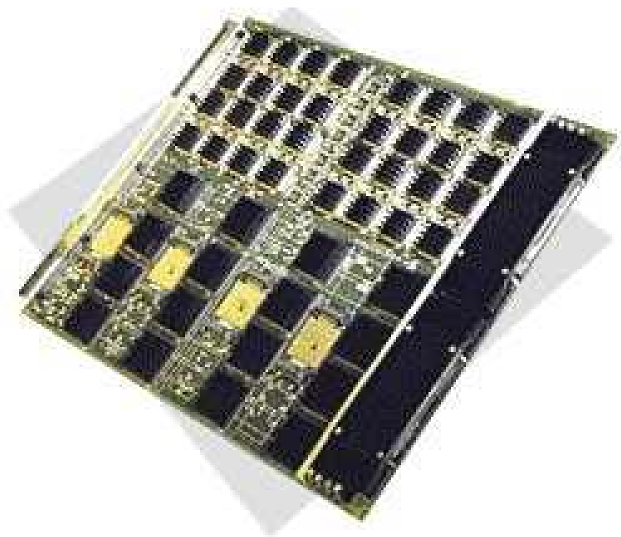
Influence of a Flux Chemical Package on the Reliability of Lead Free Assemblies

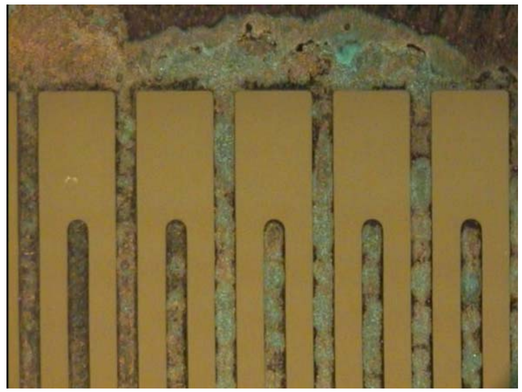
Bruno Tolla
Global R&D Dr.



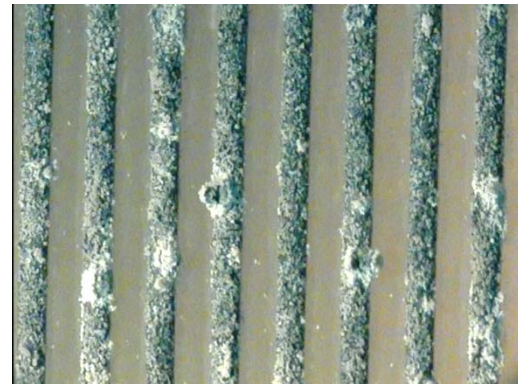
Reliability Tests
Typical Failure Modes

Dendrites

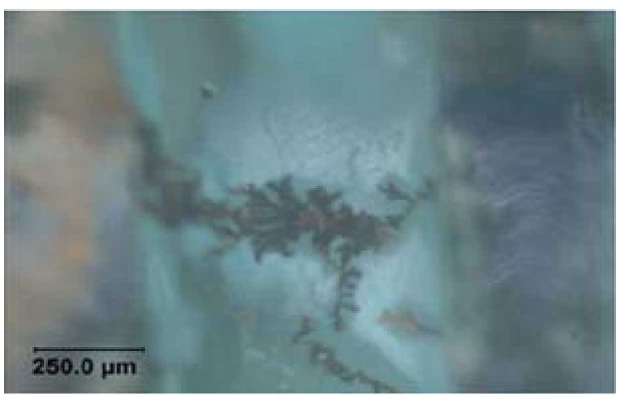
Corrosion



Precipitates



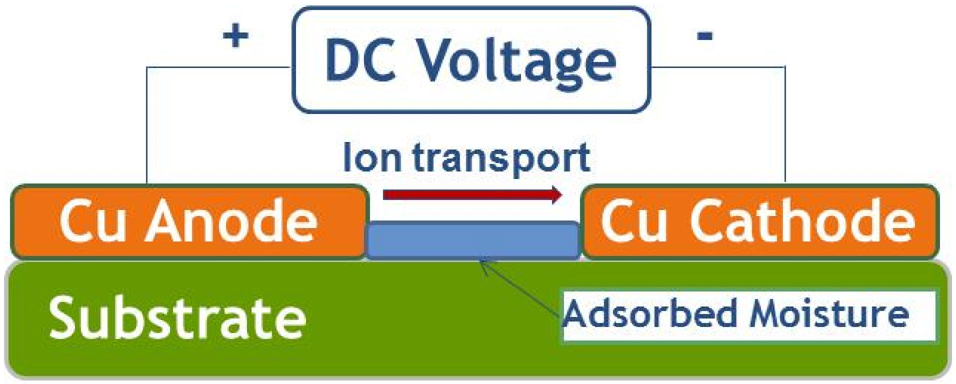
Conductive Anodic Filament (CAF)

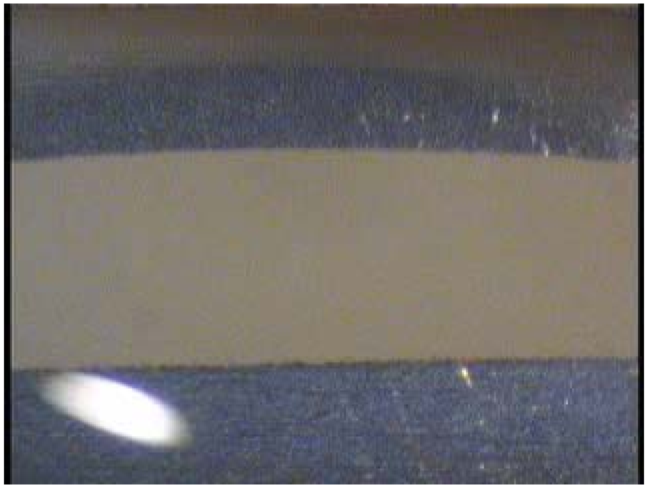


- ✓ **Current leakage**
- ✓ **Shorts**
- ✓ **Circuit Damaging**
- ✓ **Insulating deposits (relays, contacts)**
- ✓ **Cosmetic aspects**

Electrochemical Migration
The basics

- Electrochemical migration (ECM) is an electrochemical process where metal ions move between adjacent metal conductors through an electrolyte solution under an applied electric field.





- 3 Basic ingredients for the formation of an electrochemical cell
  - ✓ Moisture, Voltage bias, Ions
- 5 Sequential steps
  - ✓ Path formation → Electrodissolution → Ion transport → Electrodeposition → Dendrite growth

Chemical Ingredients for ECM
Path formation : Moisture/Ions Interaction

- Water films thickness depends on the substrate. Their conductivity is orders of magnitude lower than bulk water
  - ✓ Ionic conduction at the surface of Epoxy Laminates is negligible unless ionic contaminants are present
- The thickness and conductivity of the water film are highly dependent on the nature of the hygroscopic contaminants
  - ✓ Critical humidity level for water absorption drives SIR performance [8]

Compound	T (C)	RH (%)
NaCl	20	75
KBr	20 / 100	84 / 69.2
$LiCl.H_2O$	20	15

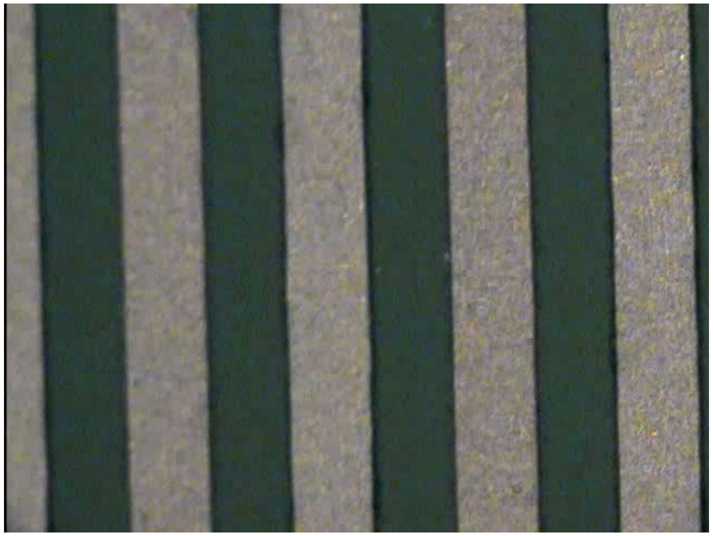
  - ✓ SIR decrease dramatically above critical humidity (and then not so much)
  - ✓ Temperature increases the moisture sensitivity of hygroscopic contaminants

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

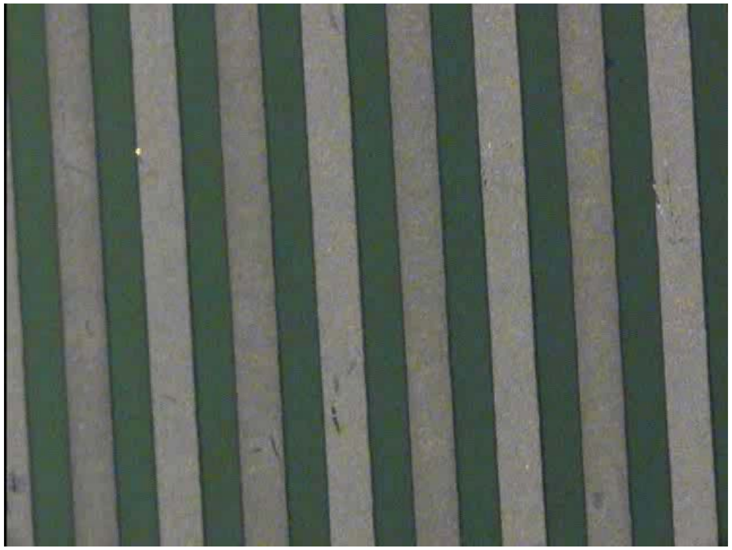
Chemical Ingredients for ECM

More than just ions : Dendrite formation in various solutions

DI Water

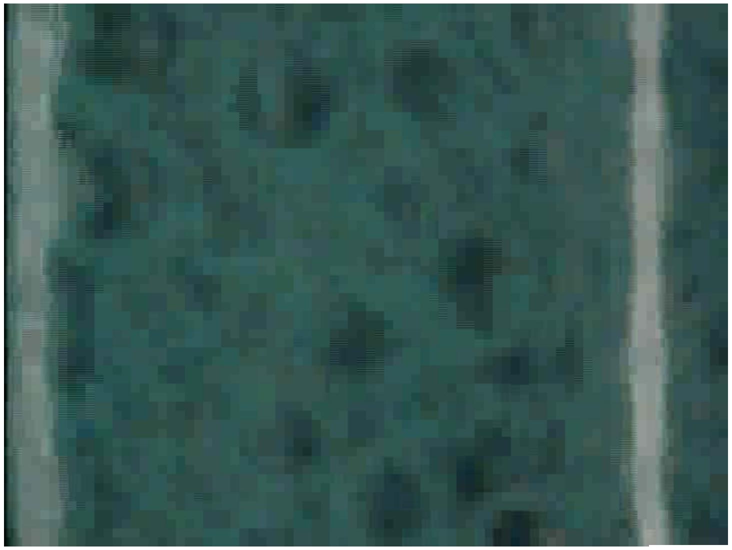


1% NaOH Solution



1% HCl Solution

5% Organic Salt Solution



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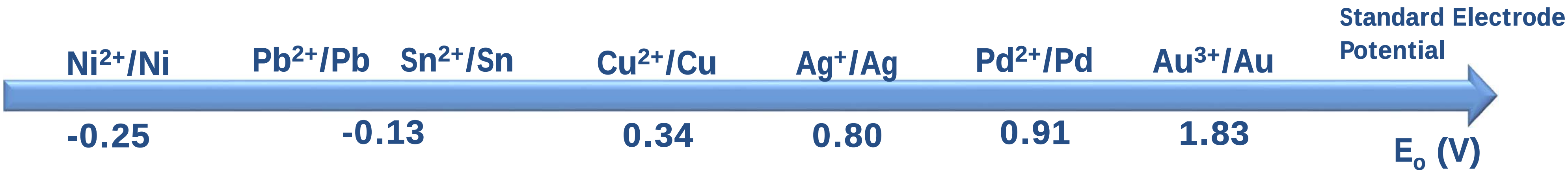
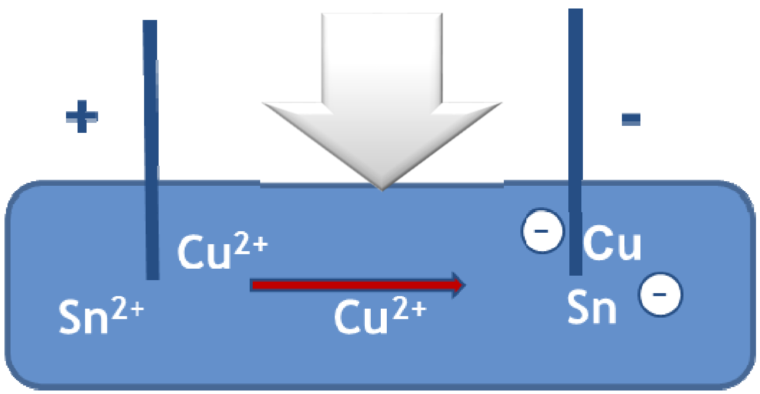
Chemical Ingredients for ECM

Dissolution/Transport/Deposition : Chemical Equilibria at Play



- Redox potentials are not a good predictor for dendritic growth
  - ✓ Pb vs Sn ability to form dendrites, Ag dendrites easy formation
- The stability of the soluble species during migration between the electrodes is key to grow a dendrite

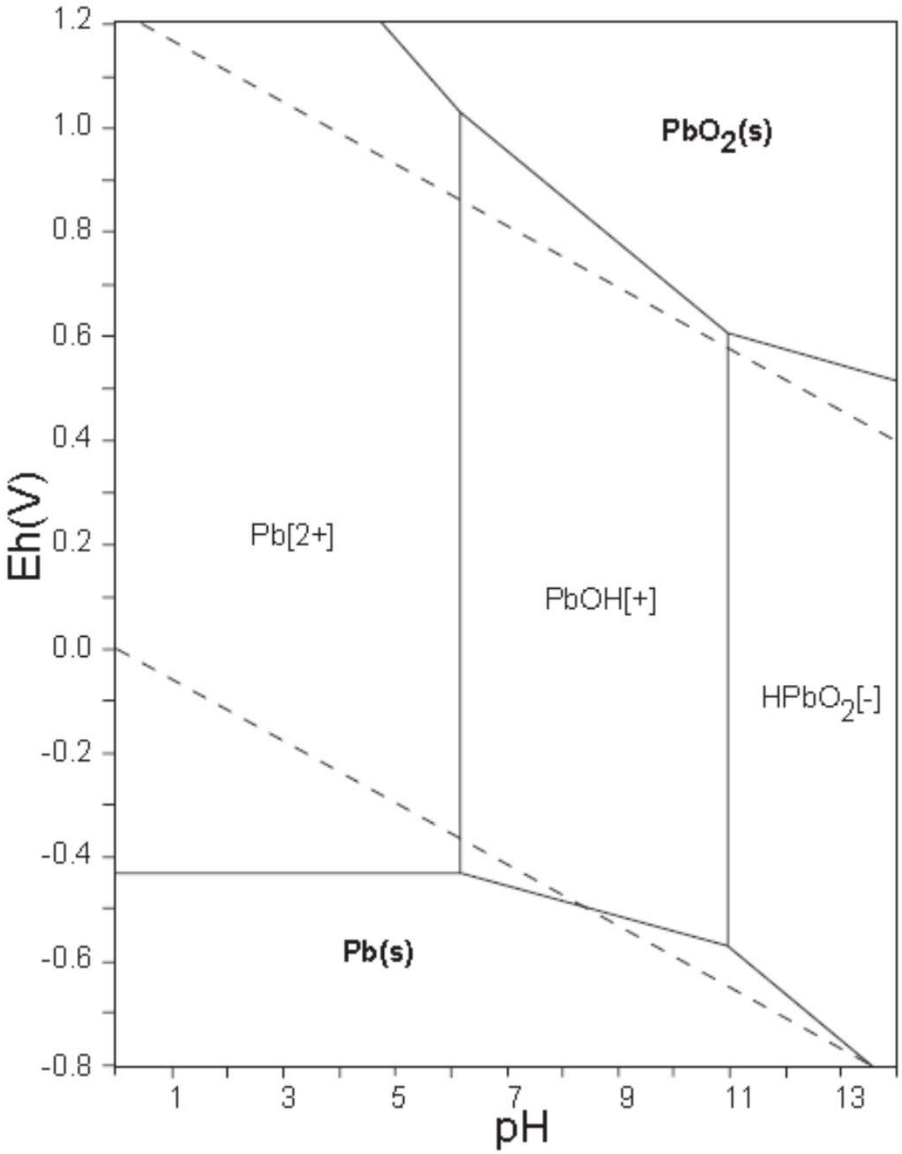
Chemistry is key !

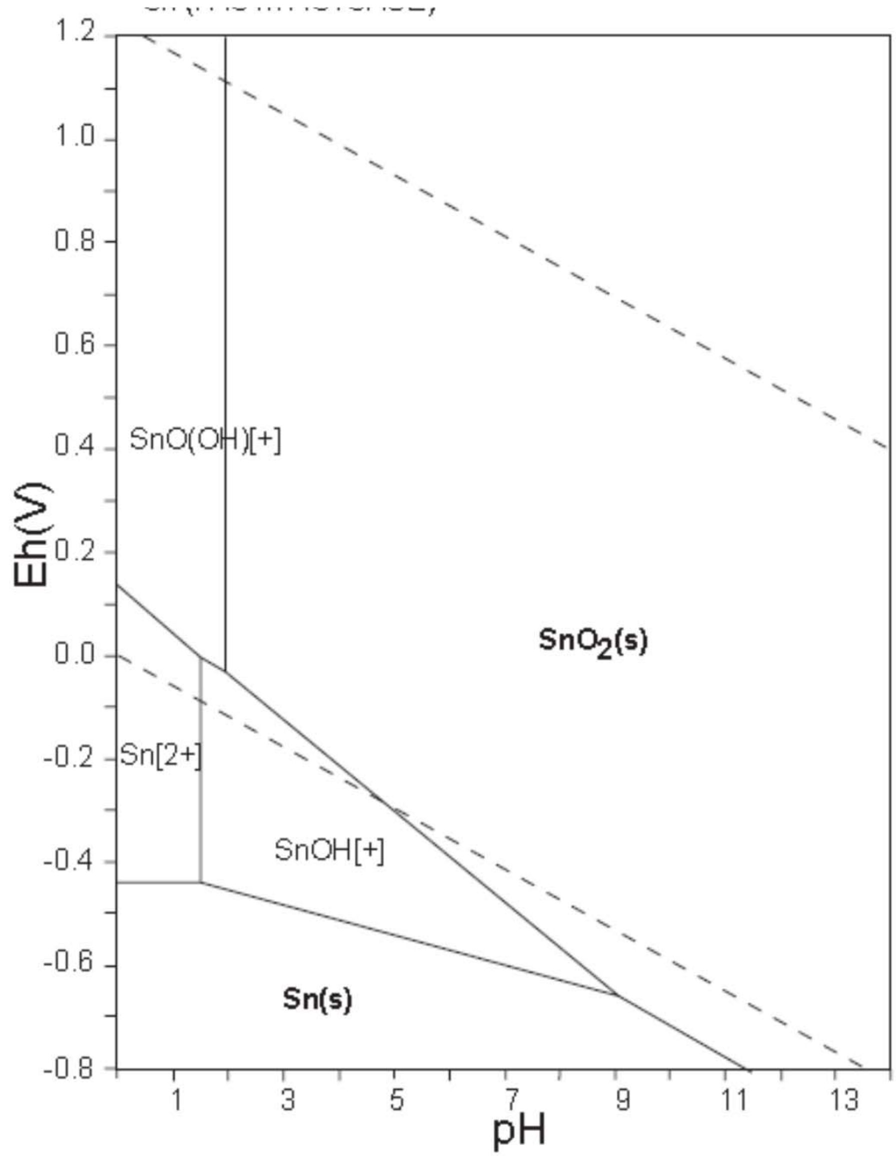


- Kind of explains the shape as well….(vs electroplating)

Pourbaix Diagrams

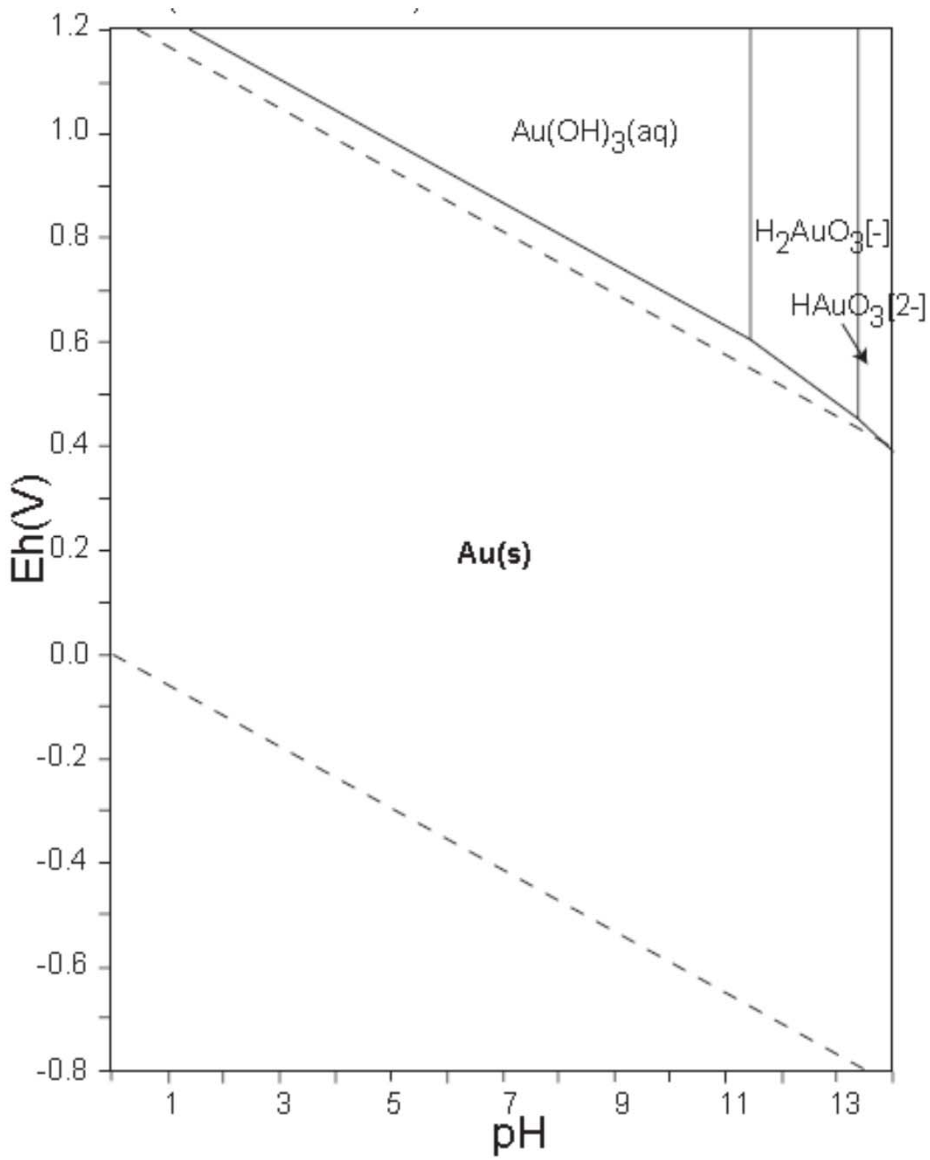
Sn and Pb Stability Range in Water

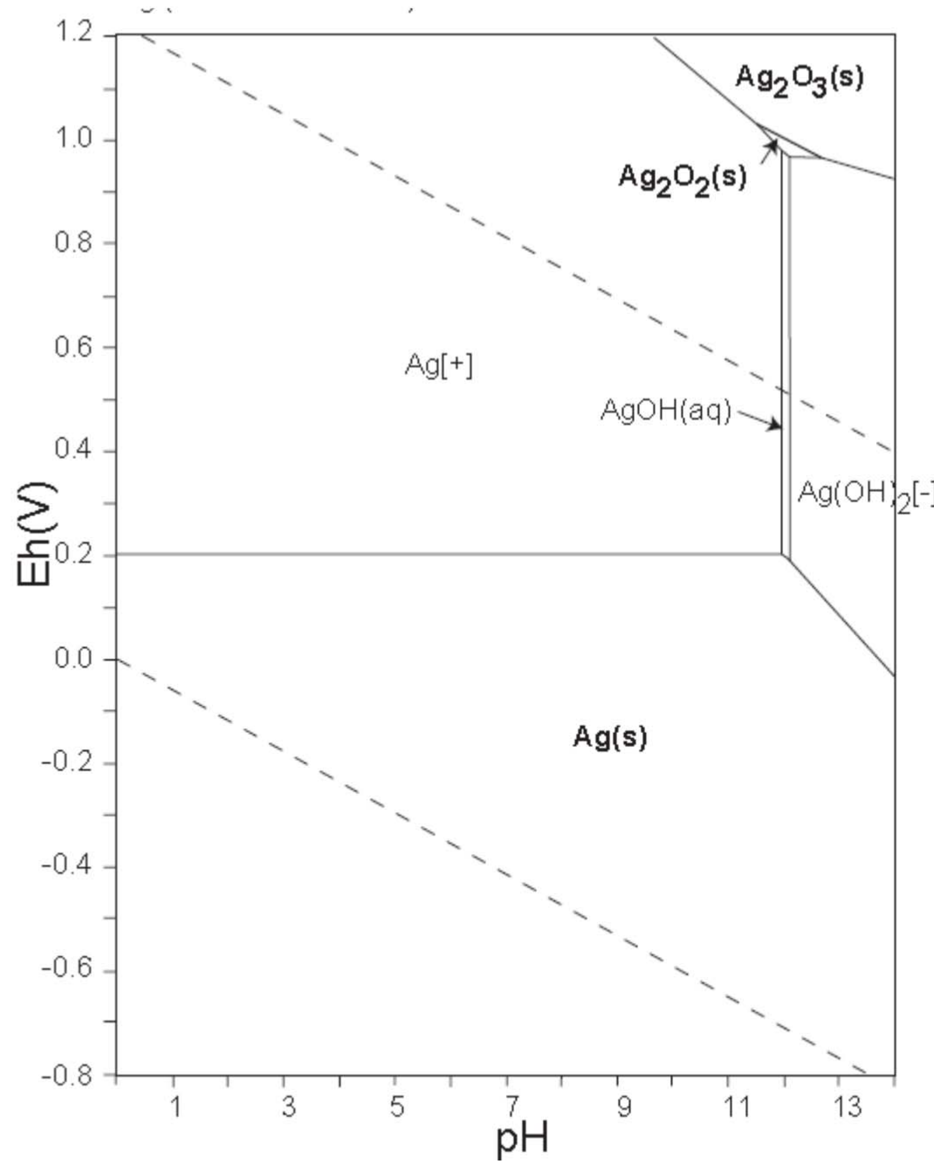




Pourbaix Diagrams

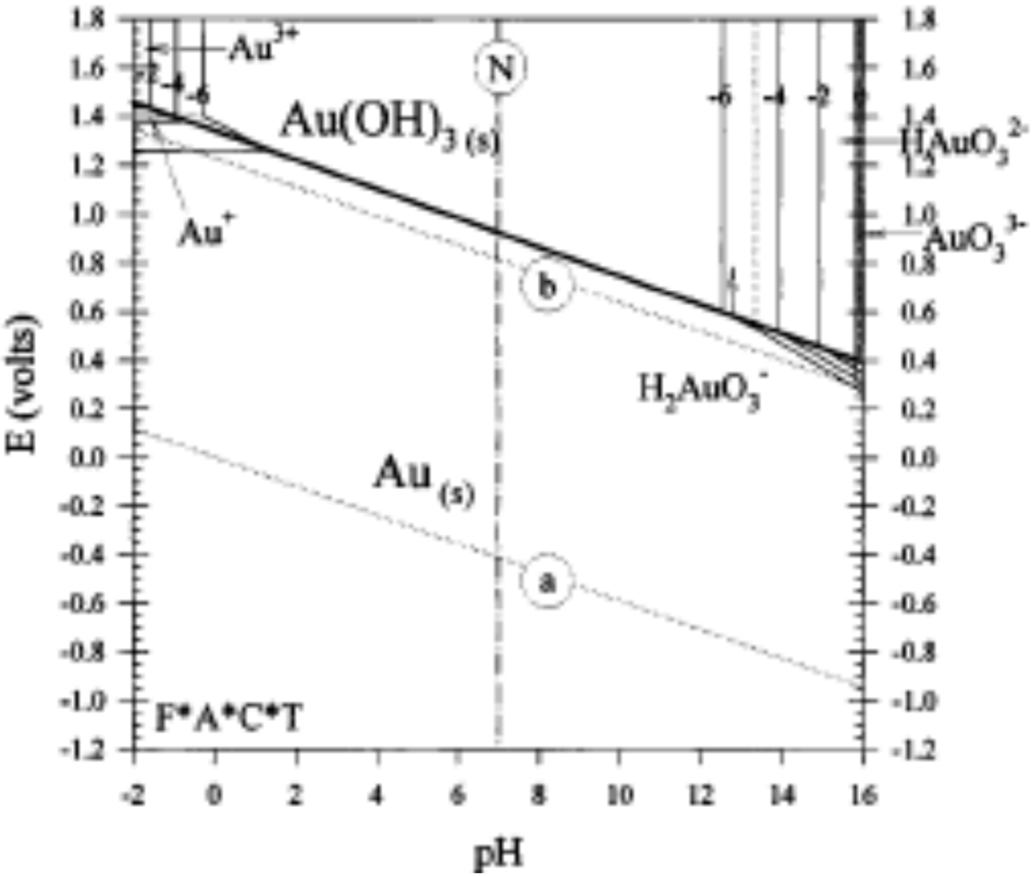
Au and Ag Stability Range in Water



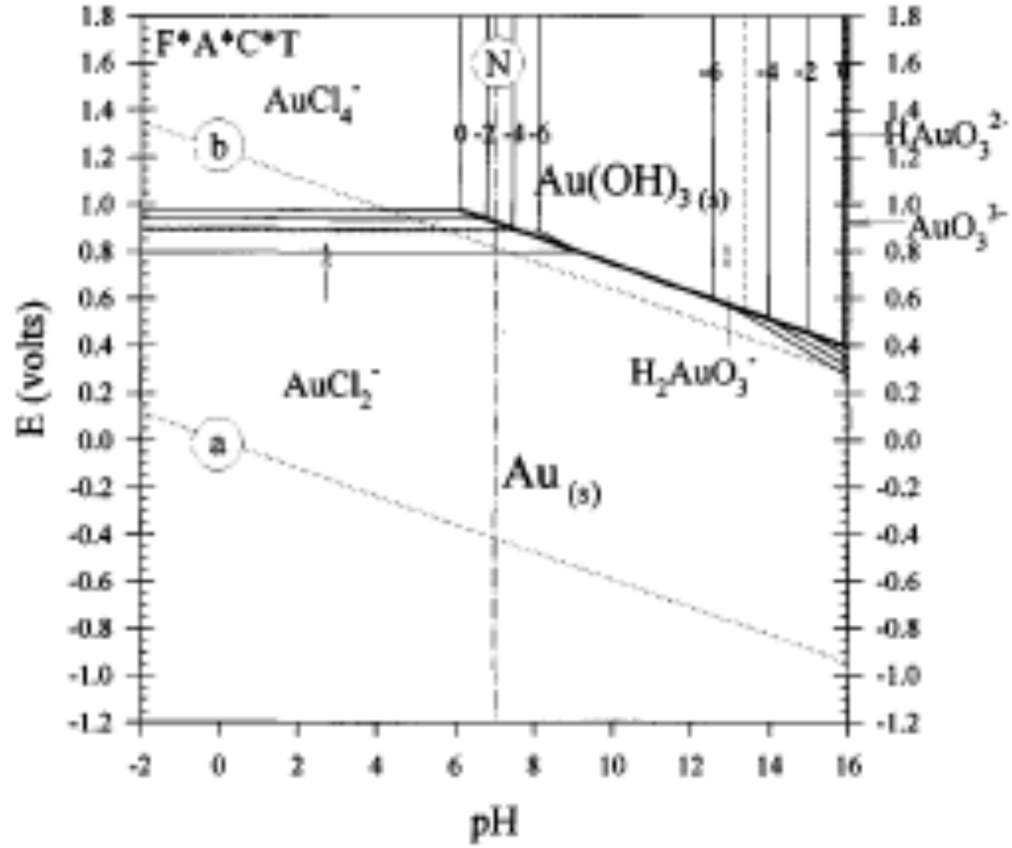


Pourbaix Diagrams

Au Stability Range in Water – Influence of Cl



Au Pourbaix diagram at 298K,
10^{-6}M Au to 1M Au



Au Pourbaix diagram at 298K in chloride solution
10^{-6}M Au to 1M Au / 1M Cl

Uhlig's Corrosion Handbook, Second Edition, Edited by R. Winston Revie.
ISBN: 0-471-15777-5

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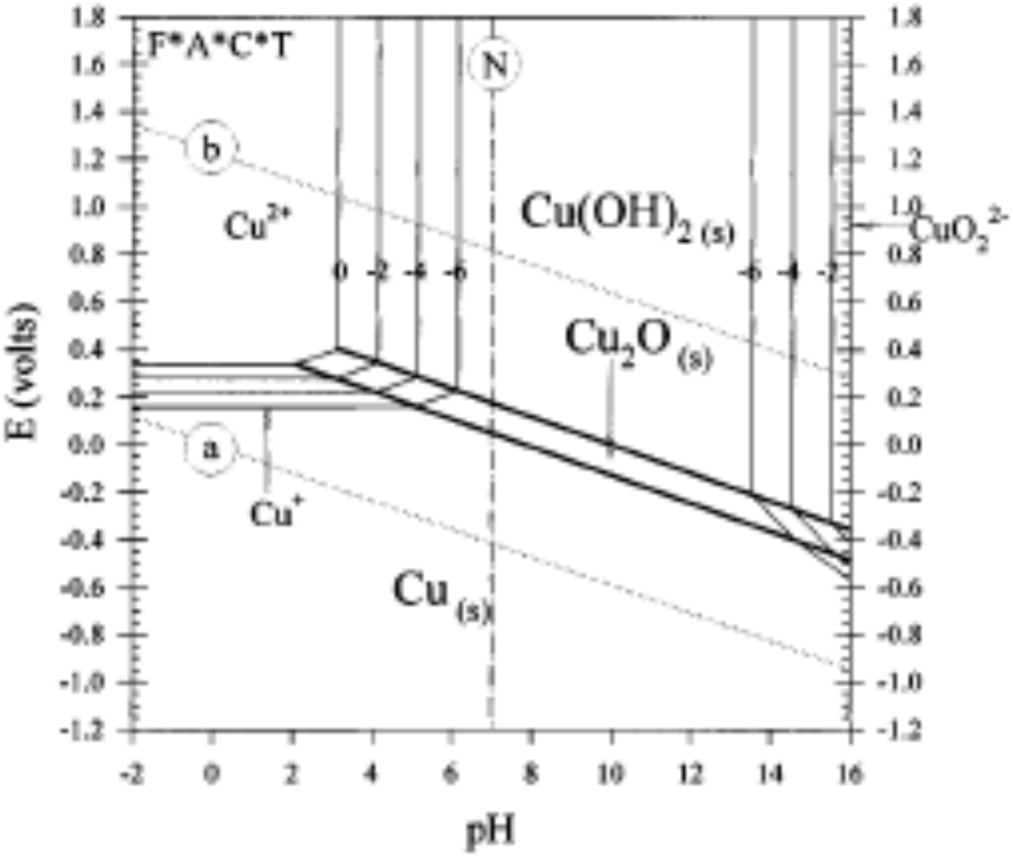
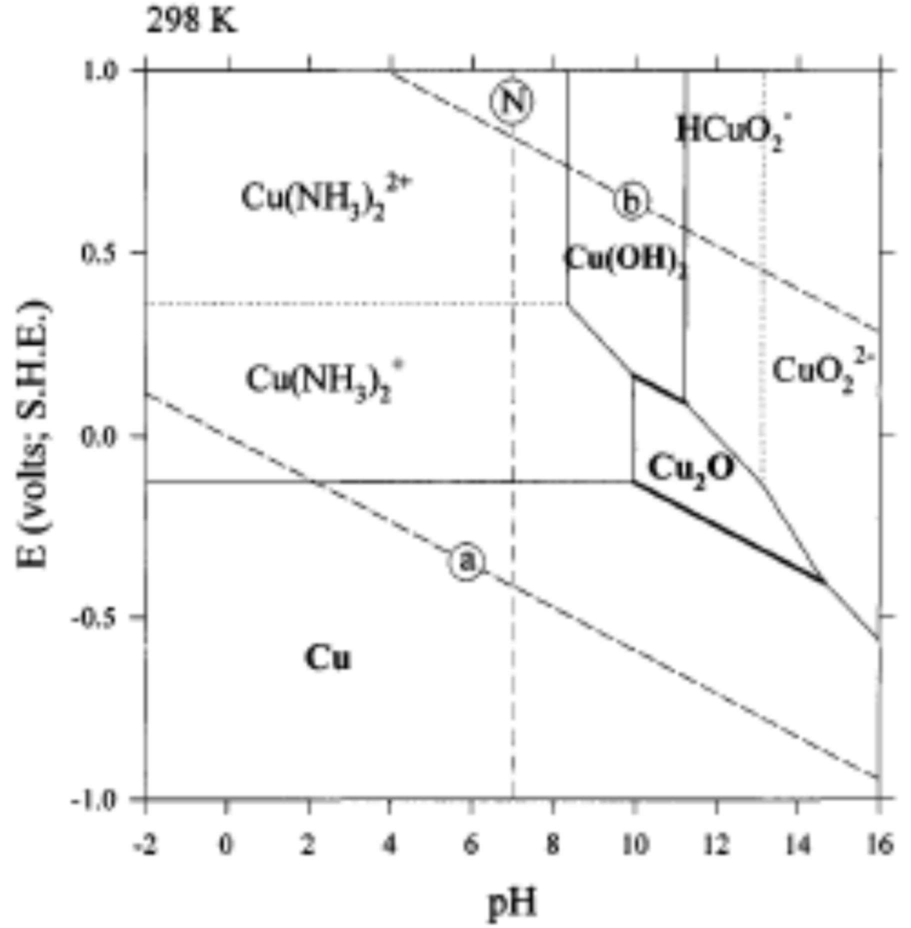
Pourbaix Diagrams

Cu Stability Range in Water – Influence of Amines



Cu Pourbaix diagram at 298K
10^{-6}M Cu to 1M Cu



Cu Pourbaix diagram at 298K in ammonia solution
10^{-6}M Cu /10^{-3}M NH_3

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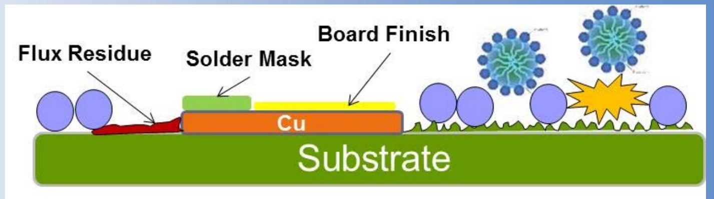
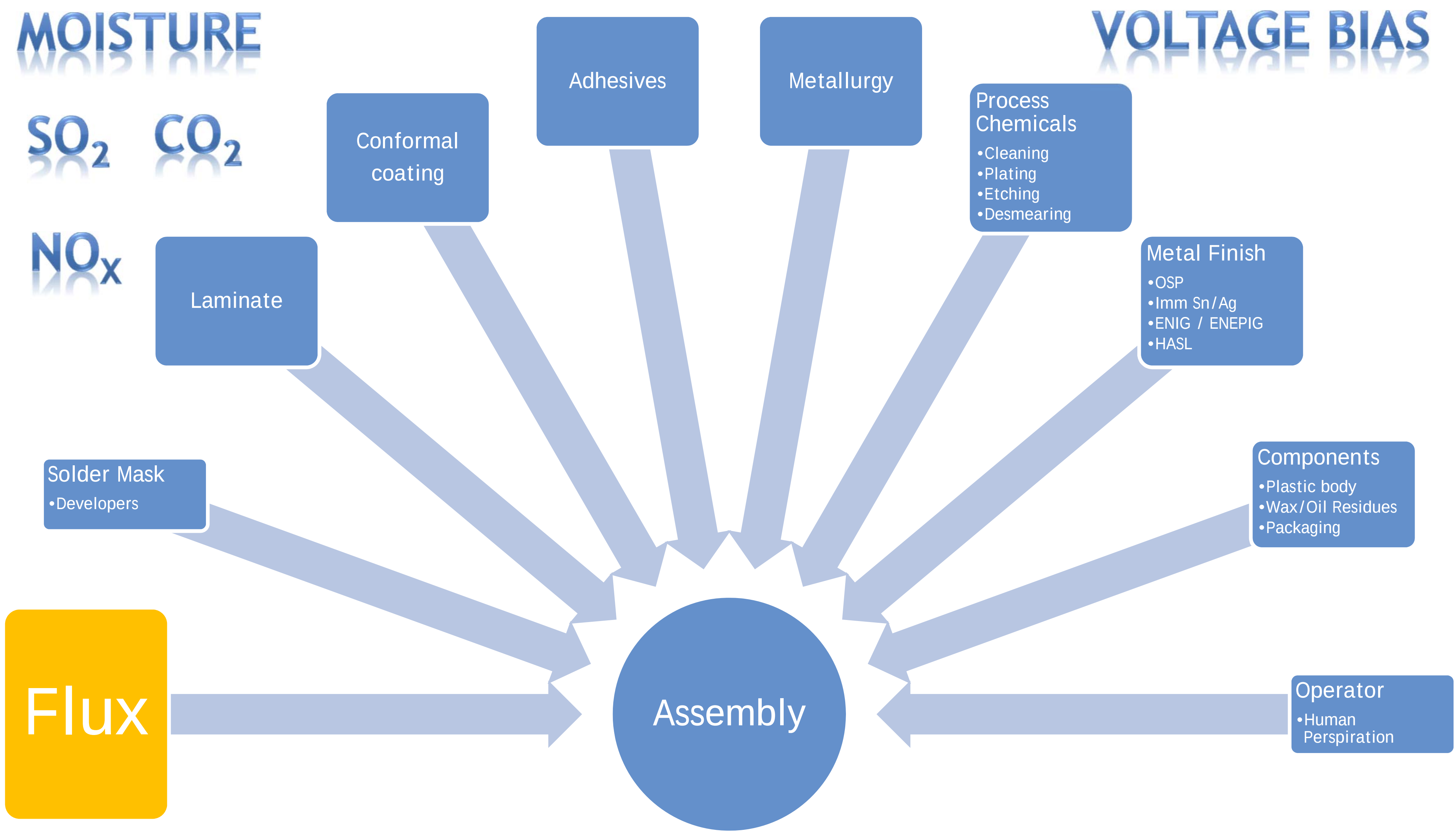
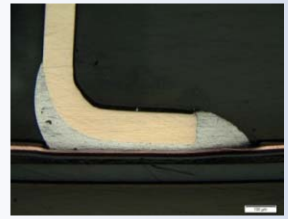
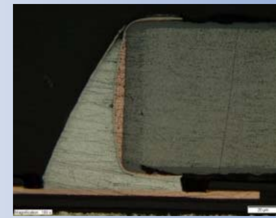
Chemical complexity of a Printed Circuit Board

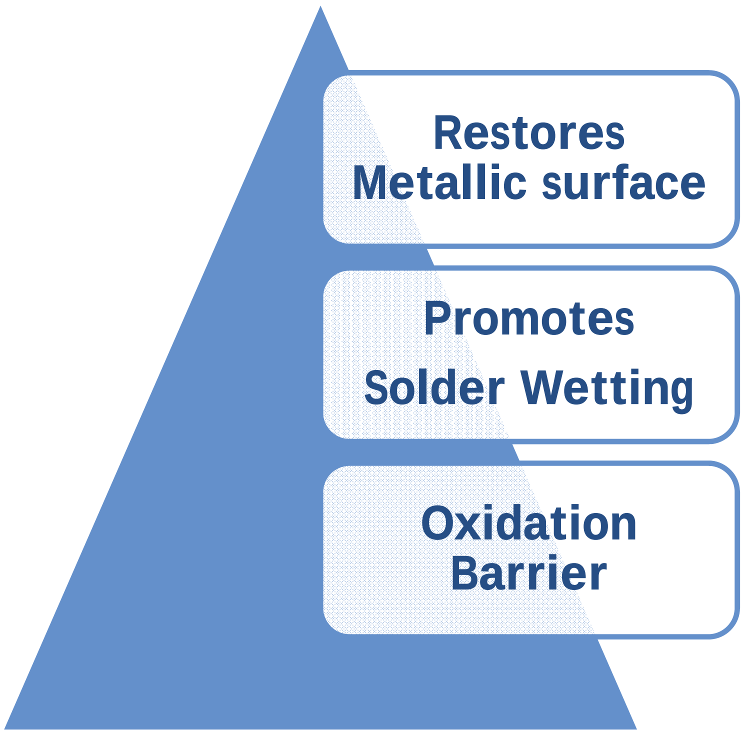




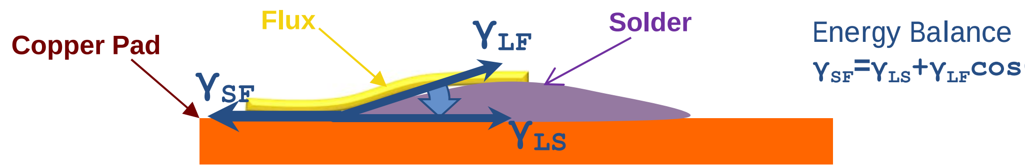

Flux Functionality

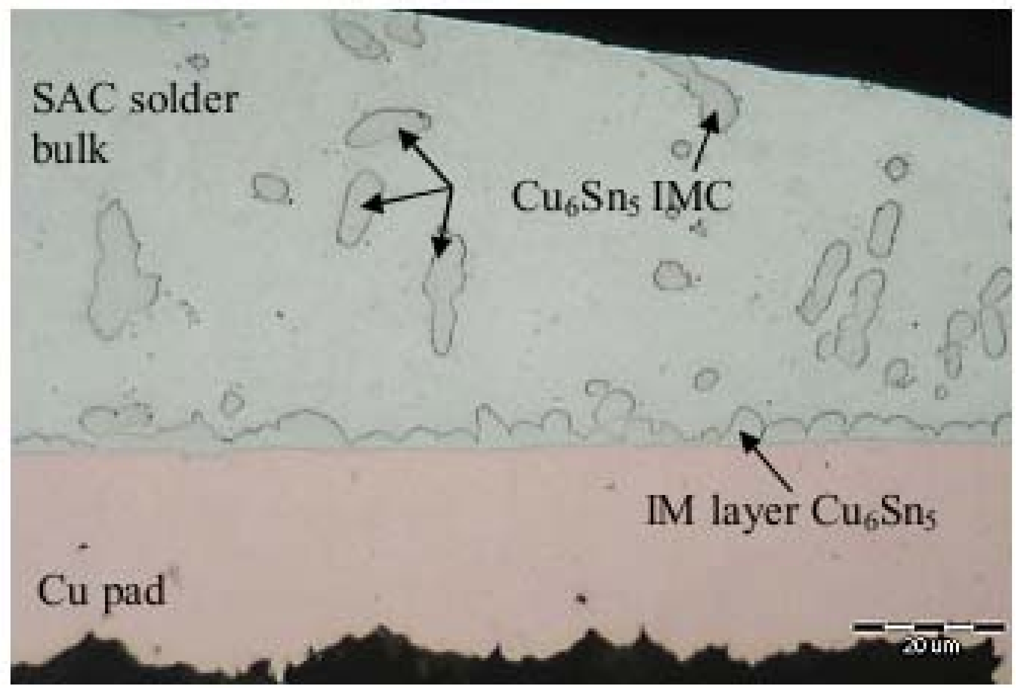
3 Fundamental Roles



The End Result: A Reliable Interconnection

- ✓ Electrical and Heat Conductivity
- ✓ Mechanical Strength





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Flux Chemistry

Carrier for Vehicle
and Activator

Solvents
Alcohols
Water

High T solvent for
fluxing byproducts
Metal protection

Vehicle
Rosin
Polyglycols

Thermal conduction
Solder Flow

Fluxes

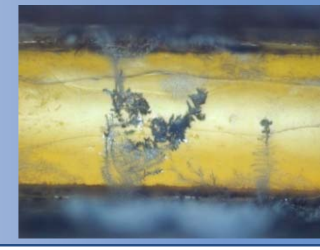
Metal oxides
layers removal

Activators
Organic acids
Rosin,Amines
Halogen/ides

Additives

Rheological additives,
Surfactants, Dispersants,
Corrosion inhibitors

Flux Impact on Reliability
1. Activators



1/ Source of ionic species

2/ Attract water

3/ Generate Metal Complexes

- Create conductive paths
- Generate more ions
- Release corrosive and ionic species

Water-mediated mechanisms

$CuO + 2HCl = CuCl_2 + H_2O$

$Cu_2O + 2HCl = CuCl_2 + Cu + H_2O$

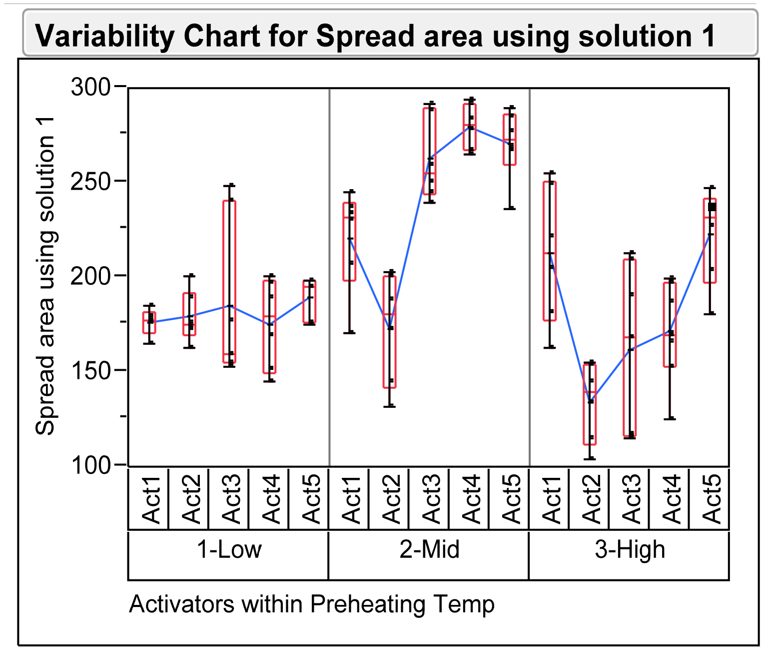
$CuO + 2RCOOH = Cu(RCOO)_2 + H_2O$

$Cu_2O + 2RCOOH = Cu(RCOO)_2 + Cu + H_2O$

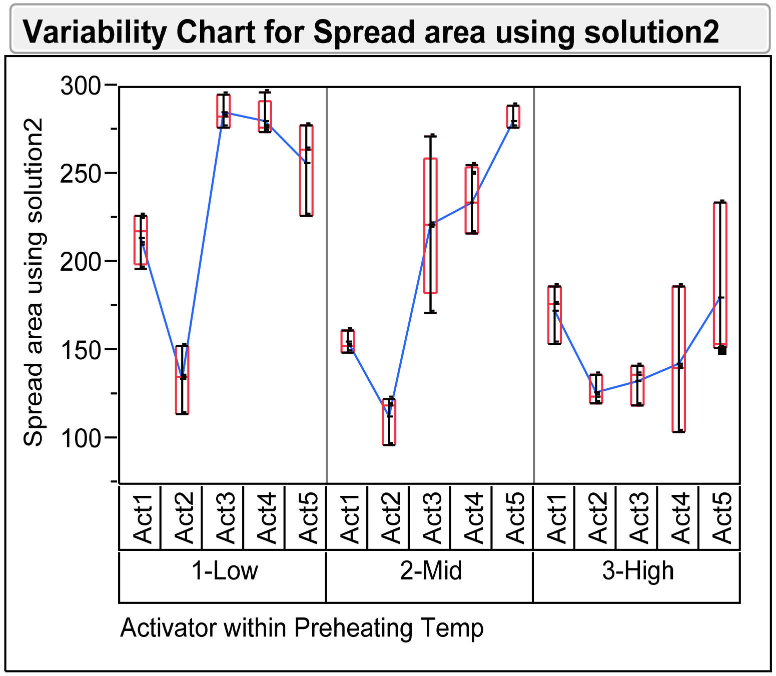
4/ Stabilize soluble metal ions between conductors by buffering the pH or creating stable charged complexes ($AuCl_4^-$)

Flux Impact on Reliability
2. Solvents

- Moisture interaction
  - Hygroscopic Solvent effect are minor (only increase H_2O layer thickness)
- Synergetic interactions are possible with some hydrophobic activators
  - Dissolution of non moisture sensitive ionic activators



in solvent 1

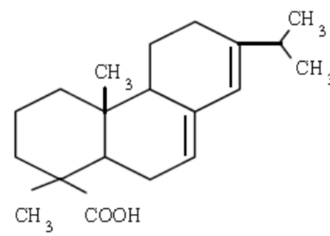


in solvent 2

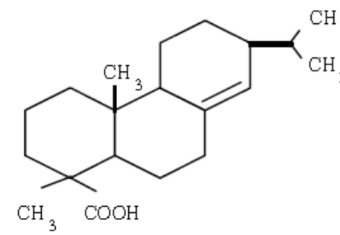
Flux Impact on Reliability
3. Rosin

Solidified resin from which the volatile terpene components have been removed by distillation is known as rosin.

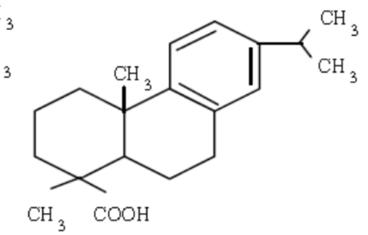
90% - Resin Acids . 6 primary acids :



ABIETIC ACID



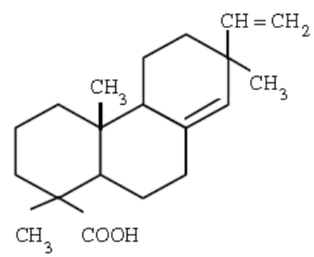
NEOABIETIC ACID



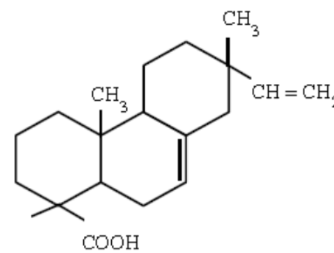
DEHYDROABIETIC ACID

10% - Non acidic materials

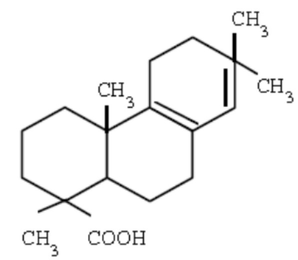
Resin acid esters
Fatty acid esters
Diterpene aldehyde and alcohols
C_{19}-C_{31} hydrocarbons
Wax



PIMARIC ACID

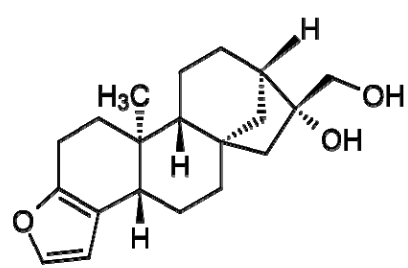


ISOPIMARIC ACID



PALUSTRIC ACID

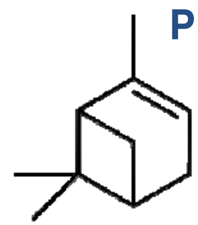
Resin (IPC) = Functionalized rosin or synthetic polymer



Cafestol

Terpene

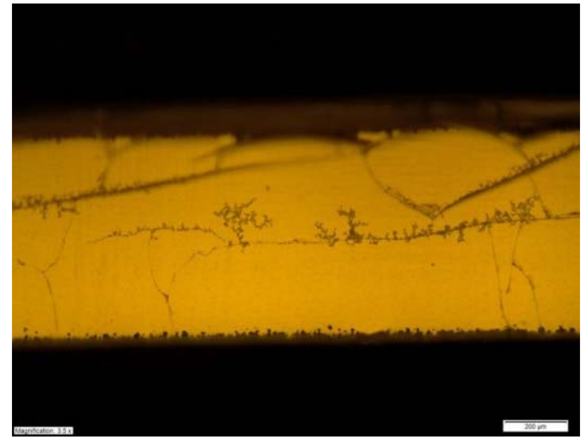
Pinene



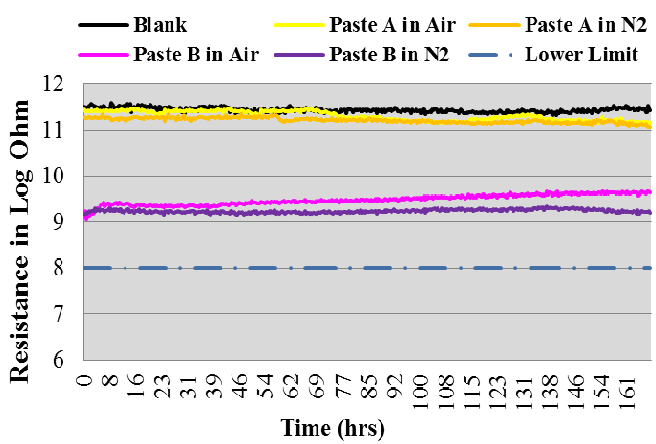
Flux Impact on Reliability
3. Rosin

- Two beneficial impacts on reliability
  - Water Repellency
  - Ion encapsulation

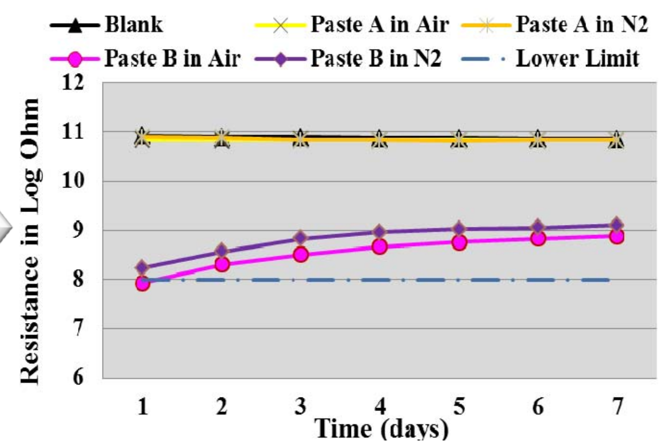
But... 3 failure modes



- Rosin can develop microcracks under environmental stress
- Rosin can oxidize during reflow (white residues)
- Rosin can release corrosive activators at higher temperatures

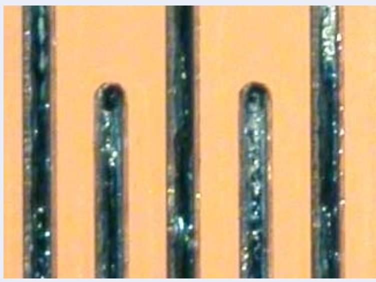
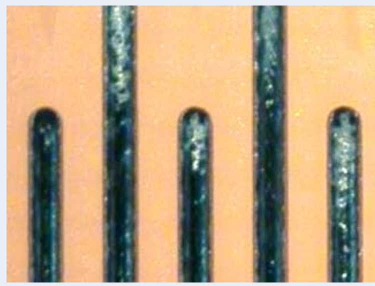
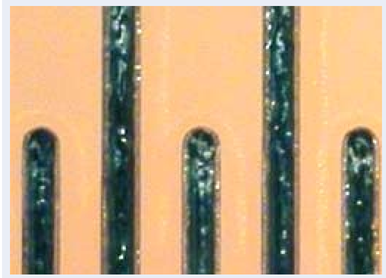
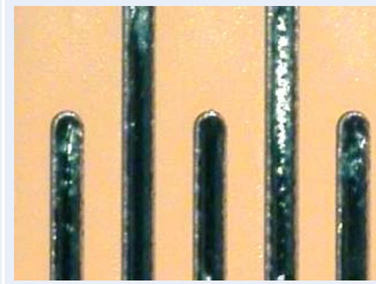
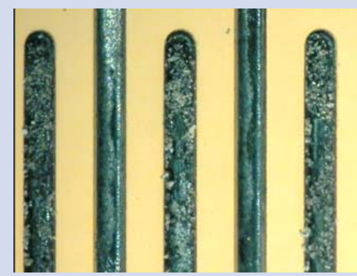


SIR 40C/90%RH (IPC 2.6.3.7)



SIR 85C/85%RH (IPC 2.6.3.3)

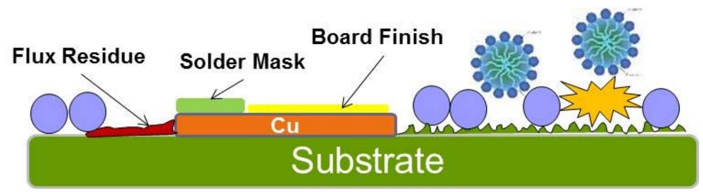
Flux Impact on Reliability
3. Rosin

	IPC 2.6.3.7		IPC 2.6.3.3	
	AIR	Nitrogen	AIR	Nitrogen
Paste A				
Paste B				

40C/90%RH **85C/85%RH**

Flux Impact on Reliability Mechanisms

- Fluxes generate a complex chemical system on the board
  - ✓ In essence, these compounds interact strongly with metal oxides



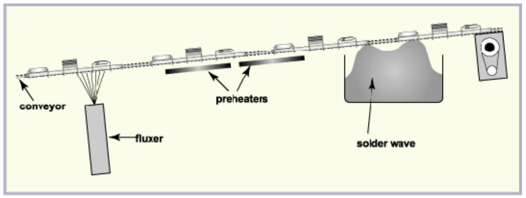
- Post-reflow residues drive reliability
  - ✓ Unconsumed activators
  - ✓ Reaction by-products in the flux residue

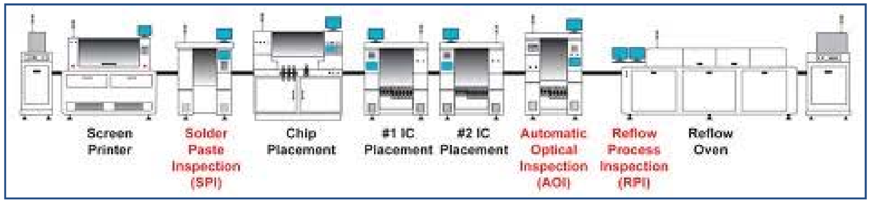
  } f(Reflow Profile and Atmosphere)

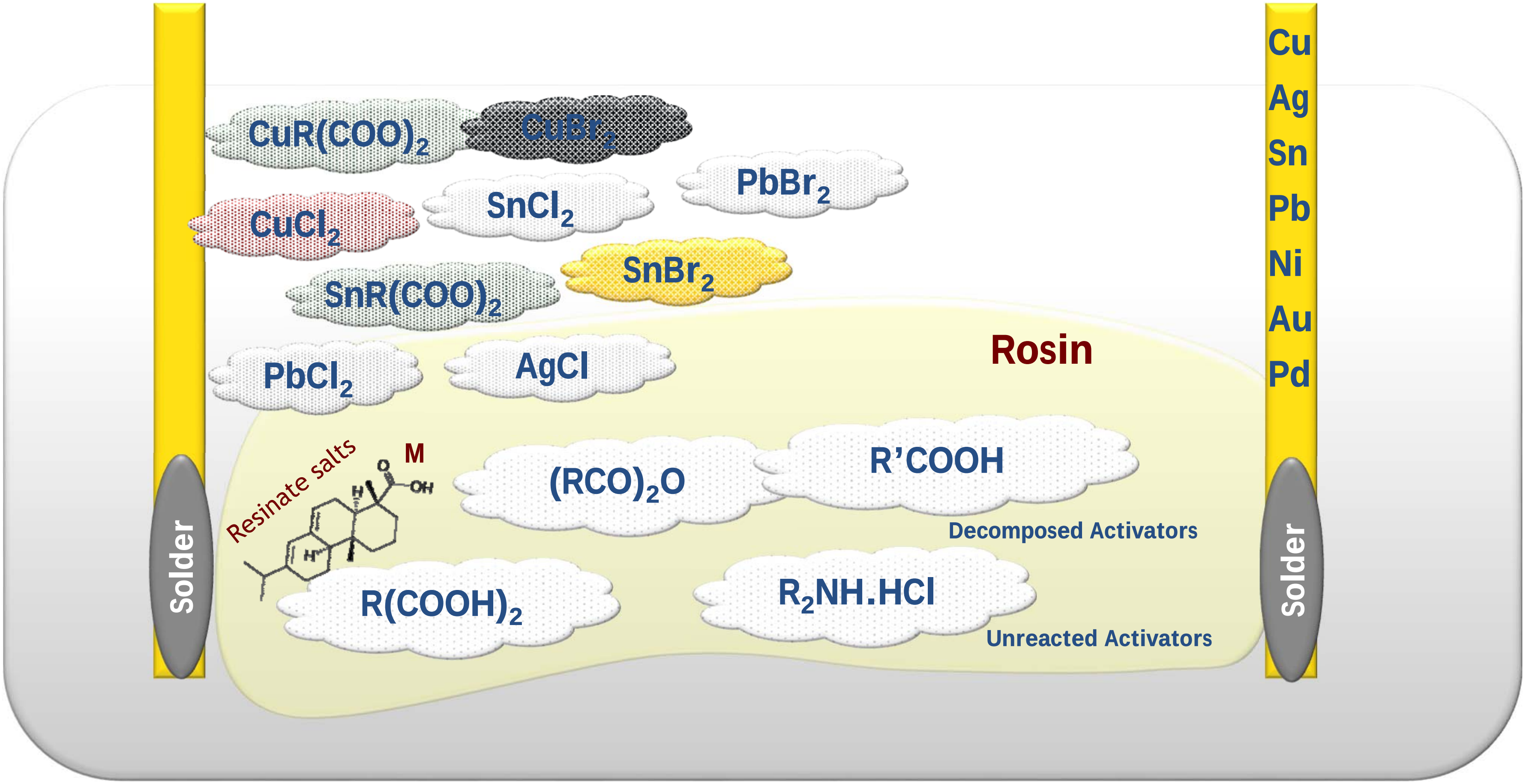
- Reliability is governed by the reactivity of these residues under environmental stress (T, RH, V)

Post-Reflow Residues
(Wave Soldering or Reflow Oven)

$CuO + 2HCl \rightarrow CuCl_2 + H_2O$
$CuO + R(COOH)_2 \rightarrow CuR(COO)_2 + H_2O$
$Cu_2O + 2HCl \rightarrow CuCl_2 + Cu + H_2O$
$Cu_2O + R(COOH)_2 \rightarrow CuR(COO)_2 + Cu + H_2O$

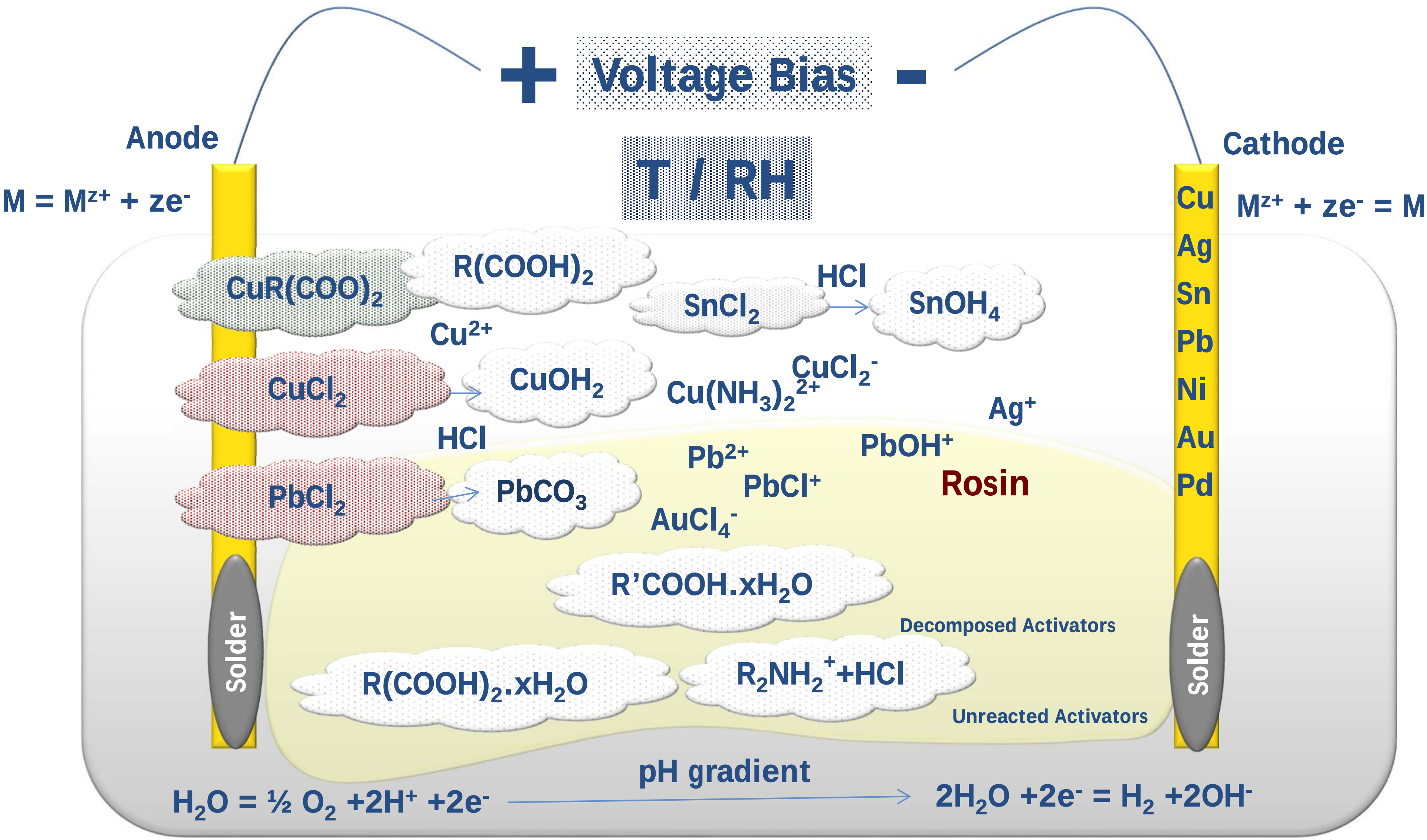






Residue composition depends on reflow conditions (Reflow Profile, Atmosphere)

Residues evolution during ageing (Reliability Tests)



T, RH, Voltage Bias are critical for the transformation of the residue
The test needs to operates in conditions representative of end-use

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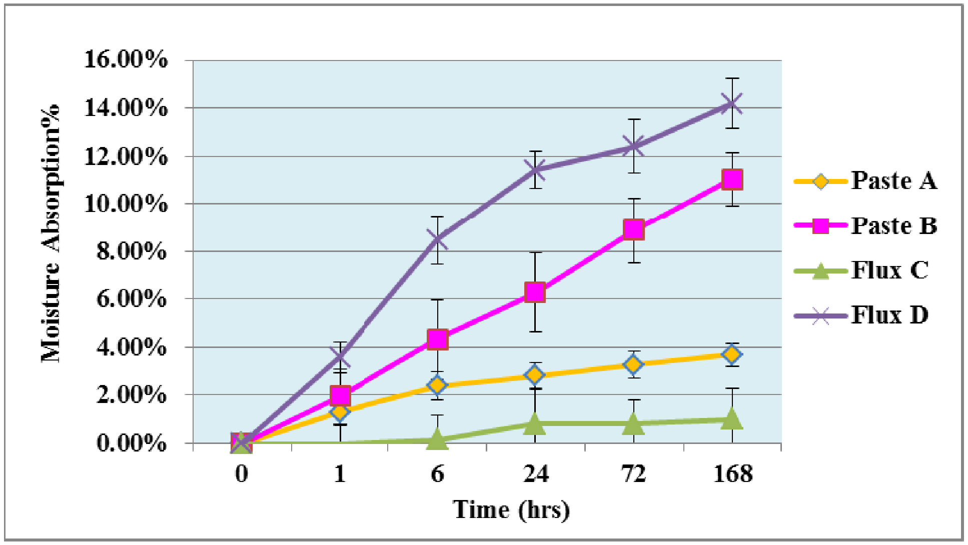
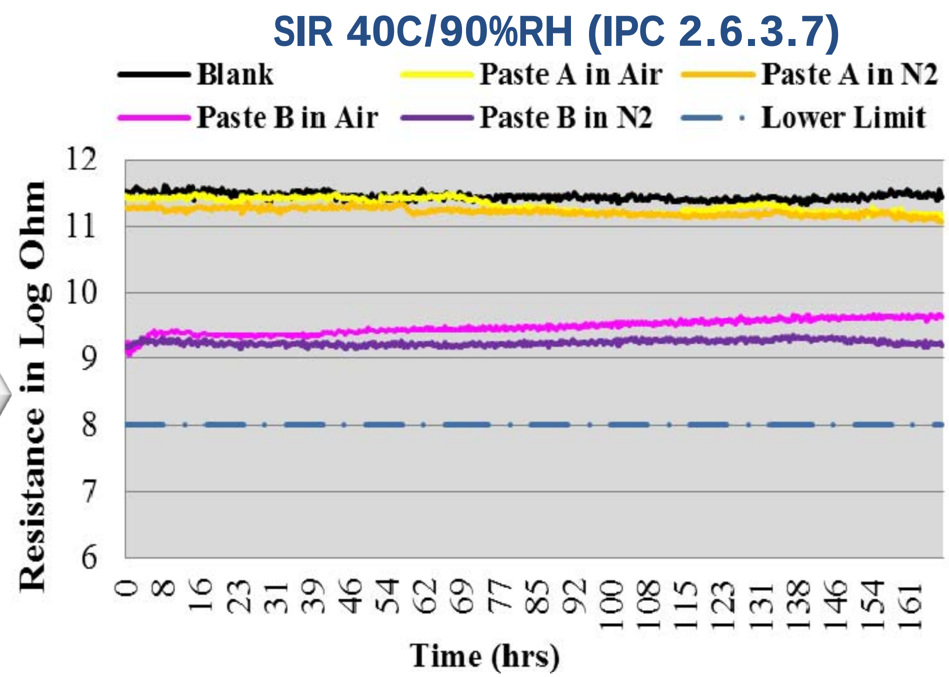
Residues Reactivity Under Environmental Stress
Key Parameters

1. Residue Hygroscopicity





2. Residue Solubility

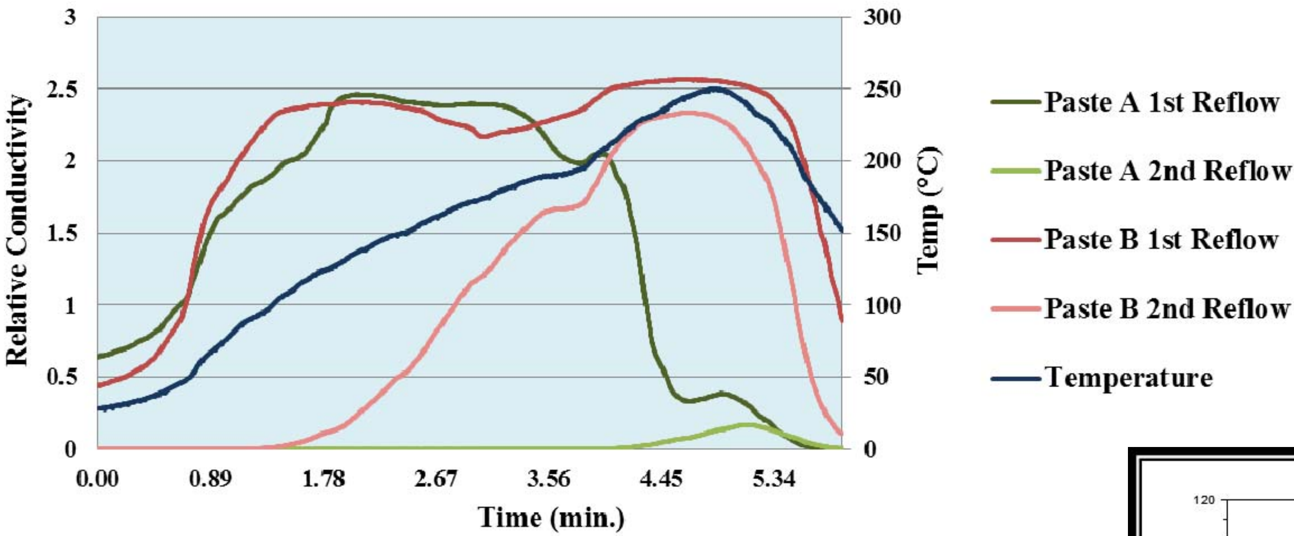
RT vs ionic liquid conditions

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

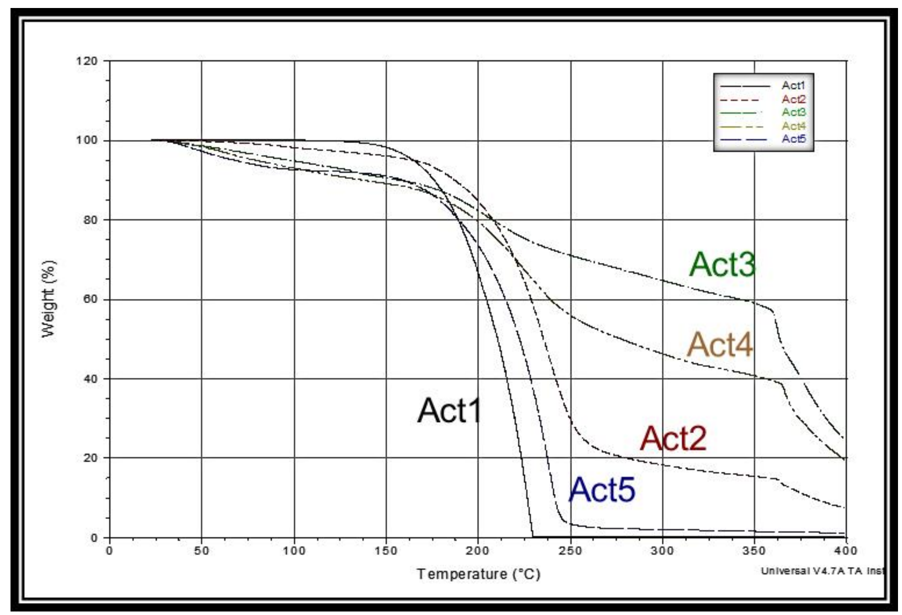
Compound	Water solubility (g/100cc)	Color
CuCl2	70.6	Green
CuCl	0.006	Green
SnCl2	83.9	White
SnBr2	85.2	Pale Yellow
PbCl2	1	White
PbBr2	0.8	White
CuOH2 / CuCO3	0.00x	Green

Residues Reactivity Under Environmental Stress
Key Parameters

3. Activator Thermal Resistance



Thermo Conductimetric Analysis



Thermo Gravimetric Analysis

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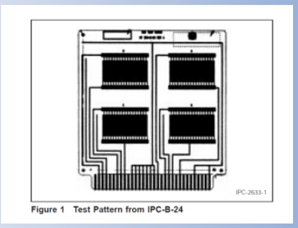
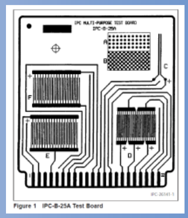
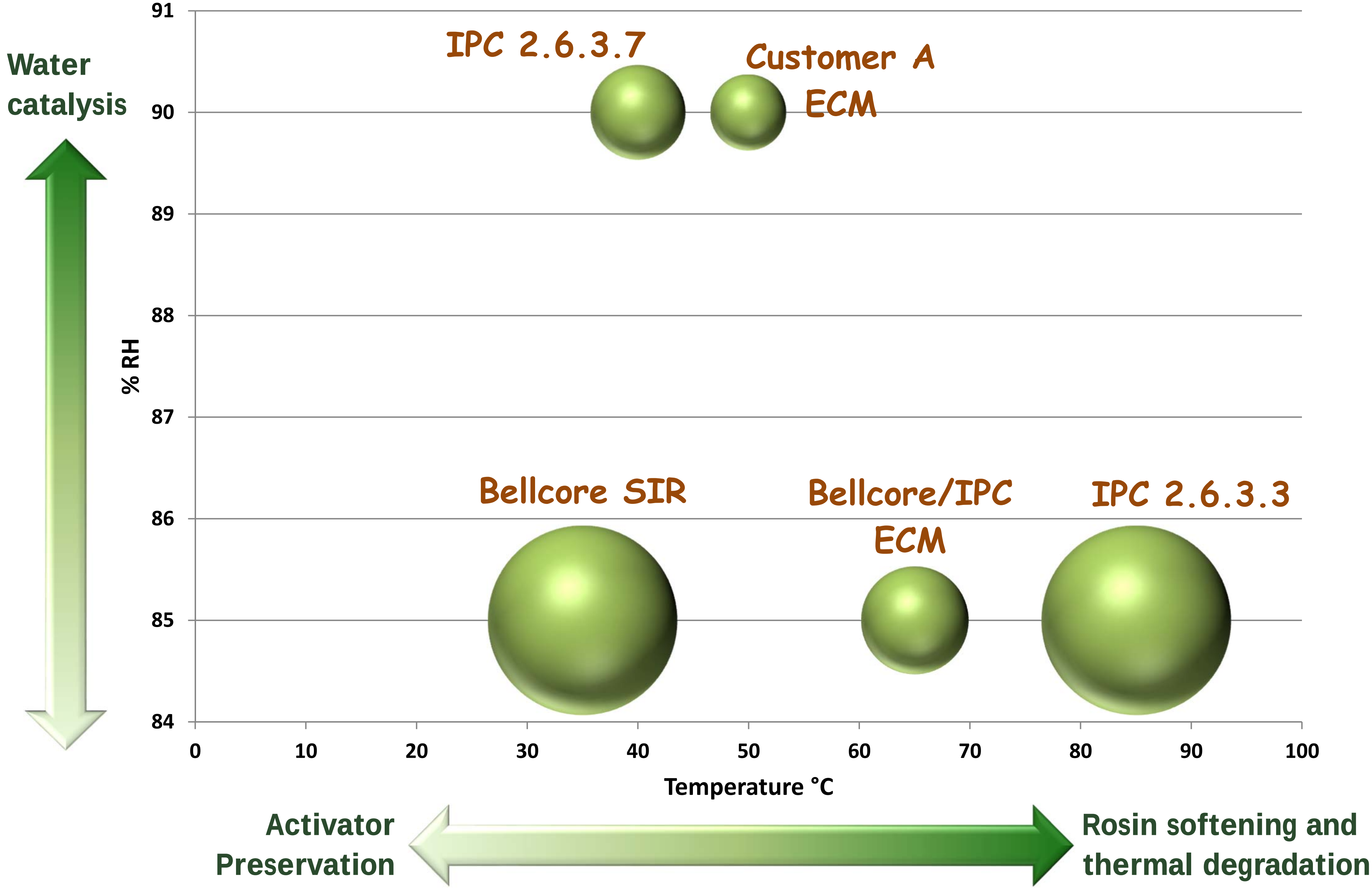
Reliability Tests Overview







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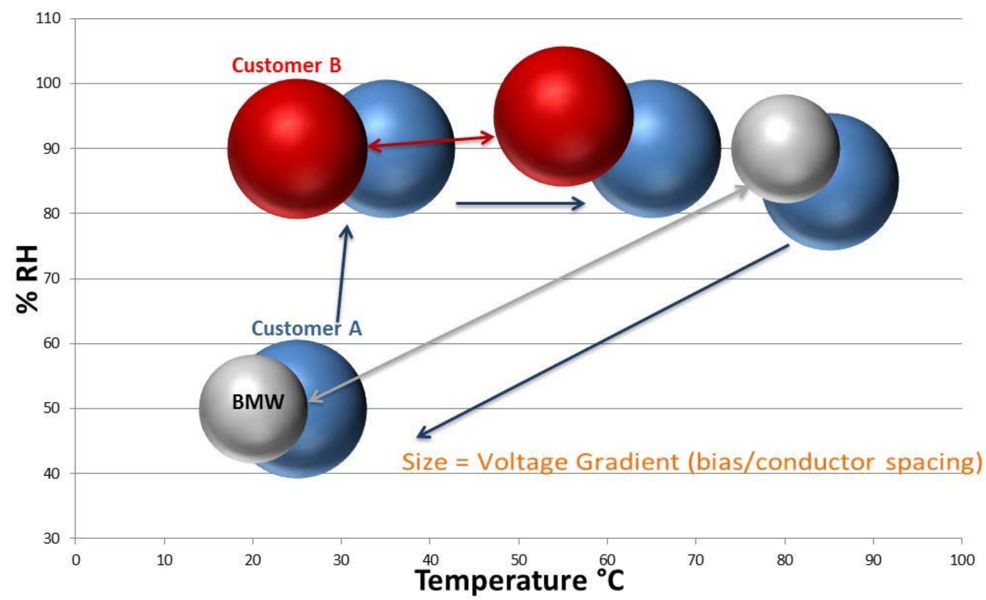
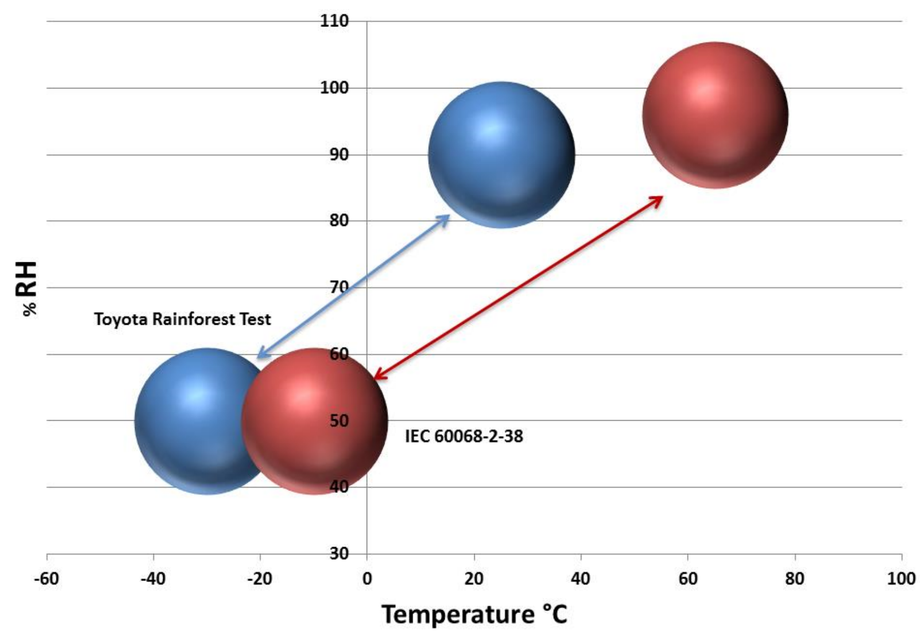
Reliability Tests Overview



Water Condensation Tests

Thermal Cycling Tests



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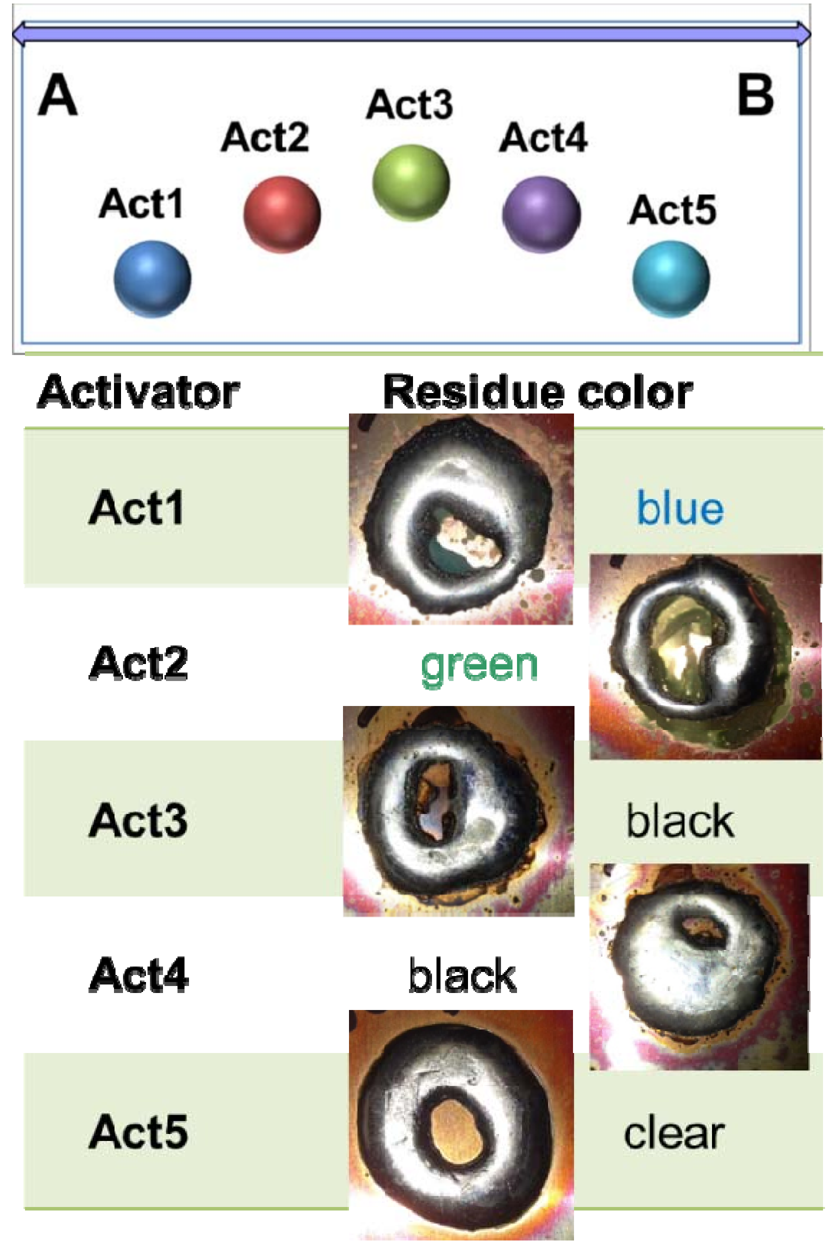
Conclusion

- The chemical systems at play are complex and heavily influenced by
  - ✓ The processing conditions (Board assembly)
  - ✓ The ageing conditions (Reliability tests)
- The reliability tests need to operate in conditions representative of end-usage for the chemical equilibria to be relevant
- Technical partnership between the flux formulator and the applicator will allow to mitigate the risks in specific end-use conditions



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Backslides

Reliability Failure Modes
How Dendrites Effect SIR Readings