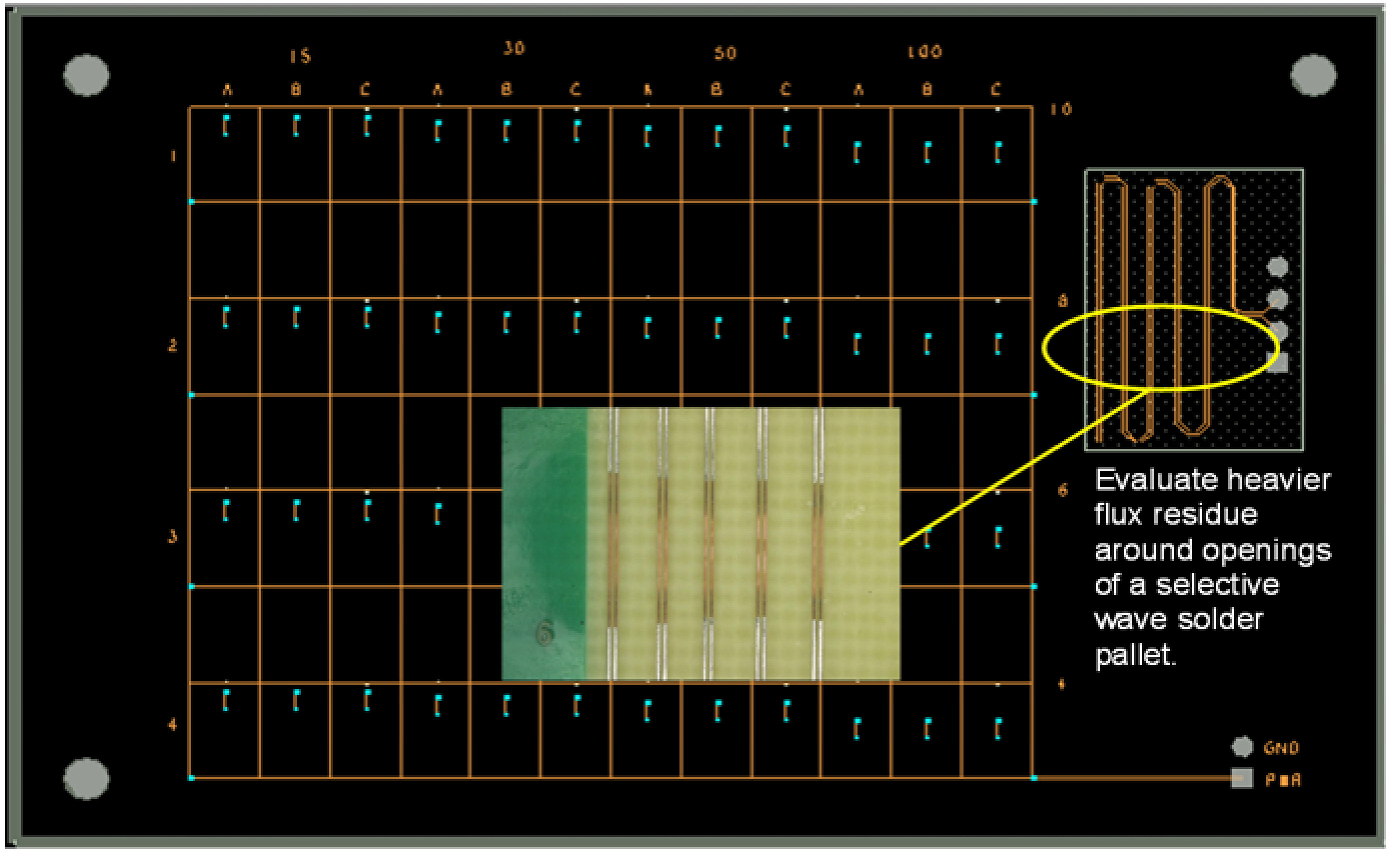


Figure 13 - Ground Pad to Trace Spacing

Resistance Comb

- Designed to test flux resistance



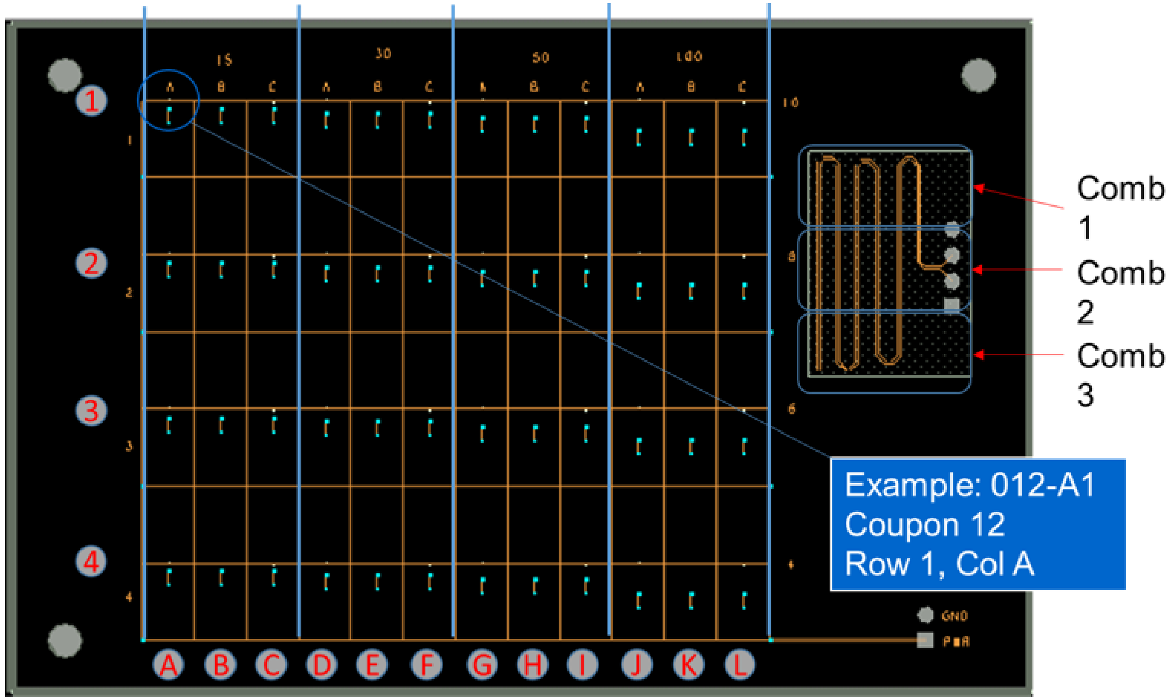
Evaluate heavier flux residue around openings of a selective wave solder pallet.

Figure 12 - Flux Residue Comb Pattern Test Site

DATA FINDINGS

Environmental Testing

- 48 solder mask opening test sites
  - Each site imaged before and after testing
  - Total data points captured: 5,780



Comb 1

Comb 2

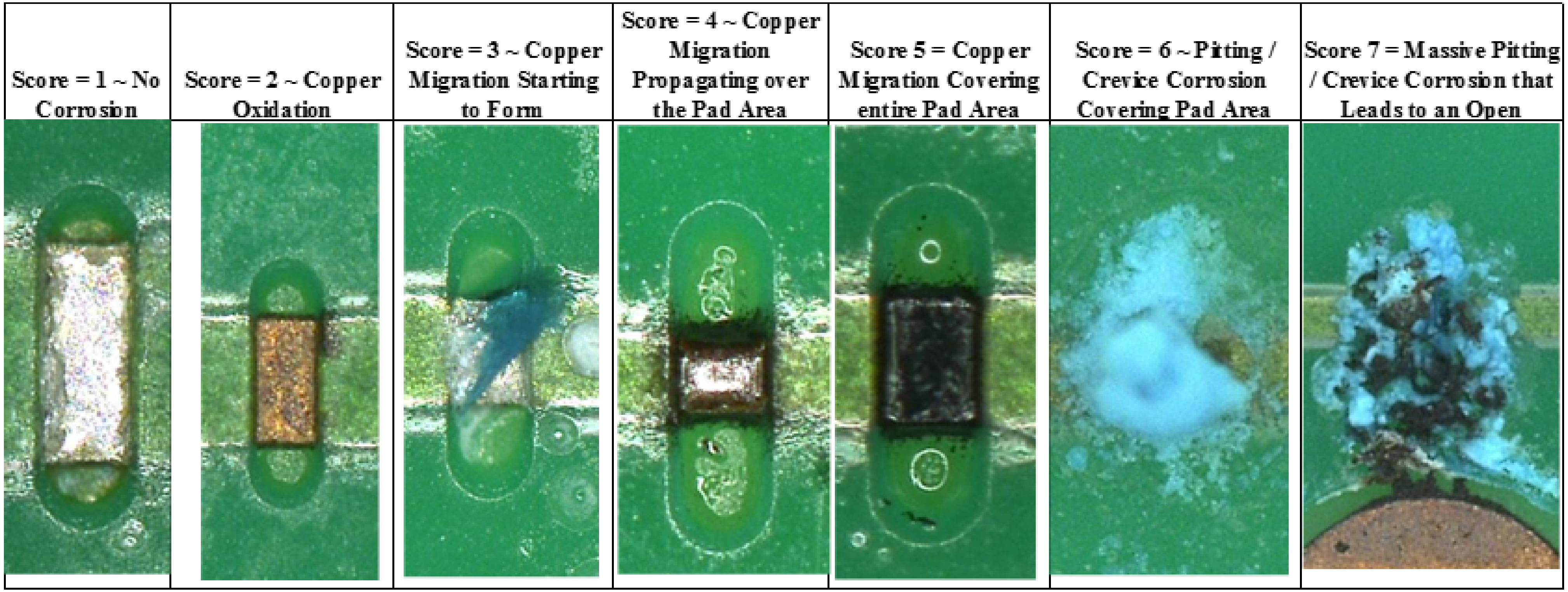
Comb 3

Example: 012-A1
Coupon 12
Row 1, Col A

Figure 16 - Test Sites Nomenclature

Grading Scale

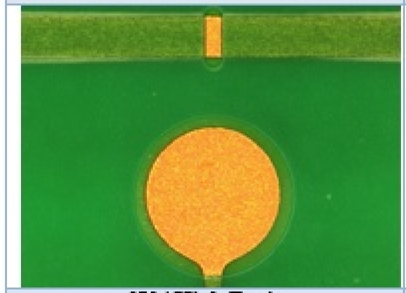
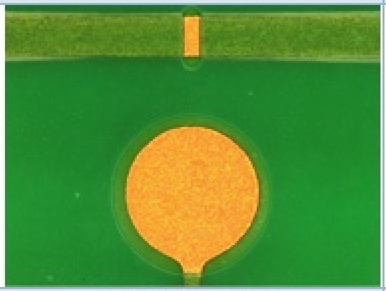
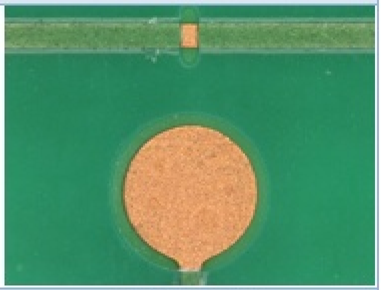
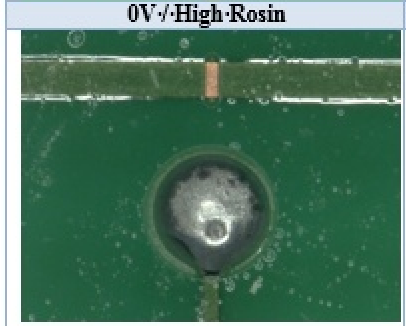
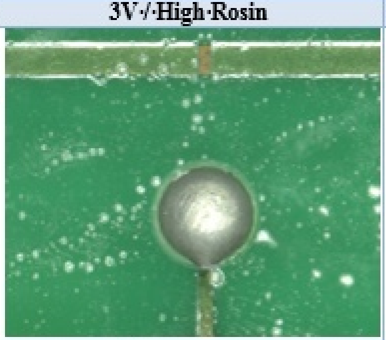
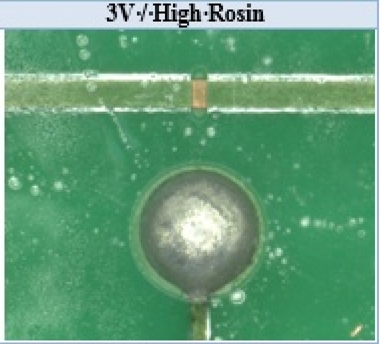
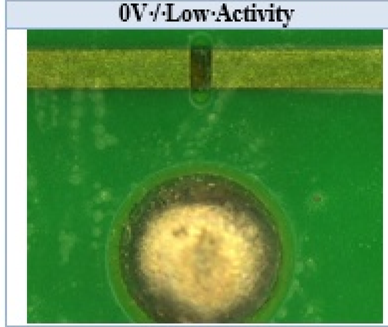
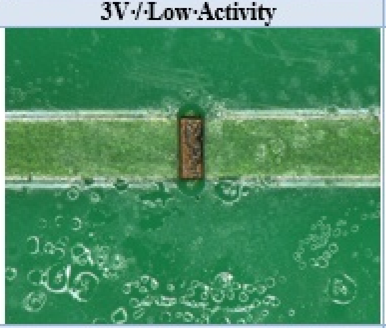
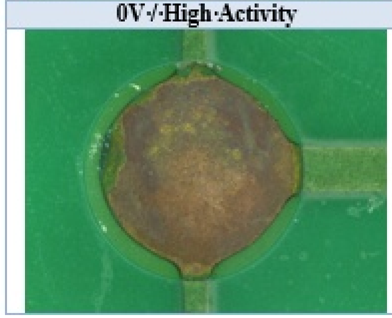
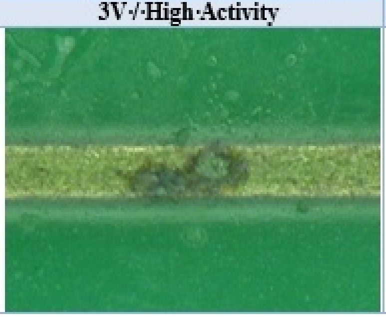
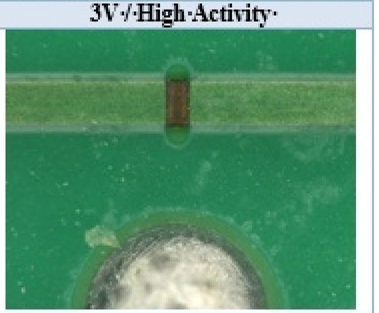
- Corrosion on boards was placed into a grading scale



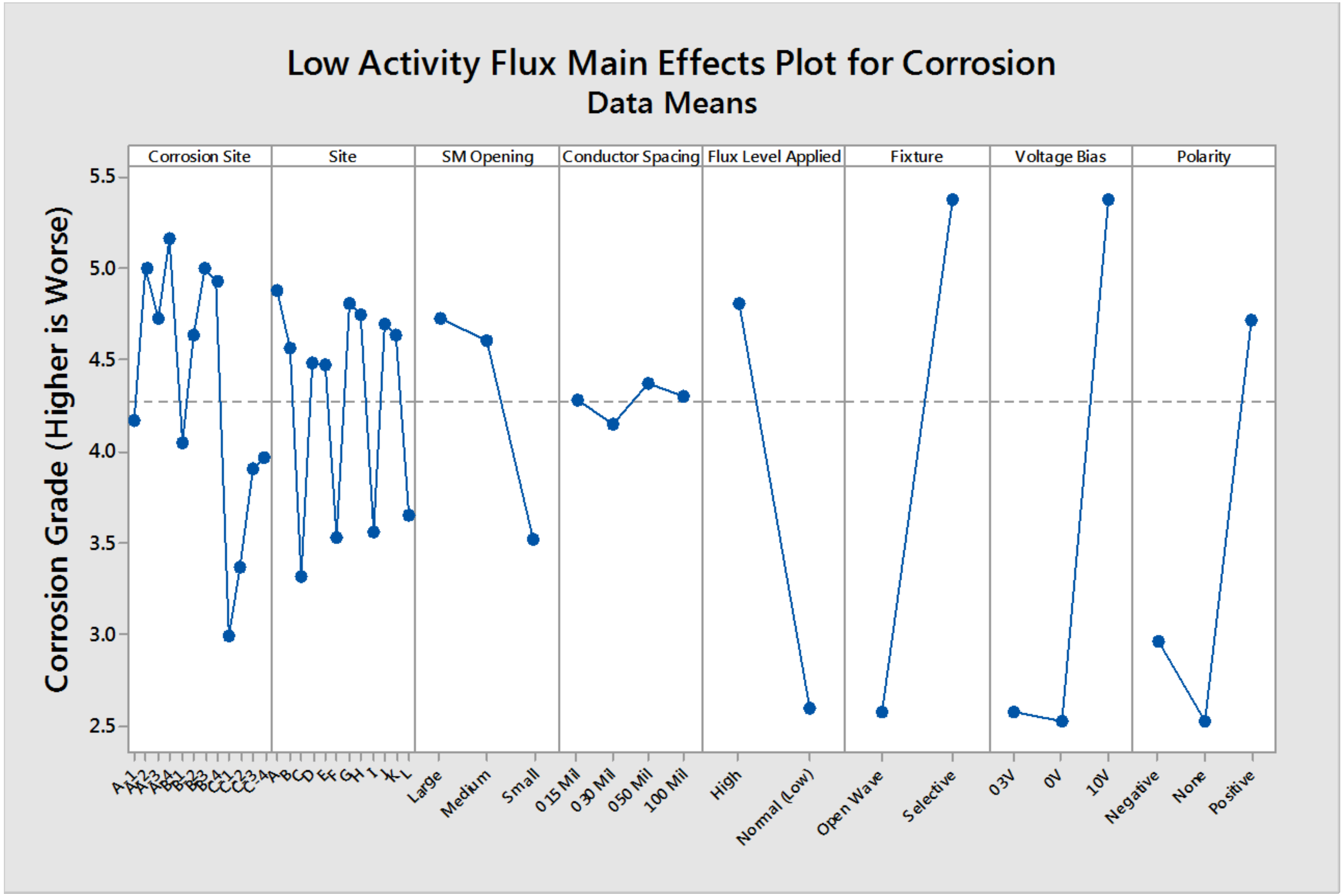
Score = 1 ~ No Corrosion	Score = 2 ~ Copper Oxidation	Score = 3 ~ Copper Migration Starting to Form	Score = 4 ~ Copper Migration Propagating over the Pad Area	Score 5 = Copper Migration Covering entire Pad Area	Score = 6 ~ Pitting / Crevice Corrosion Covering Pad Area	Score 7 = Massive Pitting / Crevice Corrosion that Leads to an Open

Figure 17 - Grading Scale Following Environmental Testing

Image Examples

No Bias	Negative Bias	Positive Bias
0V / No Flux	3V / No Flux	3V / No Flux
		
0V / High Rosin	3V / High Rosin	3V / High Rosin
		
0V / Low Activity	3V / Low Activity	3V / Low Activity
		
0V / High Activity	3V / High Activity	3V / High Activity
		

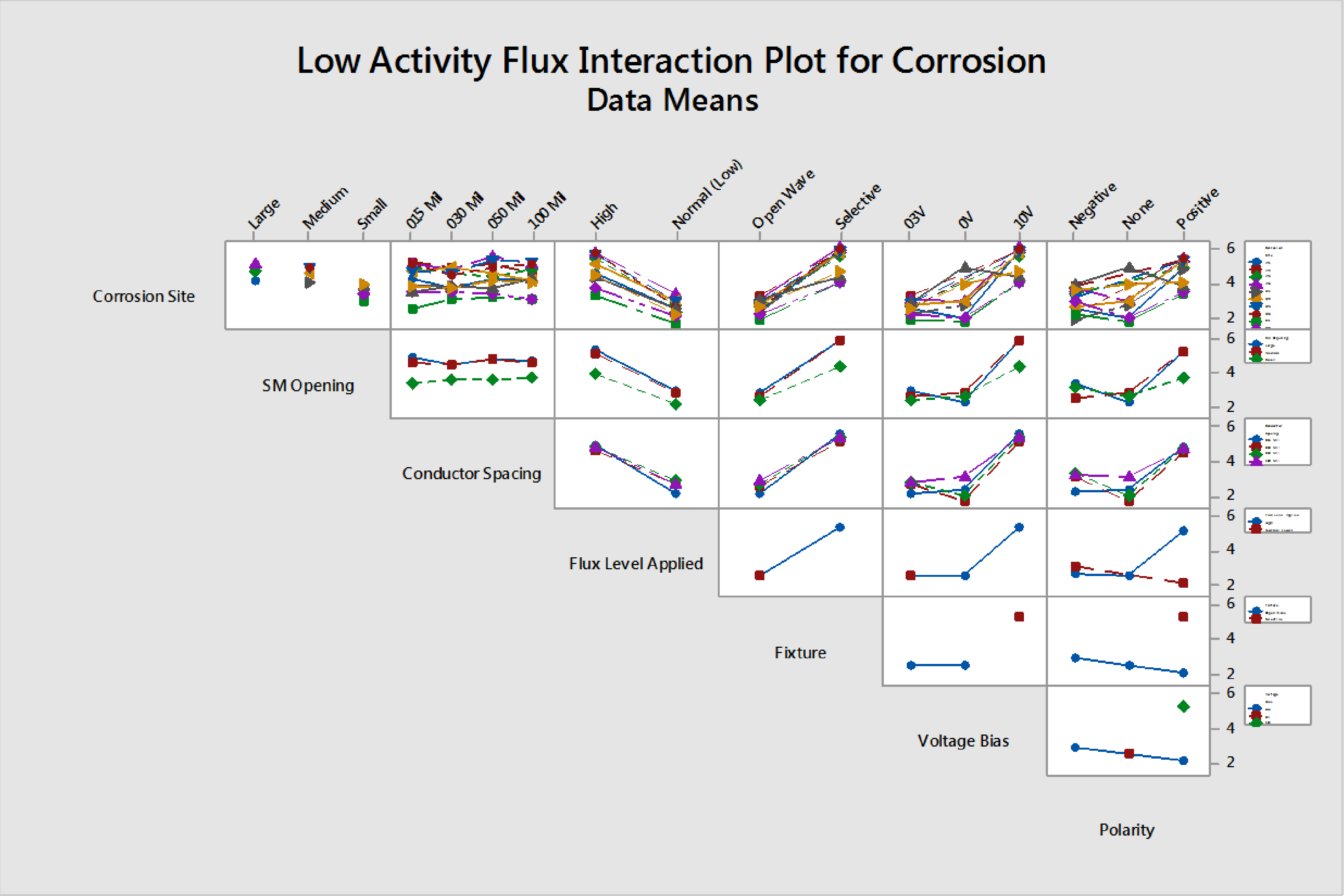
Low Activity Flux



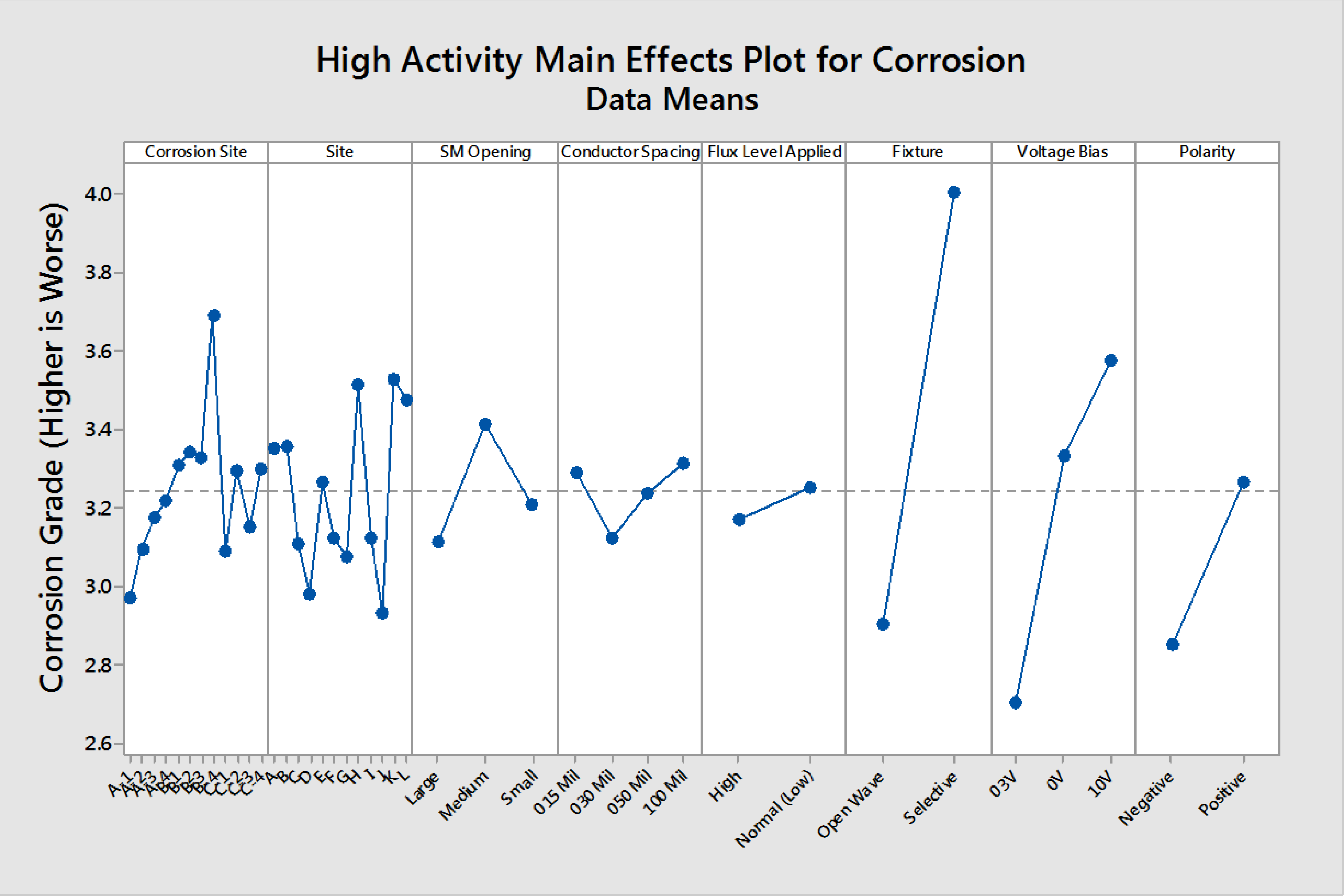
Low Activity Flux Main Effects Plot for Corrosion

Data Means

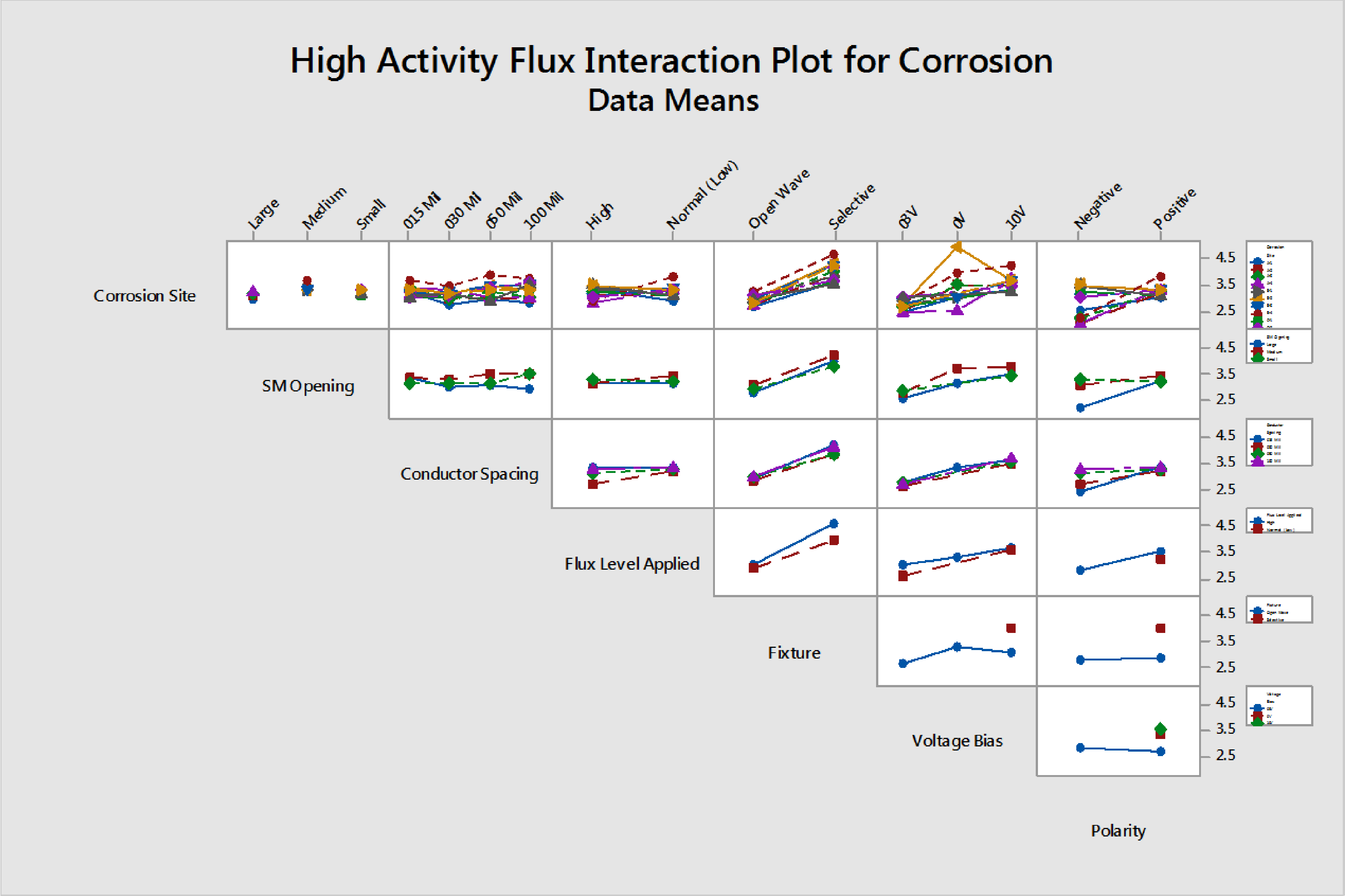
Low Activity Flux


Low Activity Flux Interaction Plot for Corrosion
Data Means

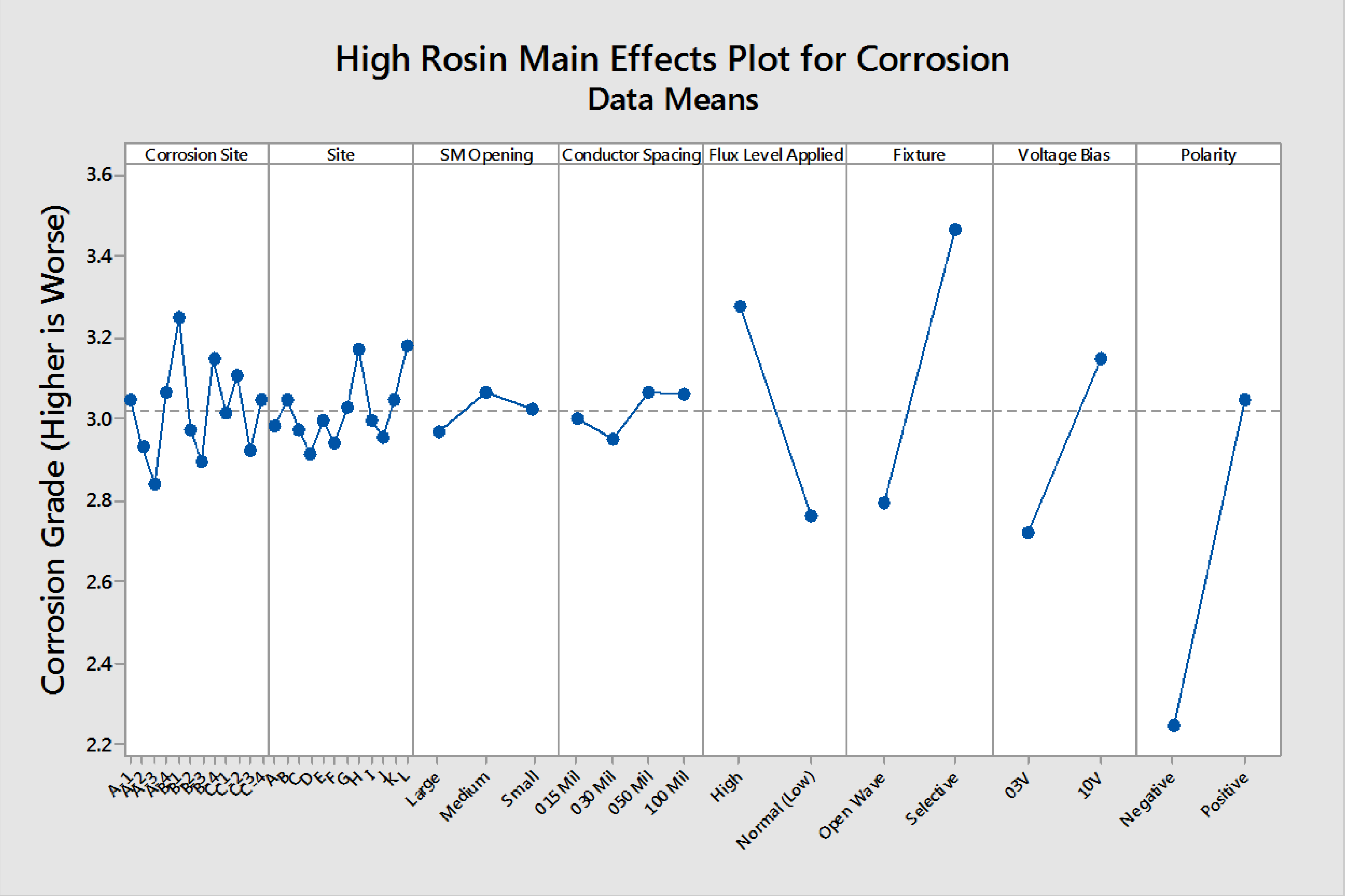
High Activity Flux



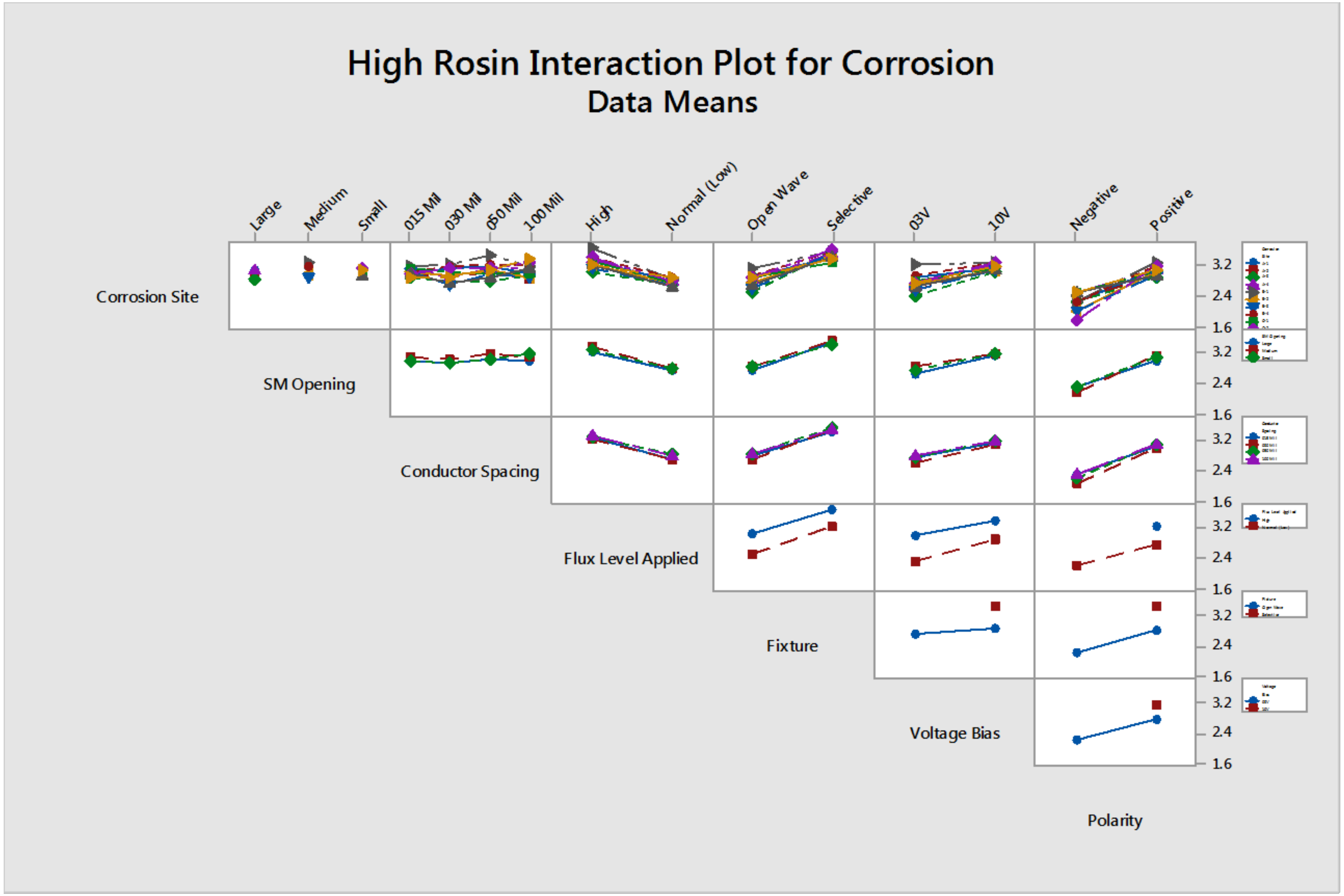
High Activity Flux



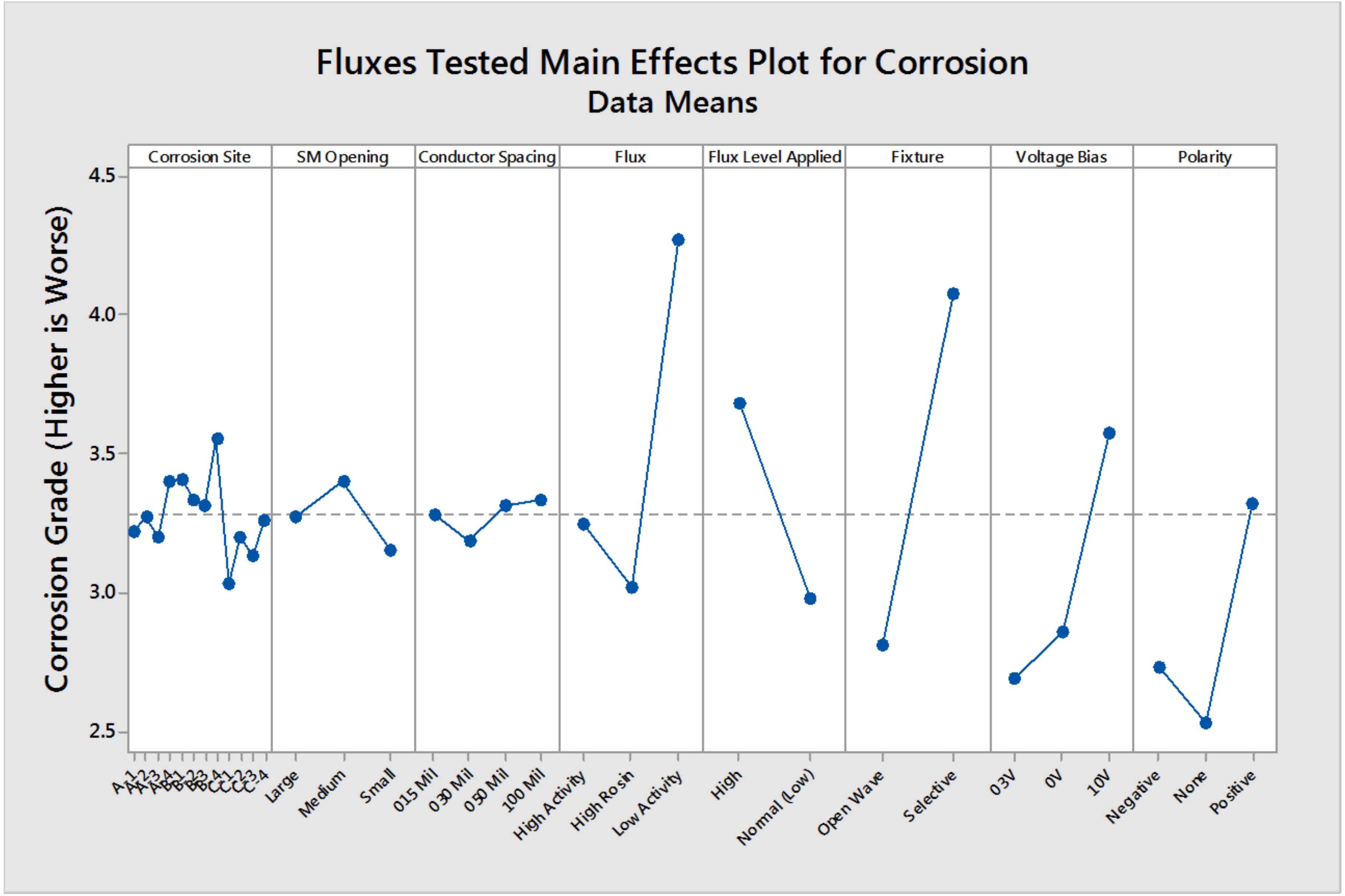
High Rosin Flux



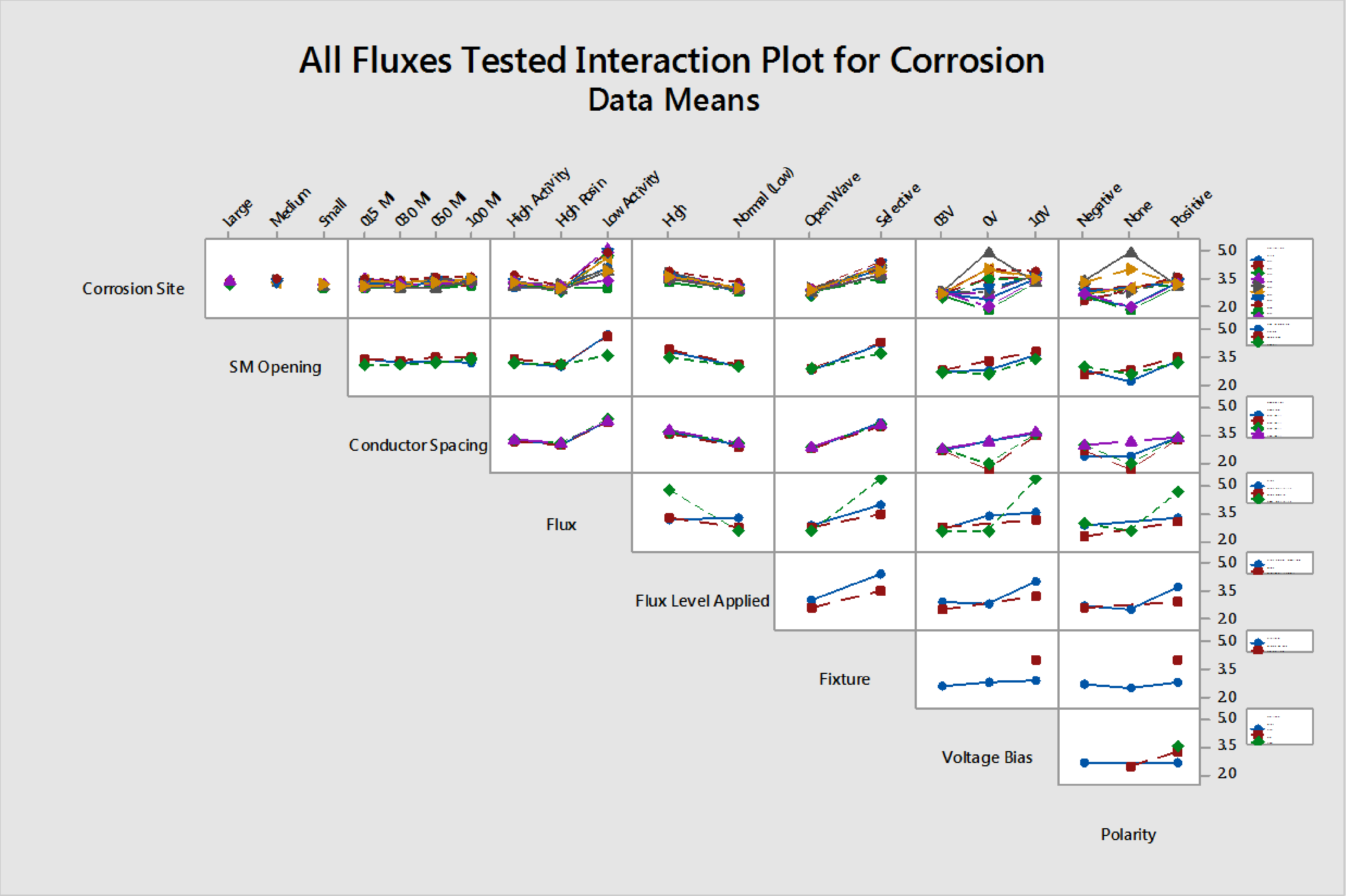
High Rosin Flux



Three Flux Comparisons



Three Flux Comparisons



CONCLUSIONS

Mixed Technology PCBs

- Quality of the solder mask construction, the assembly process and quality of design are critical
- Solder mask curing and application have been known to cause corrosion issues
- Scratches or pin holes in solder mask that expose copper traces can be problematic
- When the right conditions are present, pitting corrosion can occur

No Clean Flux

- Can find its way into solder mask imperfections
- Flux activators or other ionic substances
    - Can be present on the board
    - Can wick into solder mask gaps or flaws
- Harsh environmental exposure
    - Ions can be mobilized
    - Pitting corrosion can take place on exposed copper flaws

Pitting Corrosion

- Is primarily found on the circuit lines and solder connections that are connected to an applied voltage
- Voltage on cathode and anode must be balanced
  - Normally a low voltage on an unpowered board
  - Causes an accelerated rate of corrosion

Selective Soldering

- Showed a strong correlation with corrosion
  - Flux can be trapped around the selective fixture openings
  - Unreacted residues can be left on the board
    - Active ions
    - Remove copper oxides
    - Increase pitting corrosion reaction rates

Research Data Finds

- Pitting / Crevice factors highly correlated with corrosion
  - Selective soldering
    - Fluxes can penetrate beneath the fixture
    - Potentially shielded from heat activation
    - Flux trapped in crevices can create an active corrosion cell
  - High voltage
    - Corrosion propagation increased as voltage increased
  - Quantity of flux
    - Corrosion propagation increased as the level of flux on the board increased
    - No clean fluxes are not equal in risk levels
      - Activators used in flux formulation may be problematic
  - Harsh Environments
    - High humidity mobilizes ions
    - Atmospheric pollutants contribute to corrosion reaction

FOLLOW-ON RESEARCH

ECM Team

- Follow-on Plan
  - Complete the correlation research phase
  - Document findings into a report
  - Design a full variables research phase
    - State research hypothesis from research findings to date
    - Prove or disprove our research hypothesis
  - Present research findings to IPC for consideration in
    - Developing a new test method for pitting corrosion

Areas of Consideration for Phase III testing

- Are boards with OSP primary surface finish more susceptible to corrosion than say ENIG or Immersion Silver finished boards?
- Are some types of soldermask materials or chemistry more or less susceptible to pin-holes and/or allow more corrosion?
- Are there board design features that are more susceptible to corrosion (examples: soldermask-defined versus metal-defined SMD lands, acute trace angles on external layers, insufficient soldermask coverage beyond edges of traces, etc.)?
- What is the cause of the different forms of corrosion that occurred in the Correlation Phase of this research?
- What is the minimum voltage / polarity needed to propagate surface corrosion?
- Do larger copper surface defects take longer time to propagate surface corrosion?
- Why did all the no-clean fluxes tested fail IPC TM 2.6.15 Corrosion testing? Is this common for all no-clean fluxes?
- What are the physical properties that can create an electrolytic corrosion cell?
- Is it possible to correlate the conductivity of the no-clean residue on the surface with the corrosion potential?

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FORWARD THINKING
FOR TOMORROW'S TECHNOLOGY

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