Chemical Influences on the Reliability of Complex Assemblies

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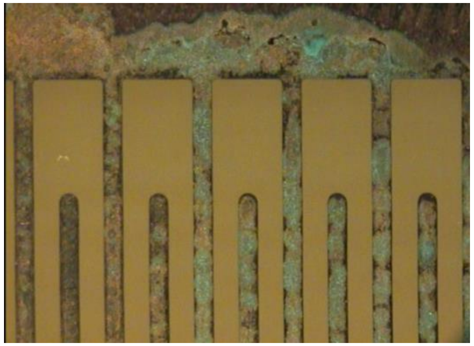
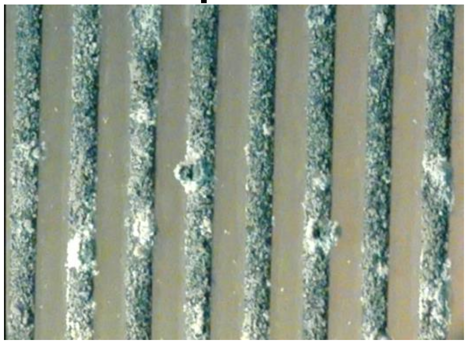
Reliability Failure Modes

Dendrites

Corrosion

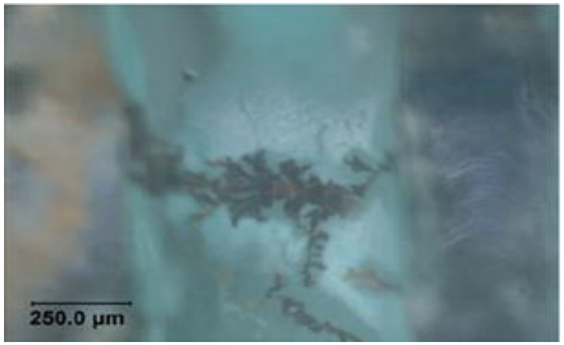


Deposits



But also

Conductive Anodic Filament (CAF), Creep Corrosion, Tin Whiskers, Black Pads,…



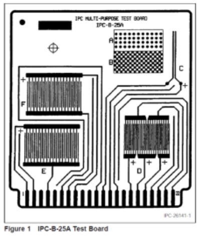
- ✓ Current leakage
- ✓ Shorts
- ✓ Circuit Damaging
- ✓ Insulating deposits (relays, contacts)
- ✓ Cosmetic aspects

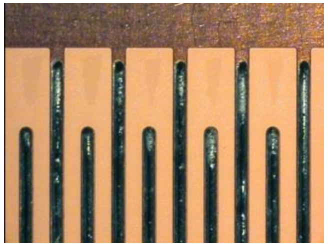
Reliability Tests

Outcome is flux classification

- Biased Tests – Applied V

Standard	Method	Temp °C / %RH	Test Voltage	Bias Voltage	Test Duration (hrs)	Test Board
IPC J-STD-004B	IPC TM650 2.6.3.3	85 / 85	-100	50	168	IPC B24
	IPC.TM650 2.6.3.7	40 / 90	12.5	12.5	72	IPC B24
	IPC ECM TM650 2.6.14.1	65 / 88.5	45 - 100	10	596	IPC B25A Pattern D
Bellcore GR-78-Core	SIR 13.1.3	35 / 85	100	45 - 50	96	IPC B25A Pattern D
	ECM 13.1.4	65 / 85	45 - 100	10	596	IPC B25A Pattern D
JIS Z 3197	SIR 8.5.3	(A) 40 / 90 (B) 85 / 85	100	0	168	IPC B25A Pattern D
	ECM 8.5.4	(A) 40 / 90 (B) 85 / 85	100	45 - 50	1000	IPC B25A Pattern D
BONO	Inventec: MO.SB.10029 Pc after 15 days	85 / 85	12	20	360	BONO Board





- Unbiased Tests
  - Quantitative Halides
  - Cu Mirror (as is)

**23C / 50% RH / 24h*

  - Cu Corrosion (residue)

**40C / 93% RH / 10d*

Confounded Testing outputs

- As defined by IPC J-STD-004B
  - **Cu Corrosion**: A chemical reaction between the copper, the solder, and the flux residues that occurs after soldering and during exposure to the above* environmental conditions

    ** §2.6.15C – 40C - 93%RH - 10d*

  - **Cu Mirror**: Corrosive properties of the flux in ambient conditions**

    *** §2.3.32D - 23C - 50%RH - 24h*

  - **SIR**: Electrical resistance of an insulating material btw conductors determined under a specified environment***

    **** §2.6.3.3 85C - 85%RH - 50V - 7d*
    **** §2.6.3.7 40C - 90%RH - 12.5V - ≥3d*

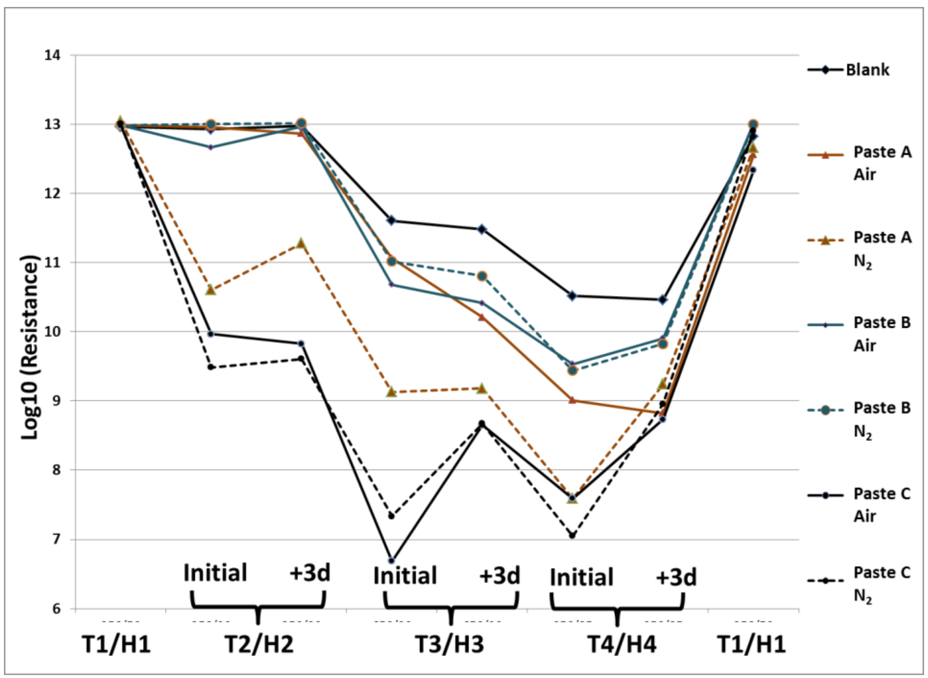
  - **ECM**: Growth of conductive metal filaments under the influence of a DC voltage bias by electrodeposition

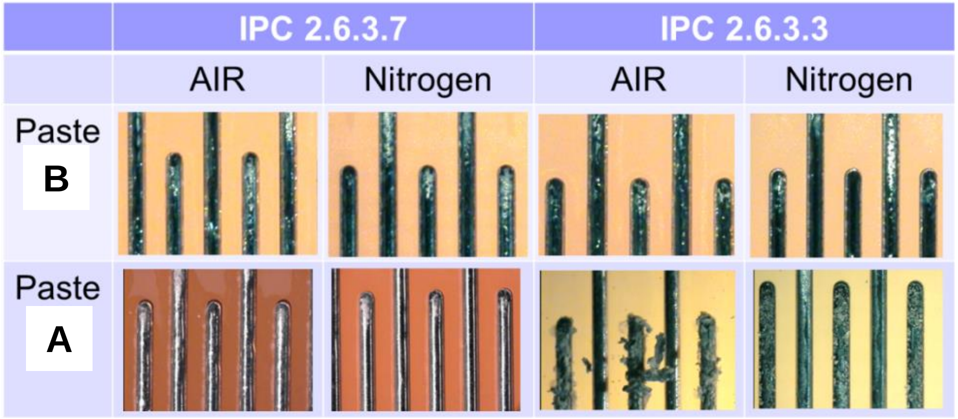
    §2.6.14.1 65C – 88.5%RH – 10V – 25d

ECM and SIR tests include Corrosion and ECM (filament growth) failures
R values affected by ions, residue hygroscopicity, dendritic growth, corrosion,…

Test variability

- Preparation procedure (reflow profile, atmosphere) and environmental conditions (T,RH,V) are critical parameters among others



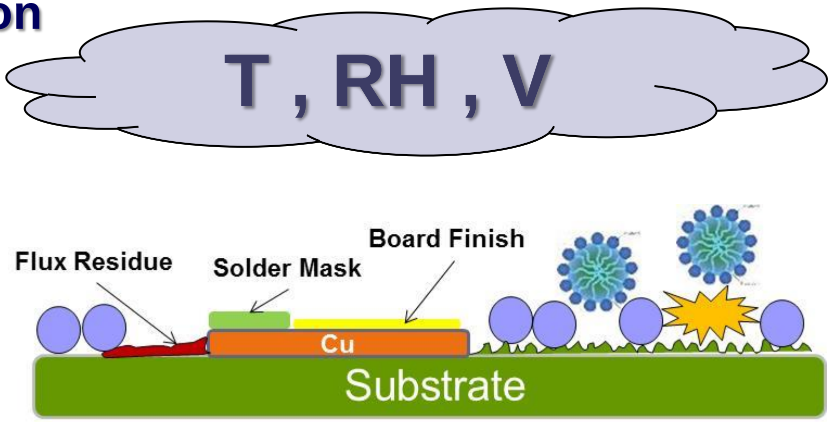


What is the predictive power of the test ?

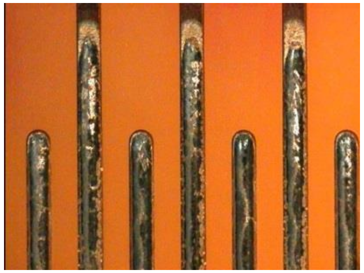
Reliability fundamentals

- Failures result from the interaction of <u>post-reflow residues</u> with board components under environmental stress

Electrochemical Migration



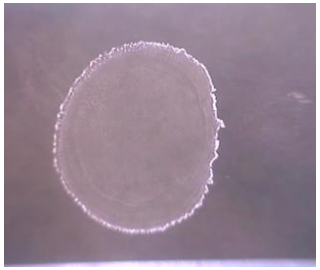
Corrosion



Precipitation

Residue composition and reactivity depend on reflow conditions (reflow profile, atmosphere)

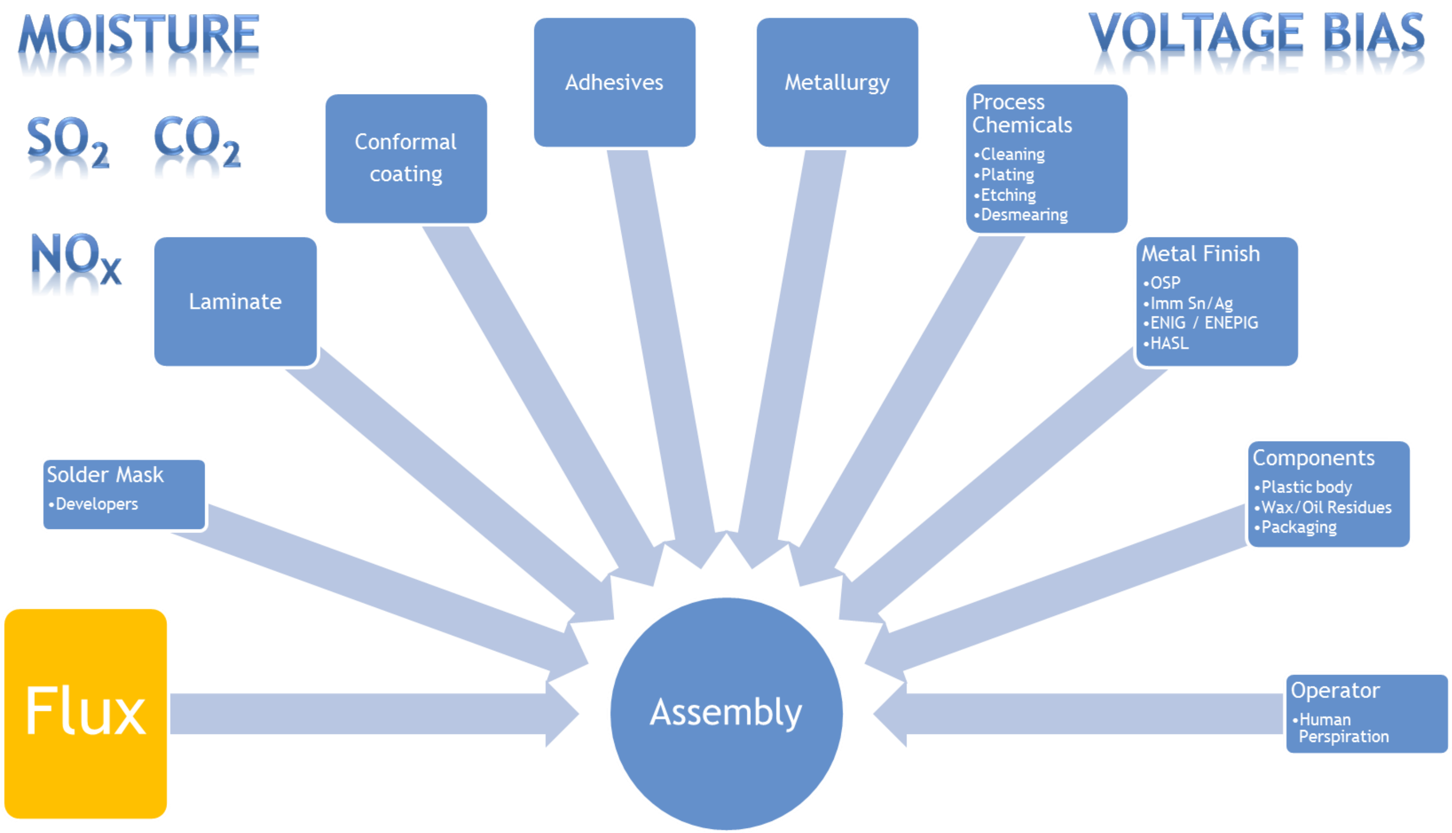
Etching



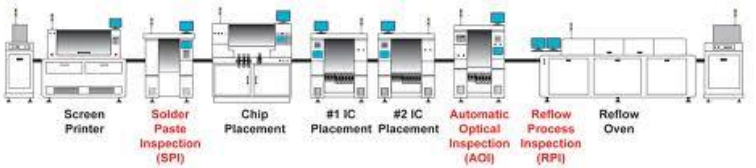
Electrochemical phenomena are preponderant in Electronic Assembly

Reliability fundamentals

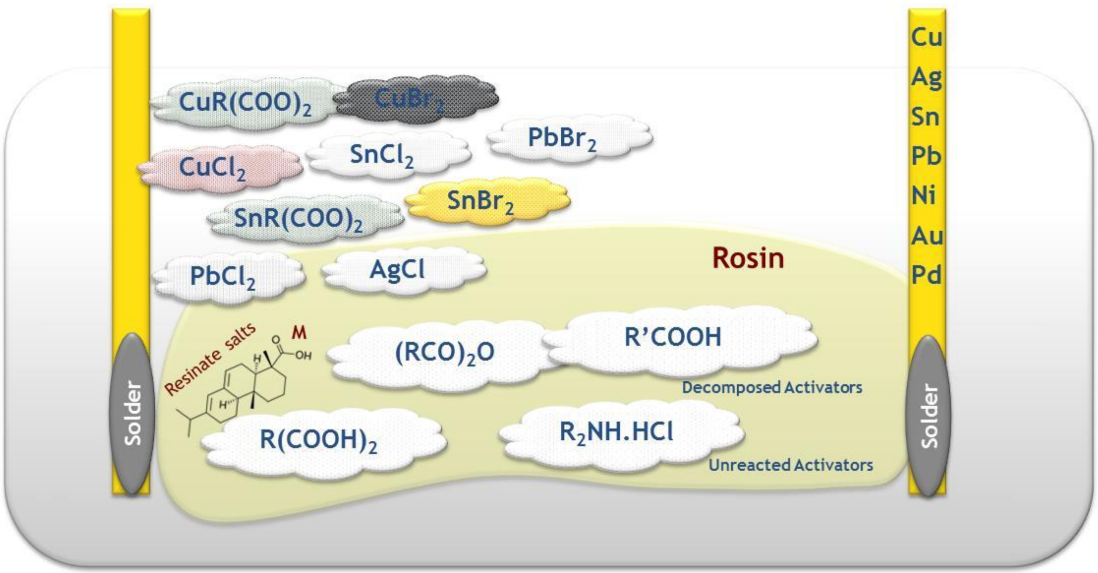
- Chemical Complexity of a Printed Circuit Board coupled with a large set of environmental conditions



Reliability fundamentals



1. Process residues formation



Compound	Water solubility (g/100cc)	Color
$CuCl_2$	75.7	Brown
CuCl	0.006	Green
$CuBr_2$	55.7	Black
CuBr	Very Slightly	White
$SnCl_2$	83.9	White
$SnBr_2$	85.2	Pale Yellow
$PbCl_2$	1	White
$PbBr_2$	0.8	White
$CuOH_2$ / $CuCO_3$	Insoluble	Green

- ✓ Unconsumed activators
- ✓ Fluxing reaction products
- ✓ Interactions by-products

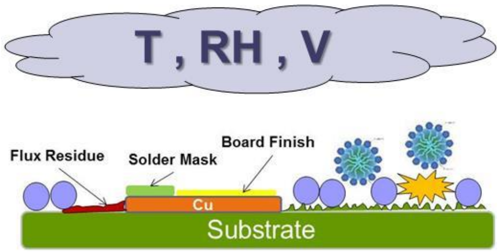
$Cu_2O + 2HCl \rightarrow CuCl_2 + Cu + H_2O$

$Cu_2O + R(COOH)_2 \rightarrow CuR(COO)_2 + Cu + H_2O$

$R(COOH)_2 \rightarrow (RCO)_2 + H_2O$, 2R'COOH

Rosin → Resinate salts, White Residues (oxidized)

Reliability fundamentals



2. Residues reaction under Environmental stress
   - Moisture Absorption
   - Hydrolysis
   - Carbonation

$CuBr_2 + 4H_2O \rightarrow CuBr_2.4H_2O$

$SnCl_2 + 2H_2O \rightarrow Sn(OH)_2 + 2HCl$

$PbCl_2 + CO_2 + H_2O \rightarrow PbCO_3 + 2HCl$

3. Corrosion of Metallic compounds
   - Oxidation
   - Complexation

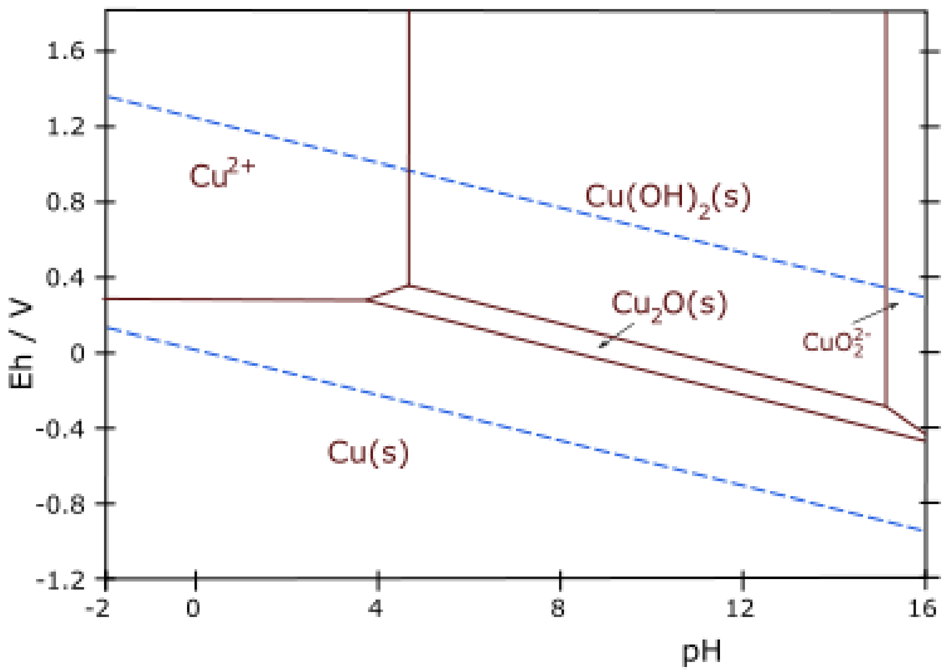
$Cu \rightarrow Cu^+ + e^-$ [E_0=0.52V]

$Cu^+ + Cl^- \rightarrow CuCl$ [pKs=6.7]

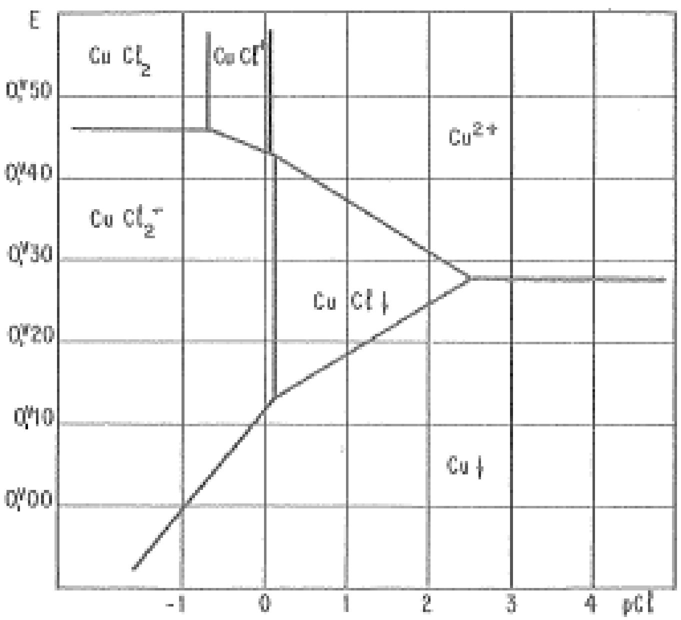
$Cu + Cl^- \rightarrow CuCl + e^-$ [E_0=0.14V]

Strong Cu complexes catalyze
Metal Oxidation

Reliability Fundamentals



Cu Pourbaix diagram at 298K
10^{-3}M Cu



Impact of Cl^- species on Cu Redox Potentials 10^{-2}M Cu^{2+}

Acidic condition favor Cu Corrosion vs passivation

Strong Cu complexation catalyzes Cu corrosion

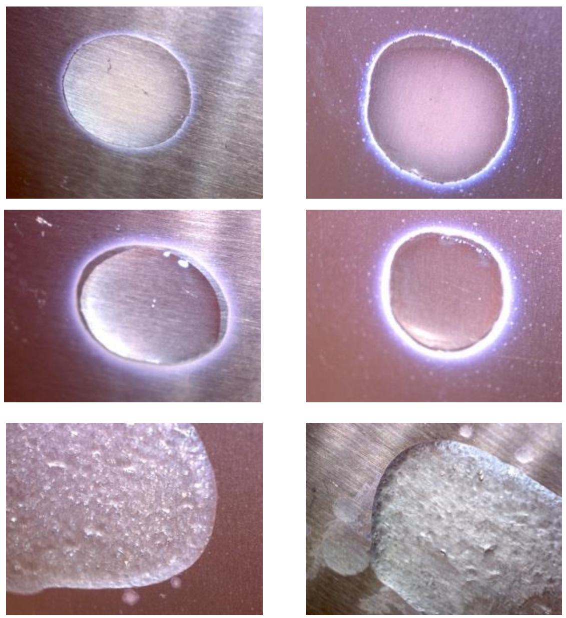
Corrosion Example - Halides

- Reactivity On Cu – Unbiased test

HCl

HBr

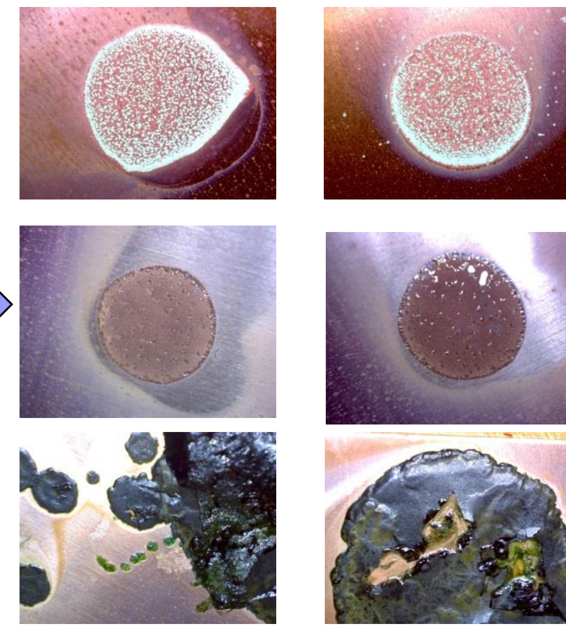
C888
Reflowed



2.5h @ 40C / 93% RH

X=Cl, Br

6h @ 40C / 93% RH



Light Brown Black	Green	Green	White/Green
$CuCl_2$ $CuBr_2$	$CuCl_2.2H_2O$ $CuBr_2.4H_2O$	$Cu(OH)_2 + 2HCl$ $Cu(OH)_2 + 2HBr$	$Cu + Cl^- \rightarrow CuCl$ $Cu + Br^- \rightarrow CuBr$

Annales de Chimie et de Physique (1903) p262

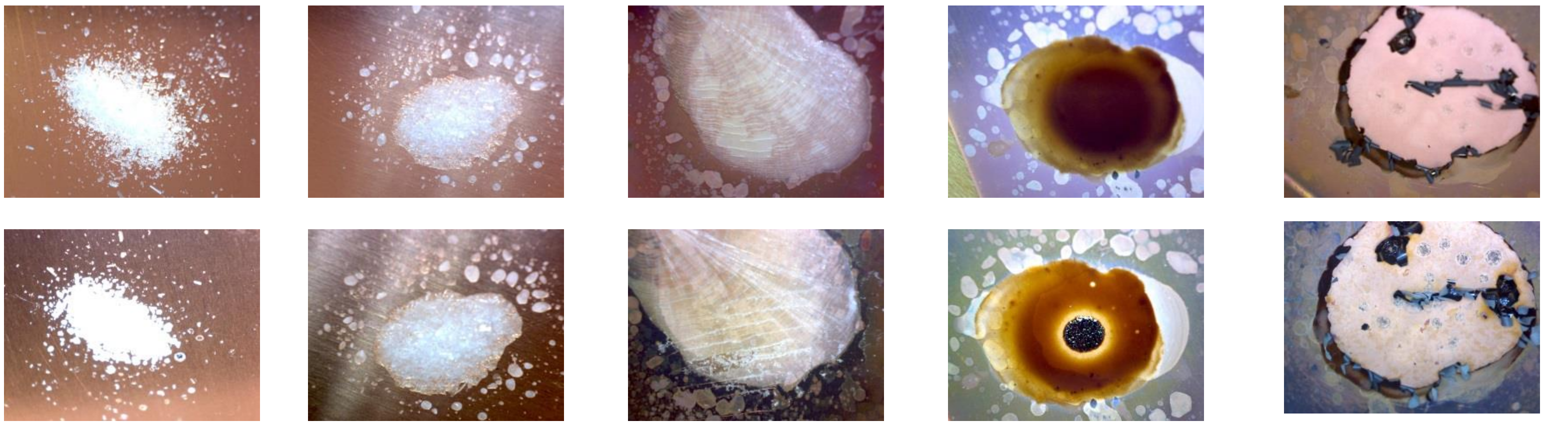
Corrosion Example - Halogens

C180 on Cu

As is | Soak 120C | Reflowed 5s | Reflowed 15s | Reflowed 25s

T=0

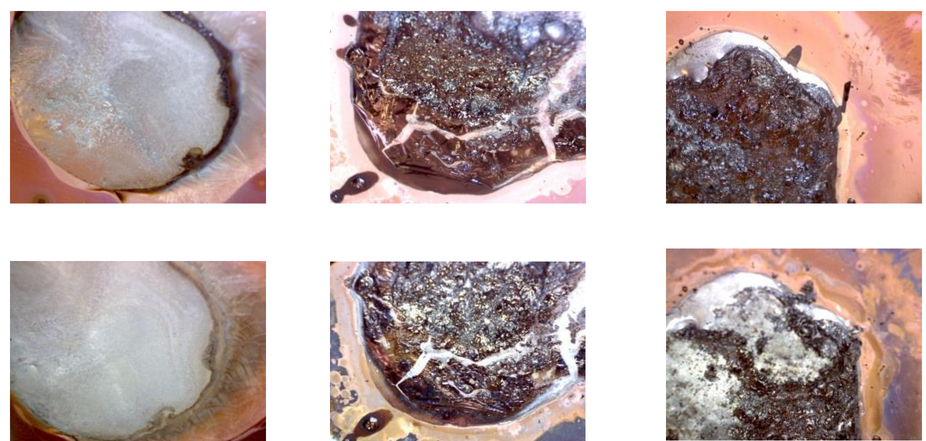
T=5d 30C/90%RH



C180 on Cu / Solder

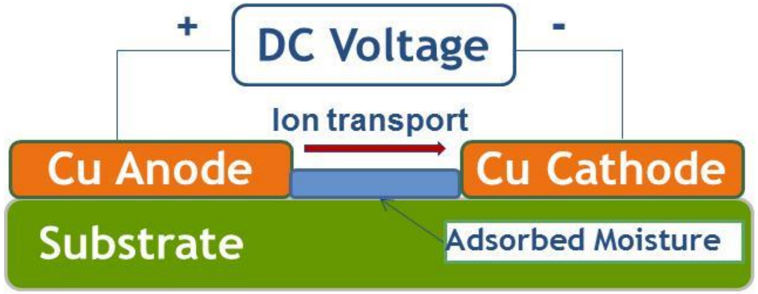
T=0

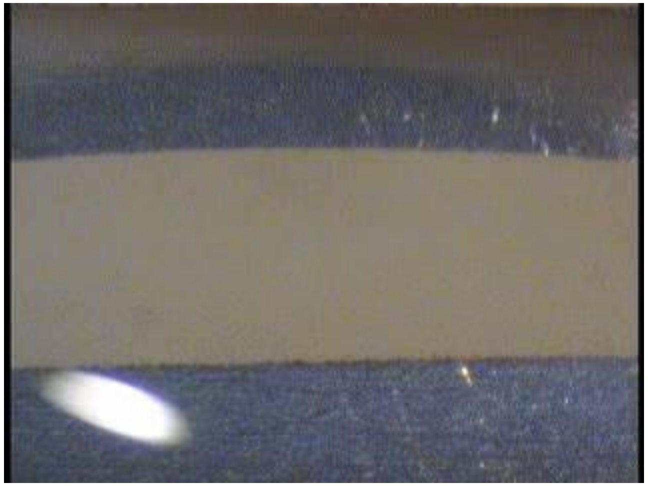
T=5d 30C/90%RH



Reliability Fundamentals
Electrochemical Migration

- Electrochemical process where metal ions move between adjacent metal conductors through an electrolyte solution under an applied electric field.

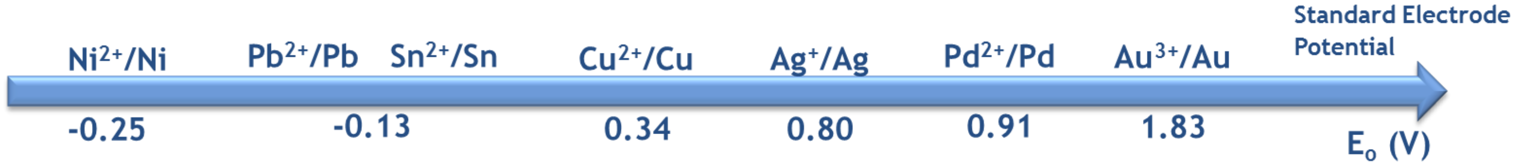




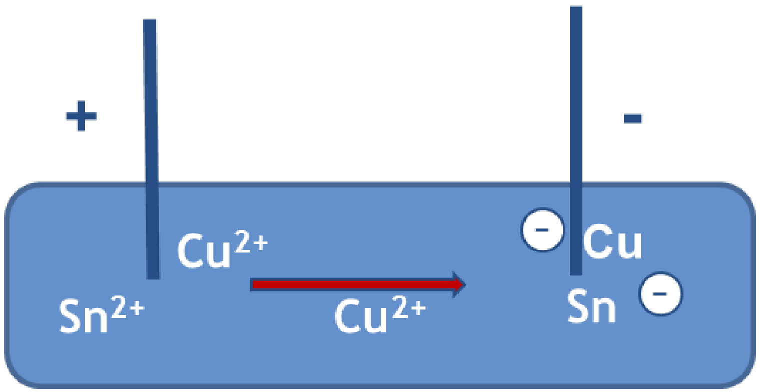
- 3 Basic ingredients
  - Moisture, Voltage bias, Ions
- 5 Sequential steps
  - Path formation → Electrodissolution → Ion transport → Electrodeposition → Dendritic growth

Reliability Fundamentals
Electrochemical Migration

- Redox potentials are not a good predictor for dendritic growth
  - Pb vs Sn ability to form dendrites, Ag dendrites easy formation



- Three concurrent mechanisms needed to grow a dendrite
  - Strongly influenced by residue chemistry

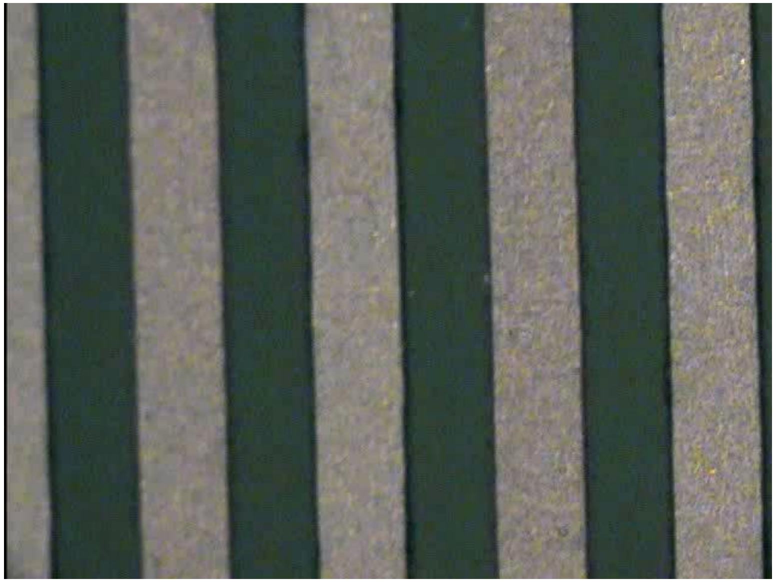


1. Formation of conductive water films at the surface of the epoxy laminate
2. Metal corrosion
3. Stabilization of charged metal complexes between the polarized electrodes

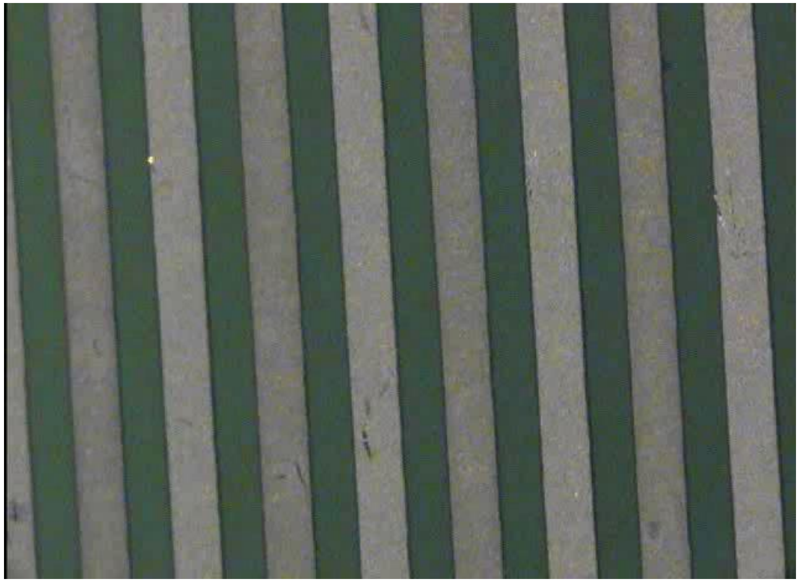
ECM Example

- Customized ECM Test [IPC B25 (Cu-FR4) / 38V/mm]

DI Water



0.25M NaOH Solution



$Cu \rightarrow Cu^{2+} + 2e^{-}$ [E_0=0.16V]

$Cu + 4OH^{-} \rightarrow CuO_2^{2-} + 2H_2O + 2e^{-}$

$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$ [E_0=0.0 V]

ECM Example - Halides

- Path formation

  $CuCl_2$

  - Water film thickness and conductivity derive from the hygroscopic and ionic nature of the residue [1]
- Electrodissolution

  $Cu + Cl^{-} \rightarrow CuCl$

  - Corrosiveness of halogenated residues demonstrated earlier
- Ion Transport
  - Halides generate a large array of stable complexes

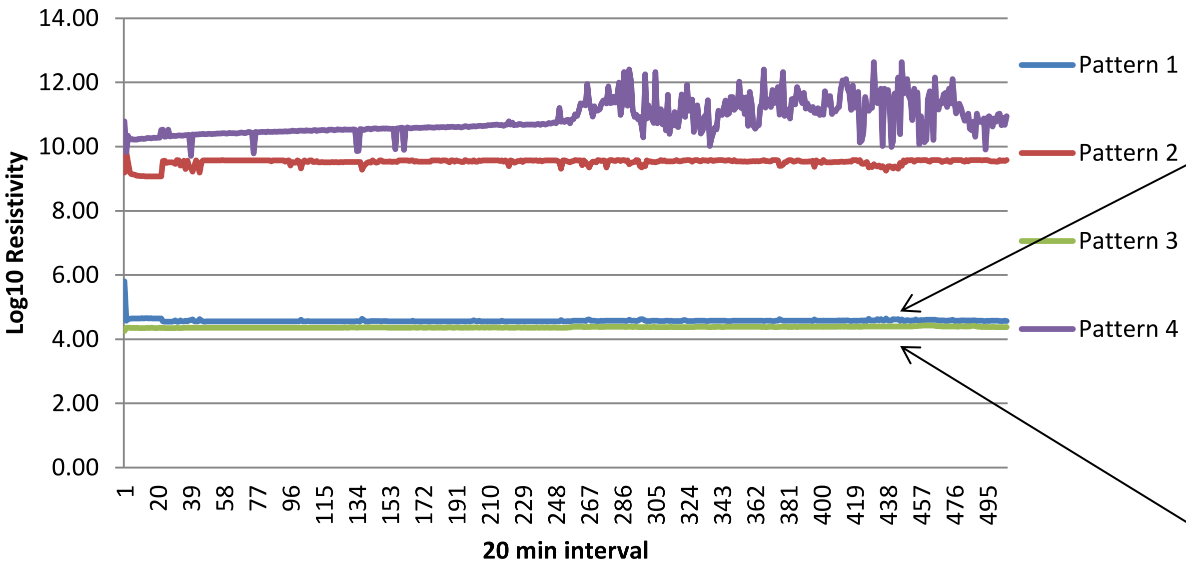
  $CuCl_2^{-}$, $CuCl_3^{2-}$
  $CuCl_4^{2-}$, $CuCl_3^{-}$, $CuCl^{+}$

0.25M HCl Solution

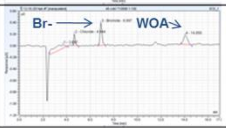
[1]: Anderson J.E., IEEE Trans. Comp., Hybrids, Manuf. Technol., 11, 1, 152-8, 1988

Real-life Example

- Halogenated flux effect on in-field failures



IPC J-STD-004B

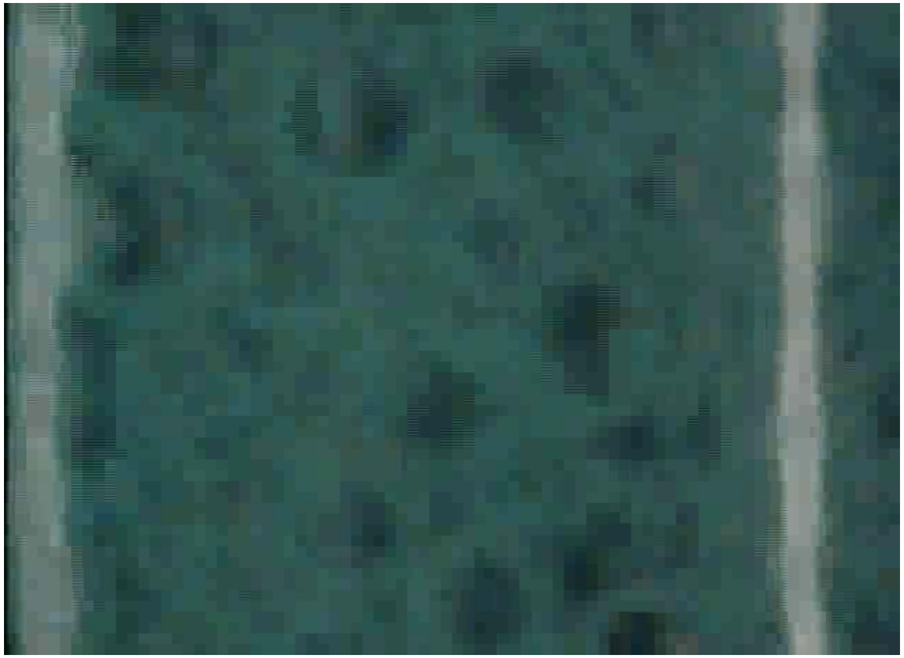
LOT	IC RESULTS	Br- ppm
W141023		3,117ppm
W141628		3,082ppm
W142181		30,487ppm
710898		2,698ppm

In-field failure correlated with an SIR failure
The failed specimen was found to have large amounts of Bromide

Non-Halogenated Fluxes

- Zero-halogen solutions can also induce Corrosion or ECM

0.5M Halogen-Free Salt Solution



Conclusion

- Reliability failures result from the interaction of post-reflow residues with board components under environmental stress
- The traditional Rosin-based approaches to protect the assembly against any chemical influence are limited
- Two basic chemical processes best model the interaction between the activators and their environment:
  - Corrosion (in its broadest definition)
  - Electrochemical Migration
- Based on these two mechanisms, we demonstrated the profound influence of the residue chemistry on the reliability failures
- Our mechanistic study also highlights the harmful effects of halogens in activator packages
- Zero-halogen solutions represent the future of Electronic Assembly
  - Fundamental knowledge of chemical influences is required to avoid similar effects as with Halogenated systems