No-Clean Flux Activity under Low Standoff Components

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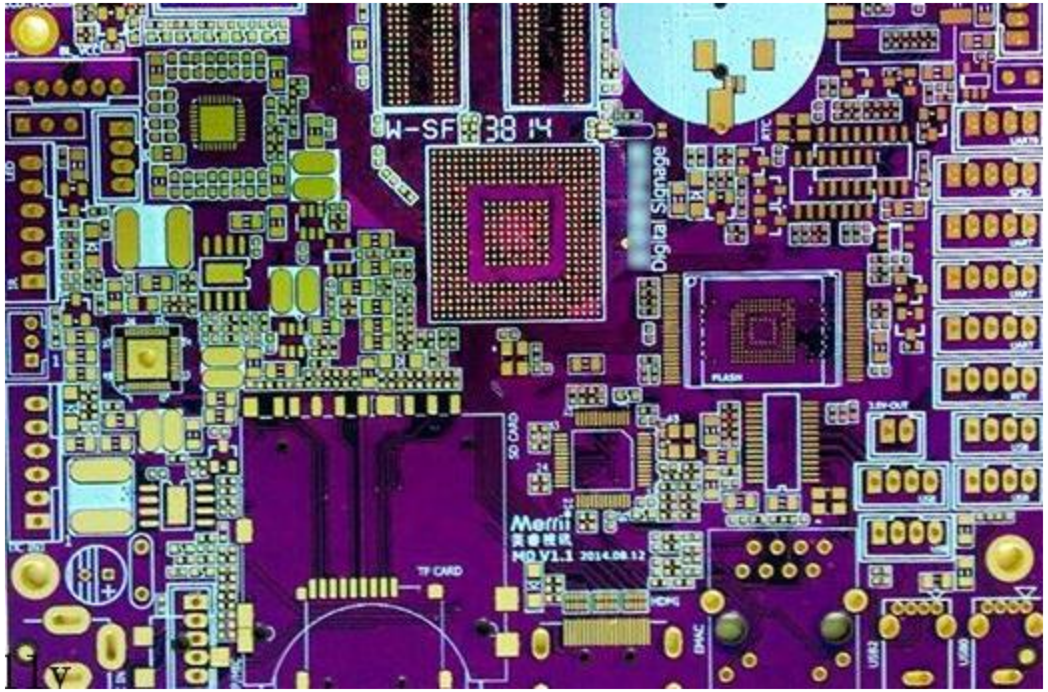
Electronic Devices

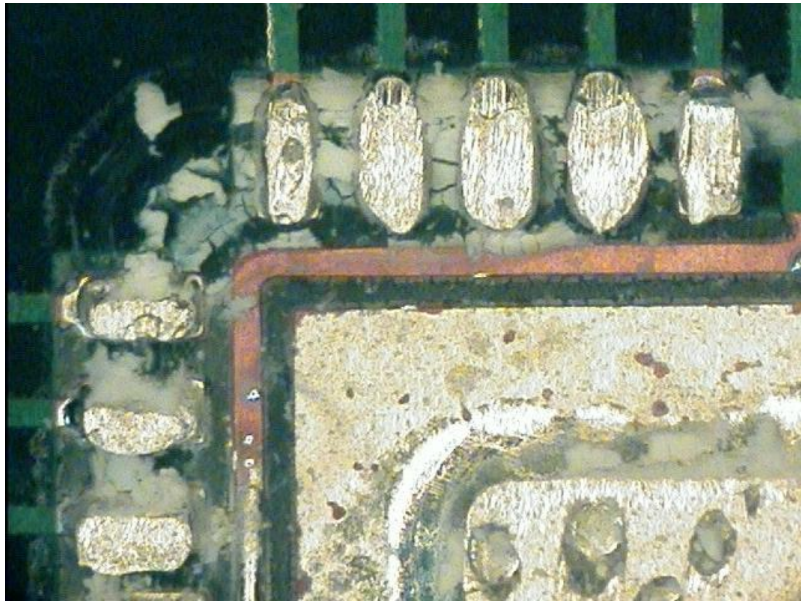
- More complex architectures and larger form factors
- Creates obstacles and challenges for
  - Partial activation
  - Outgassing



https://www.linkedin.com/pulse/high-density-interconnect-printed-circuit-board-pcb-sally-fang

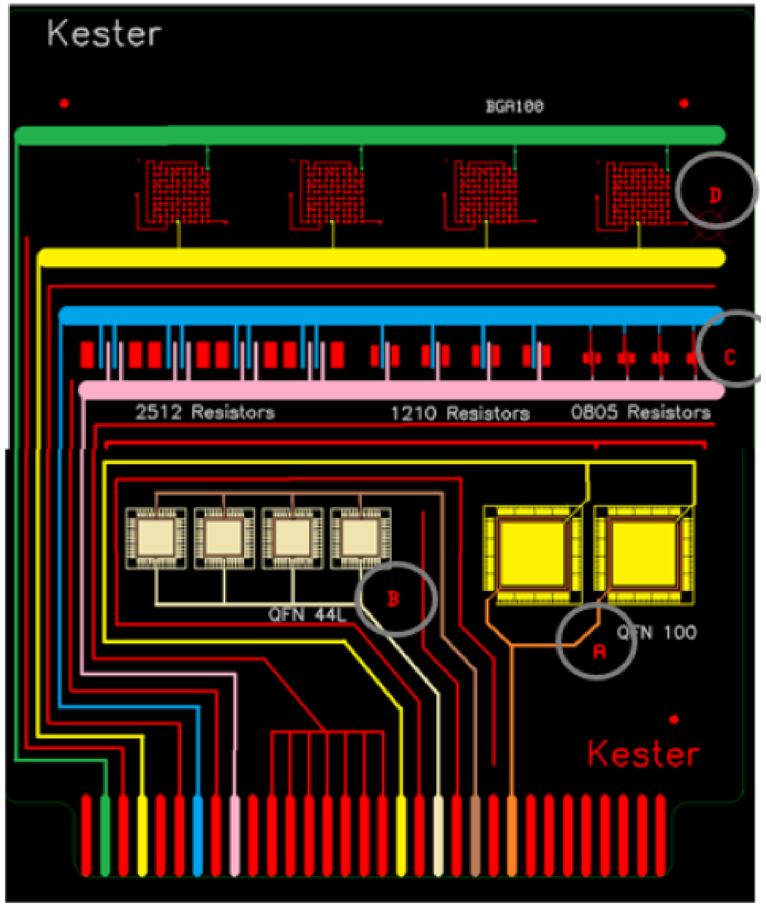
Leadless Components

- Low standoff gaps
- High number of interconnects
- Large solder mass under the component termination
- Poor outgassing channels
- Residues trapped under low standoff components
    - May not reach proper activation temperatures
    - No-clean residue may be active



Research Purpose

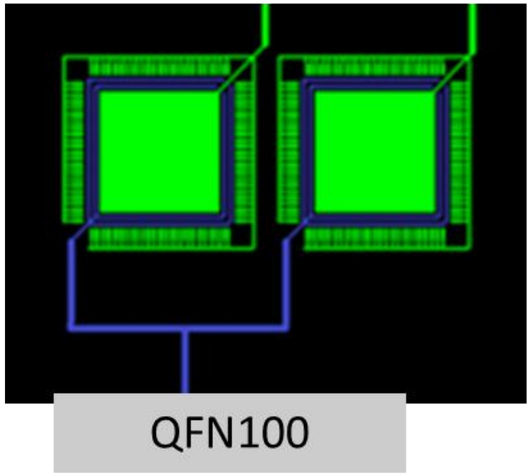
- Study the influence of flux activators under low standoff components
  - 4 Activator types
    - Halogen based: Ionic and Covalently bonded
    - Halogen-free : Two Zero-Halogen Packages
  - 2 Reflow conditions
  - 3 Residue cleaning stages
    - Not cleaned / Partially cleaned /Totally cleaned
  - 3 component types
    - BGA 100 (0.8mm pitch)
    - Resistors 2512, 1210, 0805
    - QFN44, QFN100
- Customized test board
  - In-situ SIR measurements under components

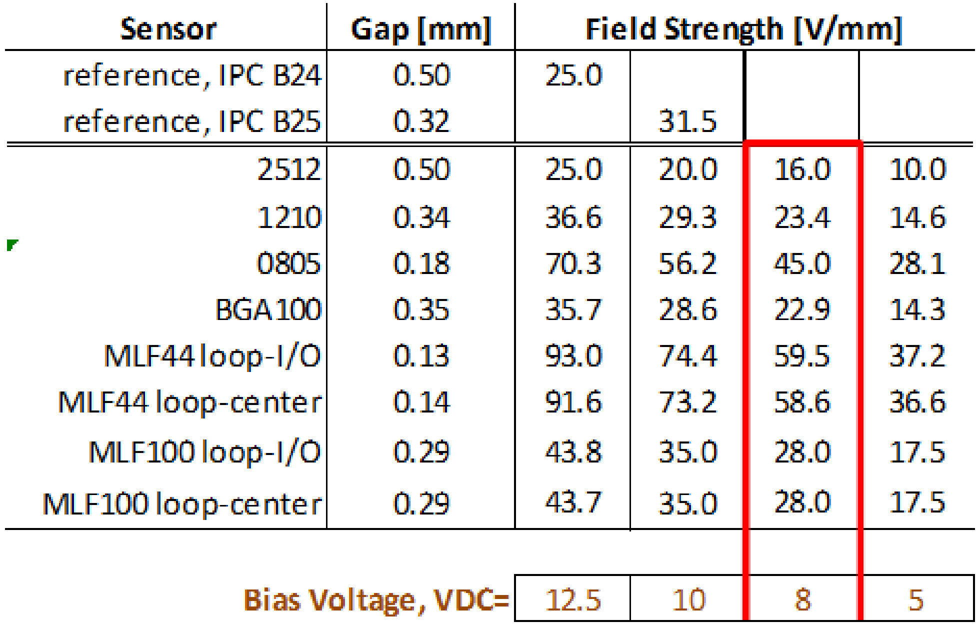


EXPERIMENTAL

SIR Flux Reliability Test Board

- The IPC SIR test method using the open format B24 pattern directs the user to setup measurement systems to obtain an electrical field strength between the positive and negative traces (gaps) to 5V for 200um of spacing (25V/mm)
- The table below shows a variety of field strengths for the IPC standard boards and the DoE board at different voltage conditions.





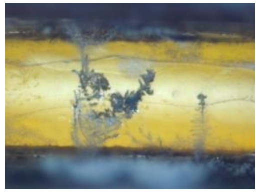
Sensor	Gap [mm]	Field Strength [V/mm]			
reference, IPC B24	0.50	25.0			
reference, IPC B25	0.32		31.5		
2512	0.50	25.0	20.0	16.0	10.0
1210	0.34	36.6	29.3	23.4	14.6
0805	0.18	70.3	56.2	45.0	28.1
BGA100	0.35	35.7	28.6	22.9	14.3
MLF44 loop-I/O	0.13	93.0	74.4	59.5	37.2
MLF44 loop-center	0.14	91.6	73.2	58.6	36.6
MLF100 loop-I/O	0.29	43.8	35.0	28.0	17.5
MLF100 loop-center	0.29	43.7	35.0	28.0	17.5
	Bias Voltage, VDC=	12.5	10	8	5

No-Clean Solder Pastes

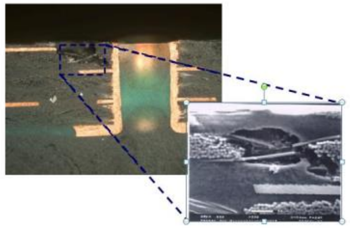
- No-Clean Fluxes
  - Chemical residues left inside the assembly
- Reliability depends on
  - Reactivity of no-clean post-reflow residues
  - Environmental stress

Corrosion

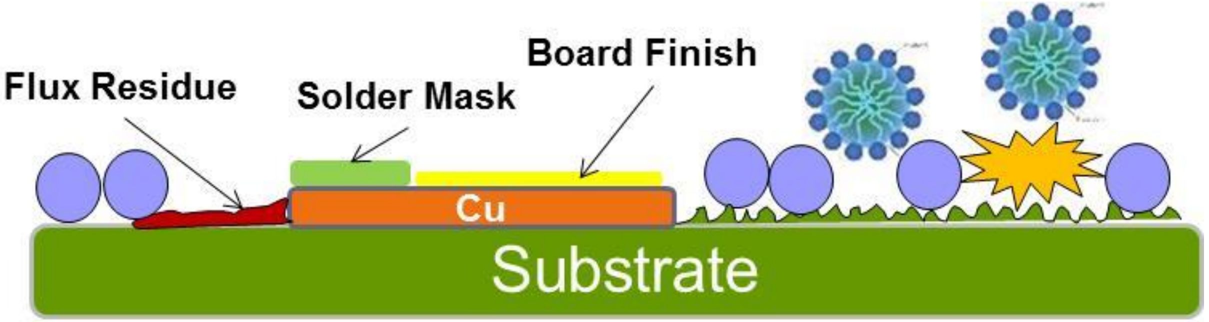
Electrochemical Migration

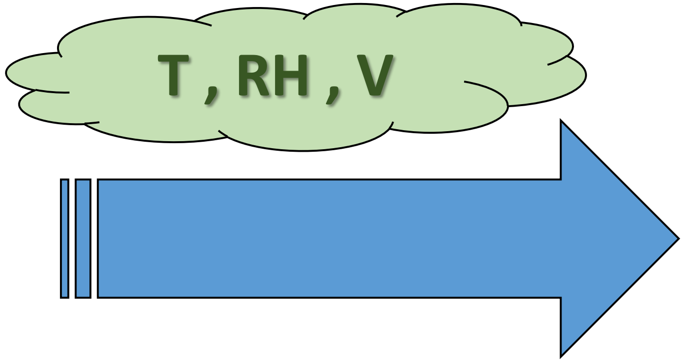


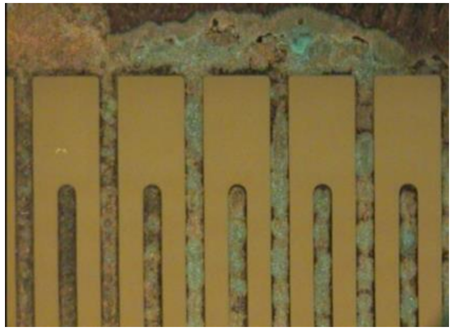
Conductive Anodic Filaments (CAF)



Creep Corrosion







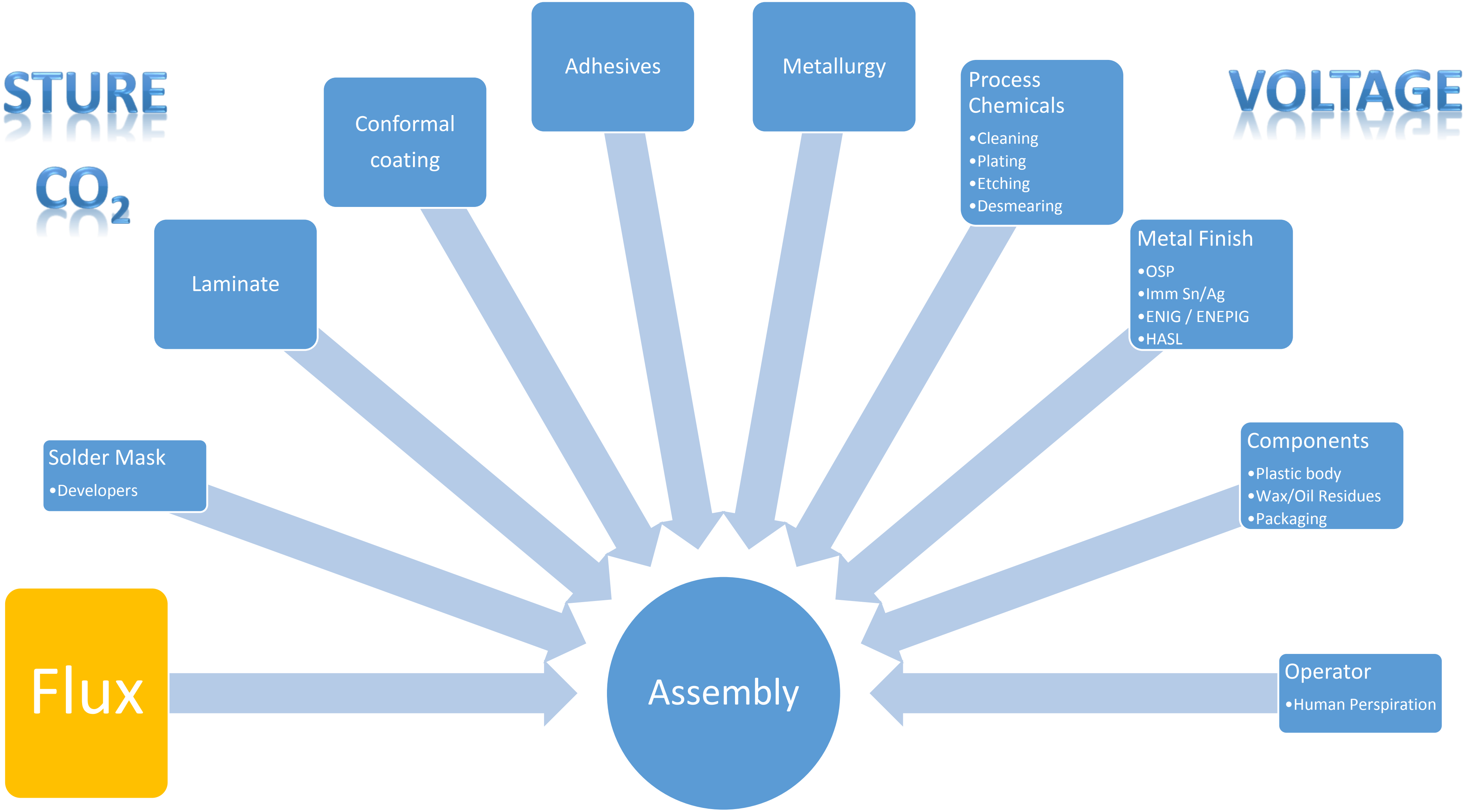
Chemical Complexity of a PCB

MOISTURE

SO_2 **CO_2**

NO_X

VOLTAGE BIAS



Conformal coating

Adhesives

Metallurgy

Process Chemicals
- Cleaning
- Plating
- Etching
- Desmearing

Laminate

Metal Finish
- OSP
- Imm Sn/Ag
- ENIG / ENEPIG
- HASL

Solder Mask
- Developers

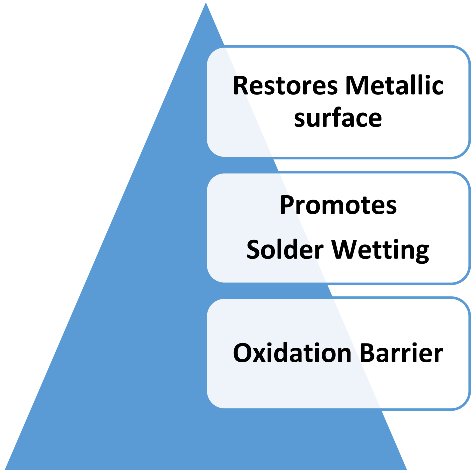
Components
- Plastic body
- Wax/Oil Residues
- Packaging

Flux

Assembly

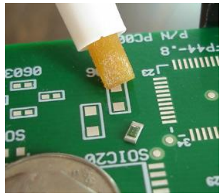
Operator
- Human Perspiration

Flux components


Restores Metallic surface

Promotes Solder Wetting

Oxidation Barrier



Solvents

Alcohols

Water

High T solvent for fluxing byproducts
Metal protection

Remove surface metal oxidation

Activators

Organic acids,
Rosin,
Amines, Halogens

Fluxes

Vehicle

Rosin

Polyglycols

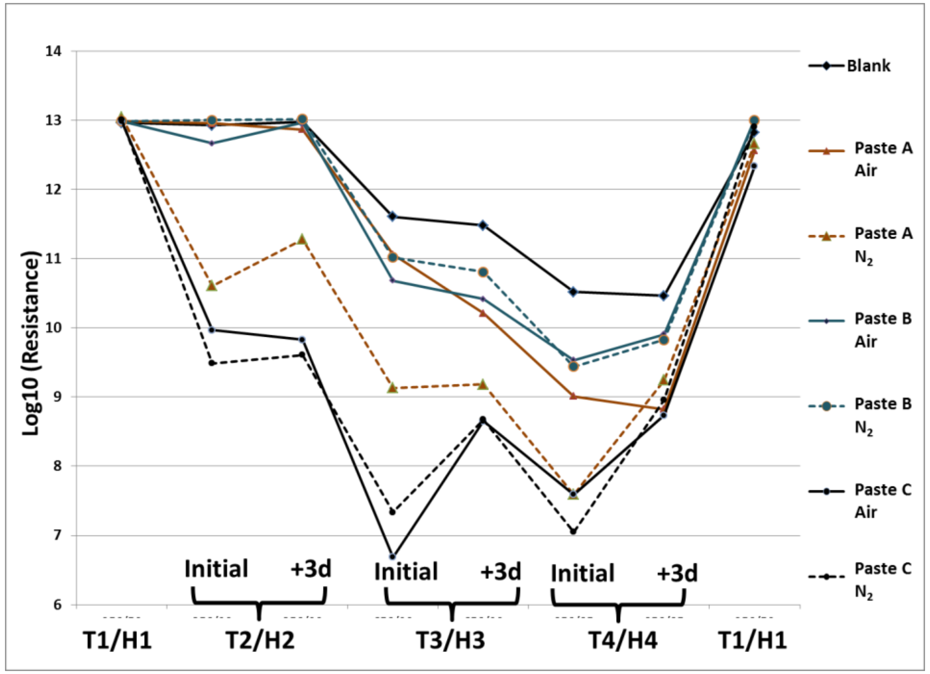
Thermal conduction
Solder Flow

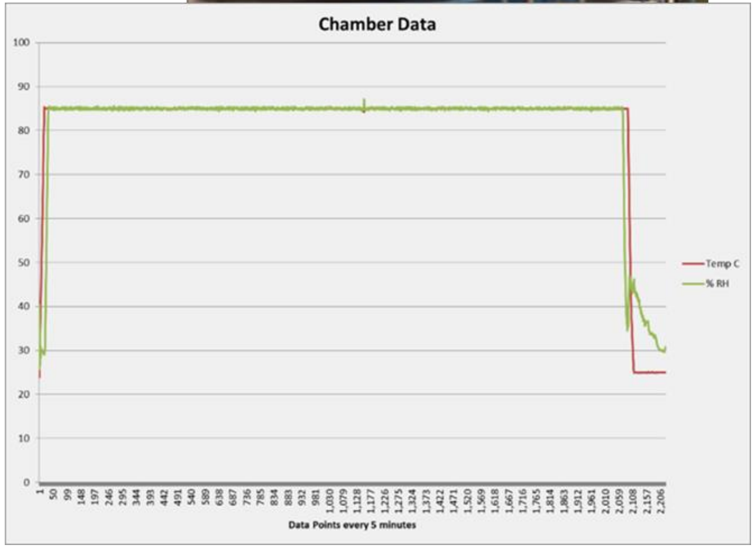
Additives

Rheological additives,
Surfactants, Dispersants,
Corrosion inhibitors

SIR Test Parameters

Test Coupon: Kester Flux Reliability Test Board
Bias: 8 volts
Test Voltage: 8 volts
Temperature: 85°C
Humidity: 85% RH
Measurement Interval: every 20 minutes at condition
Test Duration: 7 Days (168 hours)

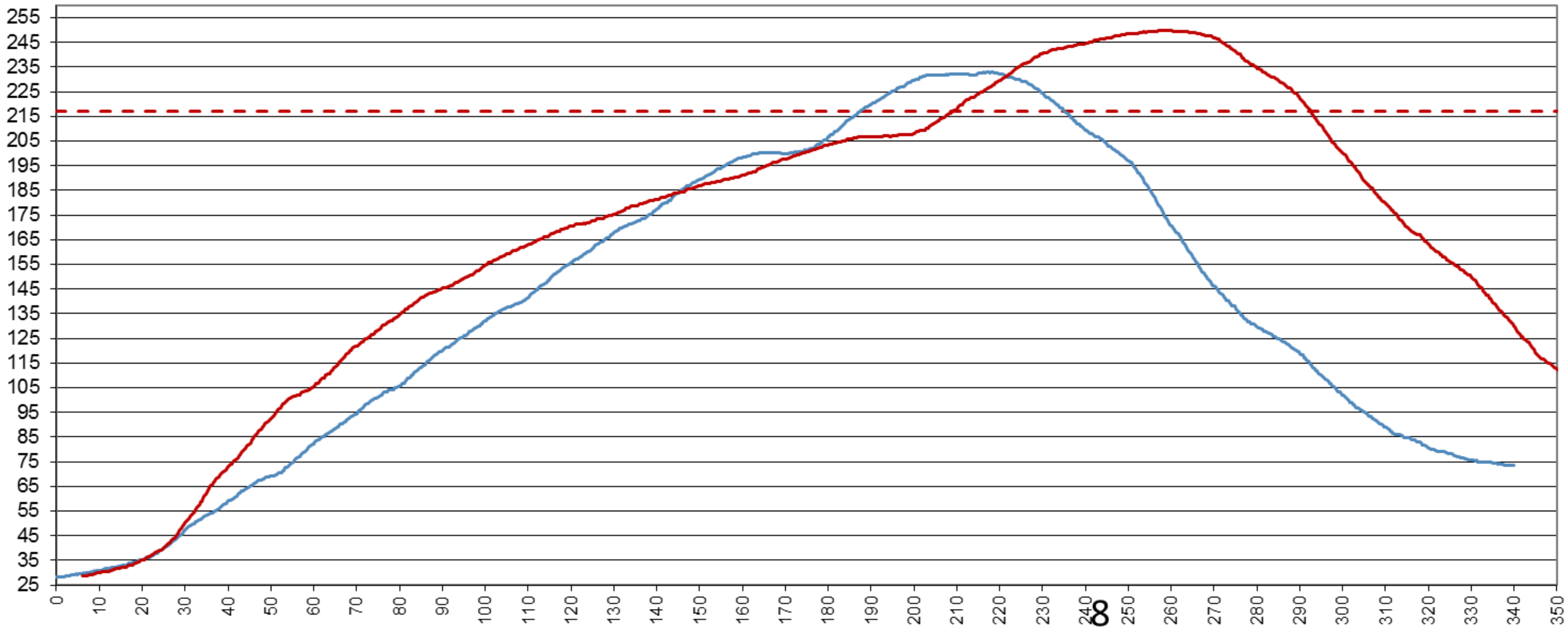




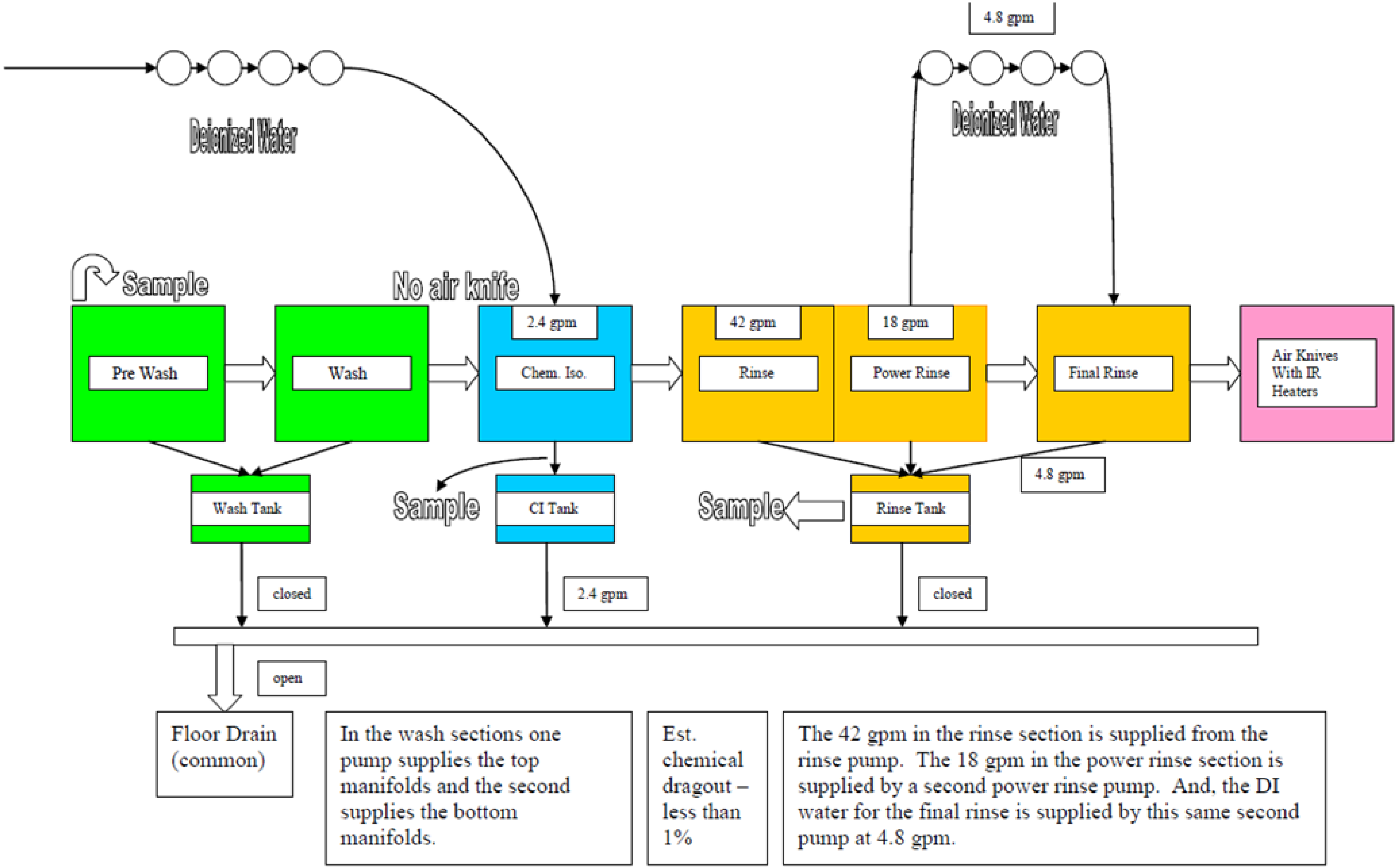
Temperature is ramped before humidity elevated to avoid reaching the dew point. Inverse applies to the recovery ramp down

Reflow Profiles

- Two different reflow conditions were used with the intent to subject the flux resides to low and high heating conditions



Cleaning Tool Setup



In the wash sections one pump supplies the top manifolds and the second supplies the bottom manifolds.

Est. chemical dragout – less than 1%

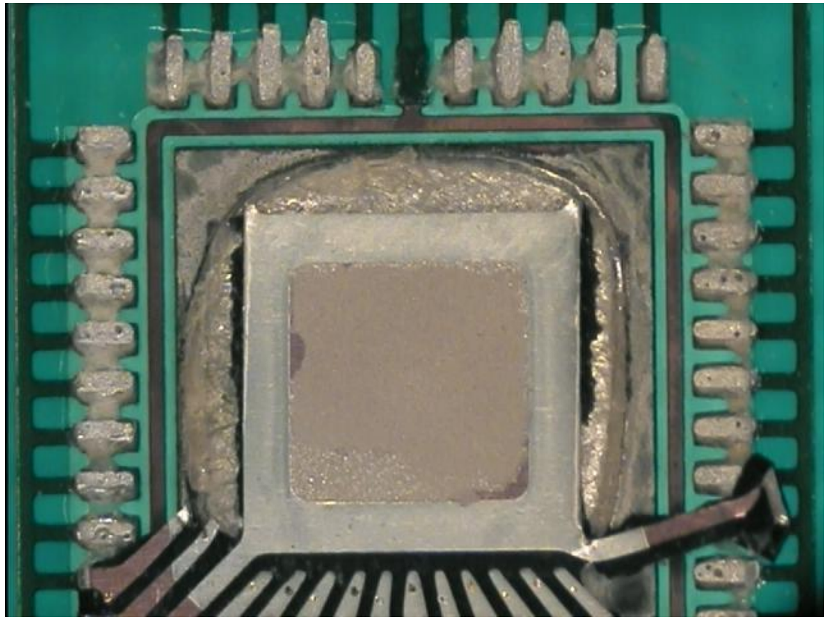
The 42 gpm in the rinse section is supplied from the rinse pump. The 18 gpm in the power rinse section is supplied by a second power rinse pump. And, the DI water for the final rinse is supplied by this same second pump at 4.8 gpm.

Cleaning Parameters

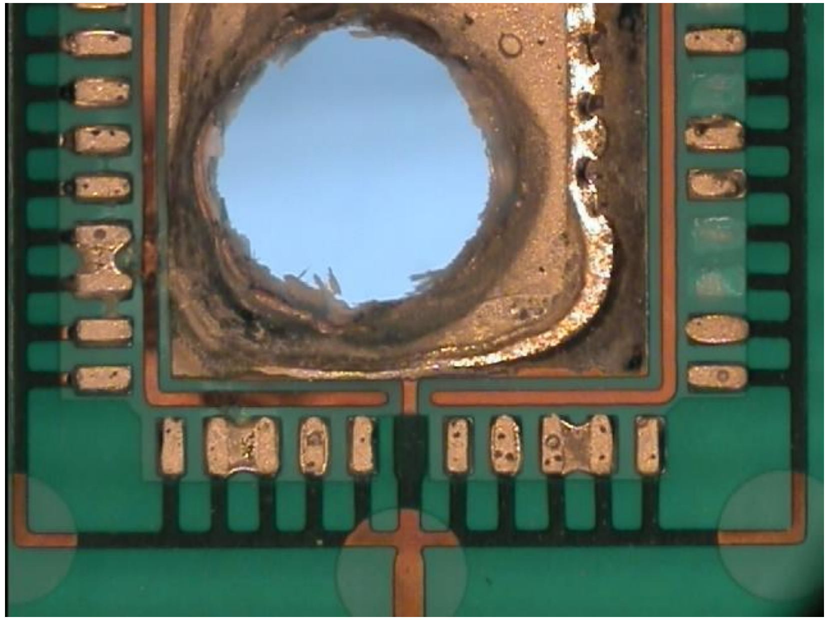
- Cleaning Conditions
  - No-Cleaning
  - Partial Cleaning
    - Inline spray-in-air, 2 FPM, 3 min wash
  - Total Cleaning
    - Inline spray-in-air, 0.5 FPM, 10 minute wash
- Wash Temperature: 65°C
- Subset of parts where removed during setup to assure partial and total cleaning effects

RESULTS AND DISCUSSION

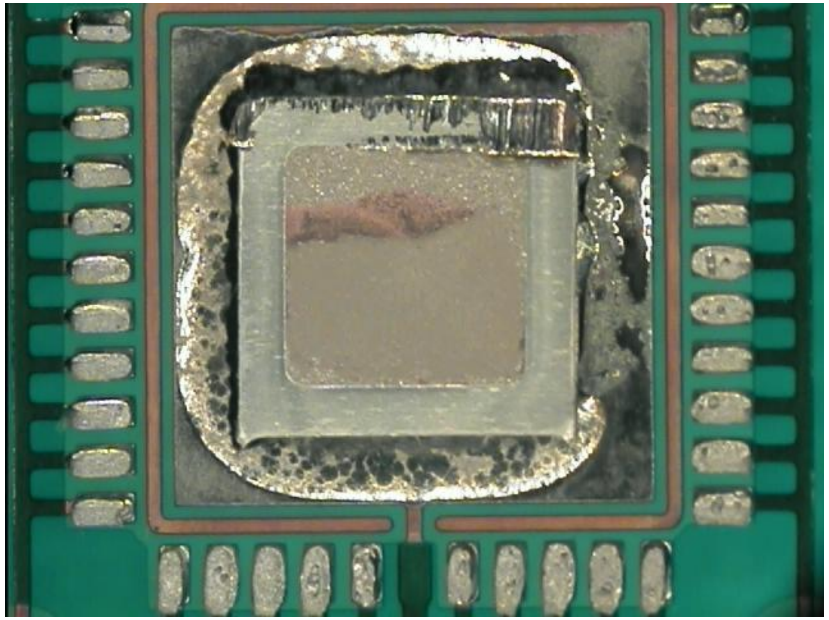
Flux Residue



Not Cleaned



Partially Cleaned



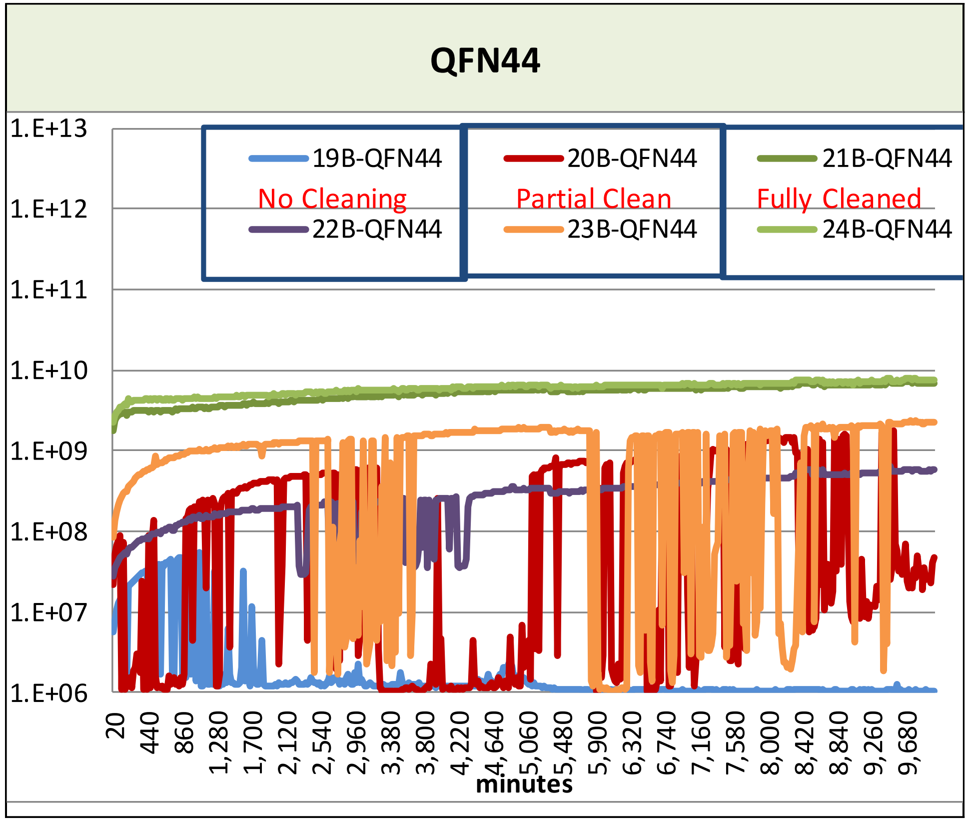
Totally Cleaned

Activator #4

$$CuO + 2HCl = CuCl_2 + H_2O$$

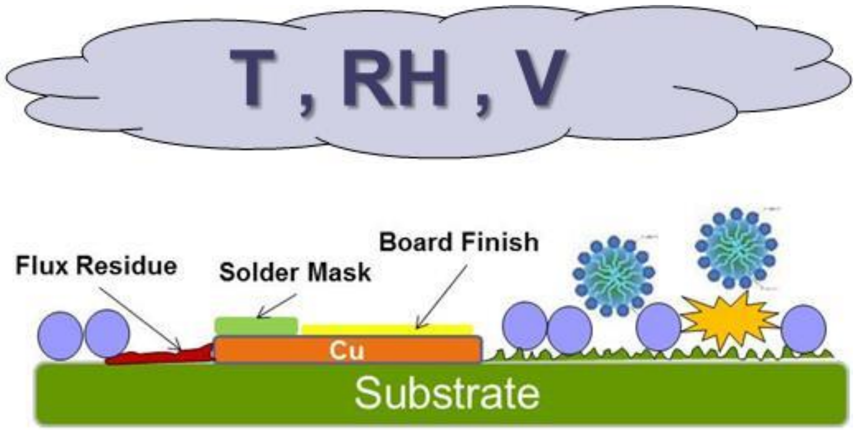
$$Cu_2O + 2HCl = CuCl_2 + Cu + H_2O$$

- Halide based solder paste
  - Ionic form of Halogens (R.HCl)
  - Large doping levels (>1,500ppm)



- Worst reliability under components of the four solder pastes tested
  - Chlorine based residues
  - Electrochemical activity independent of reflow conditions

Reliability fundamentals



- Why do halide generate active residues ?

1. Highly Ionic
2. Environmental interactions
   - Moisture Absorption
   - Hydrolysis
   - Carbonation
3. Corrosion of Metallic compounds
   - Oxidation
   - Complexation

$CuCl_2 + 2H_2O \rightarrow CuCl_2.2H_2O \rightarrow Cu(OH)_2 + 2HCl$

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

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

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

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

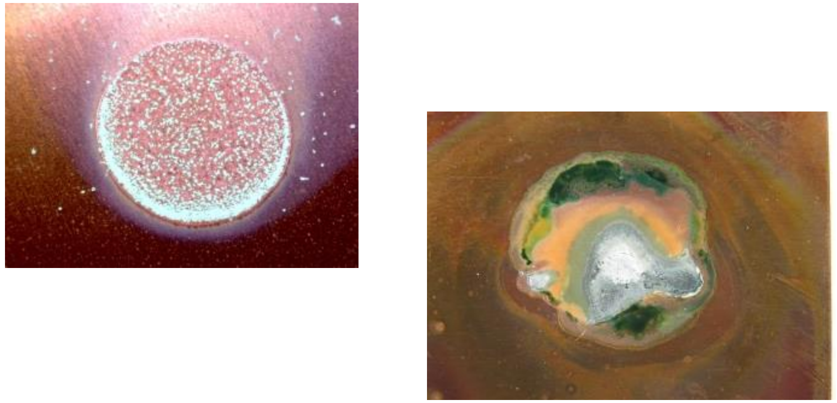
$Cu + Cl^- \rightarrow CuCl + e^-$ $[E_0=0.14V]$

Strong Cu complexes catalyze
Metal corrosion

Activator #4

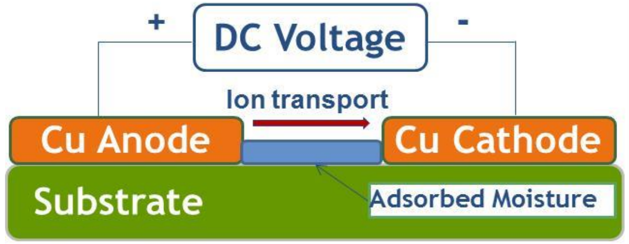
- Why do halide generate so active residues ?

Corrosion → Electrochemical Migration



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

Strong Cu complexes catalyze metal corrosion



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

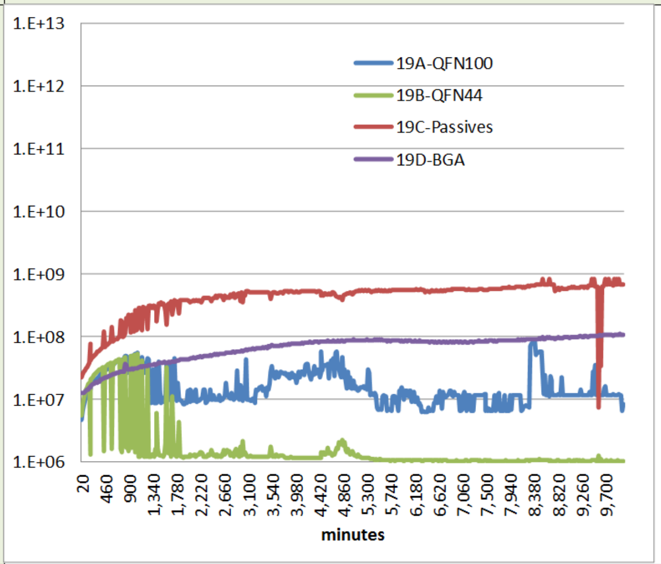
Halides generate a large array of stable complexes

Activator #4

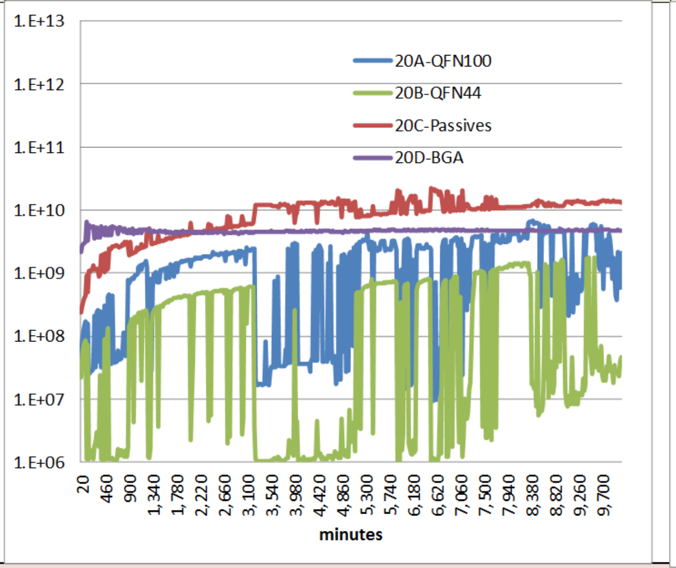
Processing impacts

Activator 4 Ramp to Spike

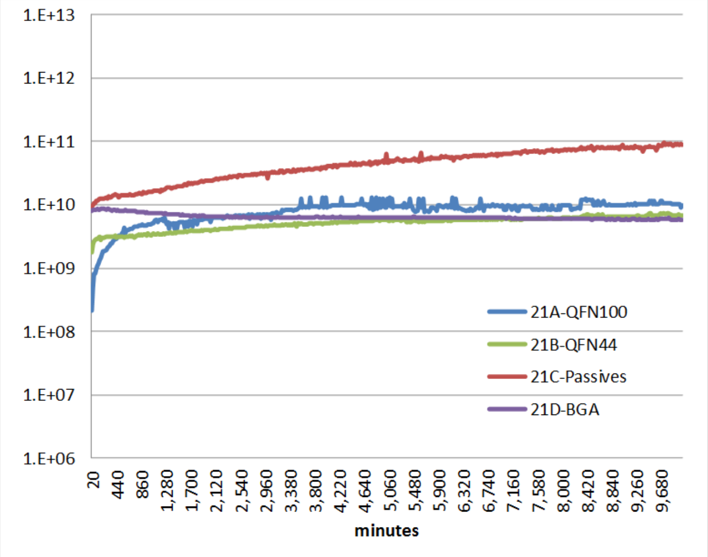
NoCleaning



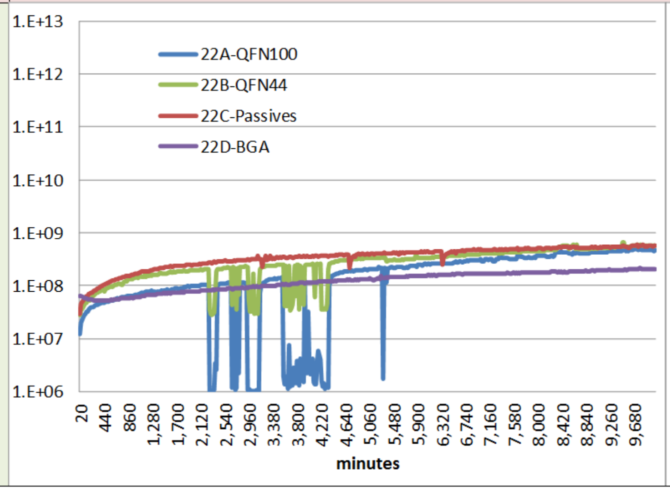
Cleaning 2 FPM / 3min

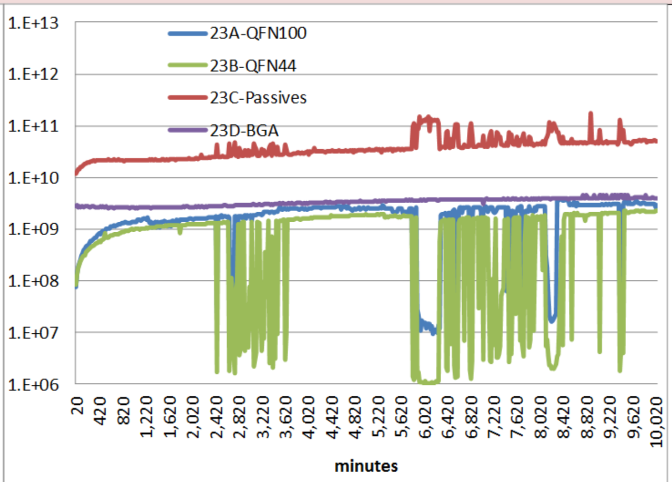


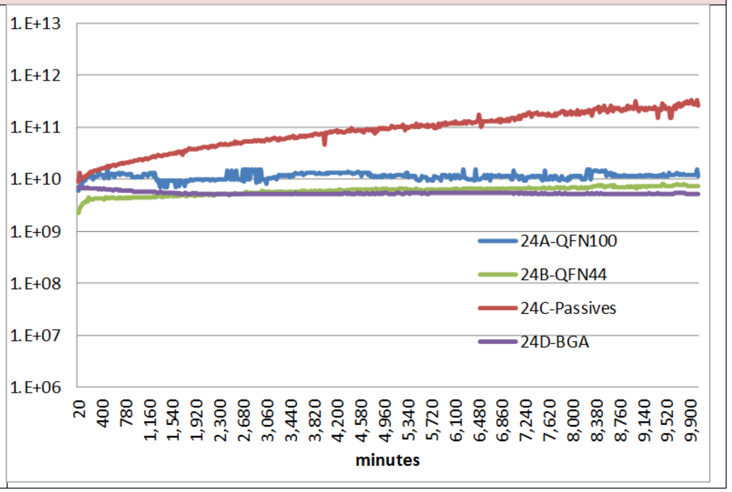
Cleaning 0.5 FPM / 10 min



Activator 4 Soak





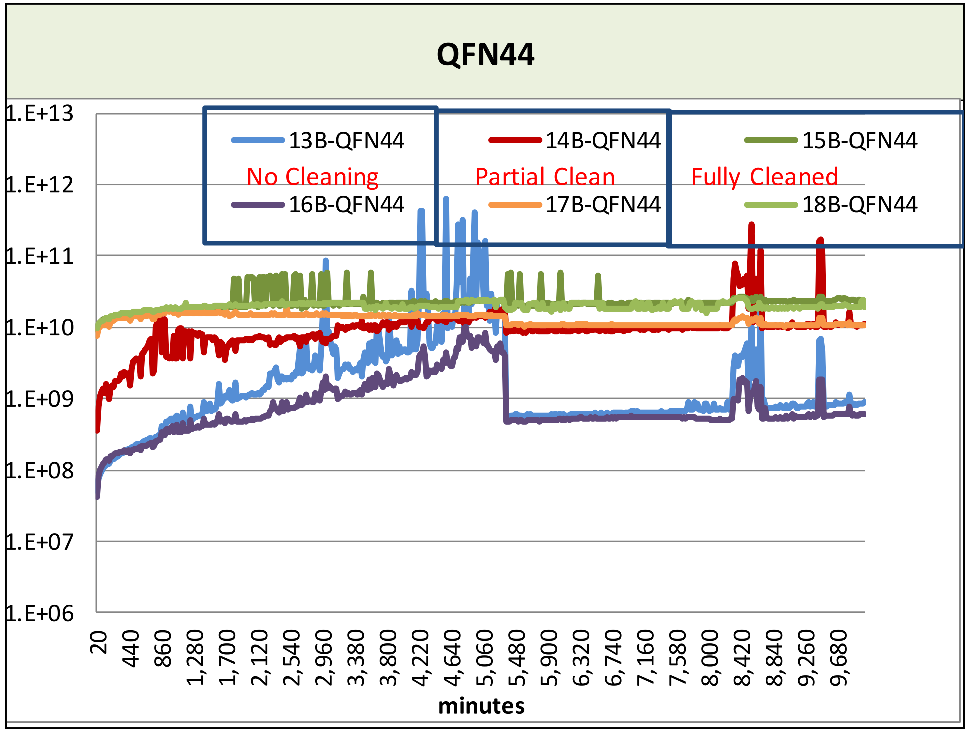


Activator #3

$$CuO + 2HBr \rightarrow CuBr_2 + H_2O$$
$$Cu_2O + 2HBr = CuBr_2 + Cu + H_2O$$

- Halogen based solder paste
  - Halogenated Organic Compounds (R-Br)
  - Large doping levels (>1,500ppm)

- Best reliability under components of the four solder pastes tested
  - Interplay between processing conditions
    and end use environments

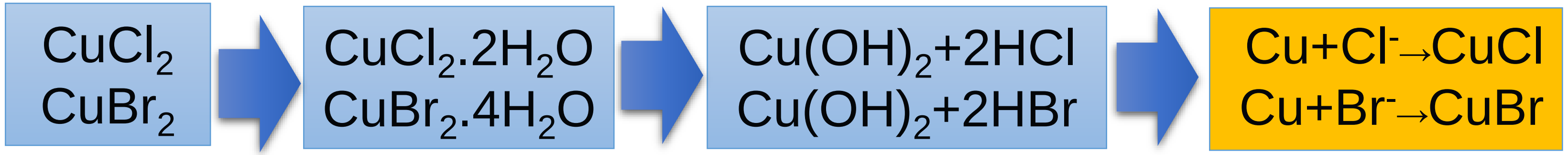


Activator #3

$$CuO + 2HBr \rightarrow CuBr_2 + H_2O$$

$$Cu_2O + 2HBr = CuBr_2 + Cu + H_2O$$

- Why did brominated organic components generate safer residues ?
  - Similar Chemistries and physicochemical properties



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

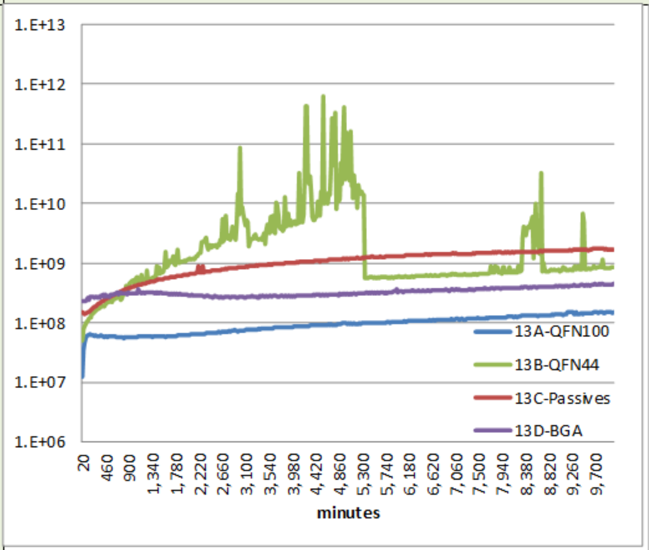
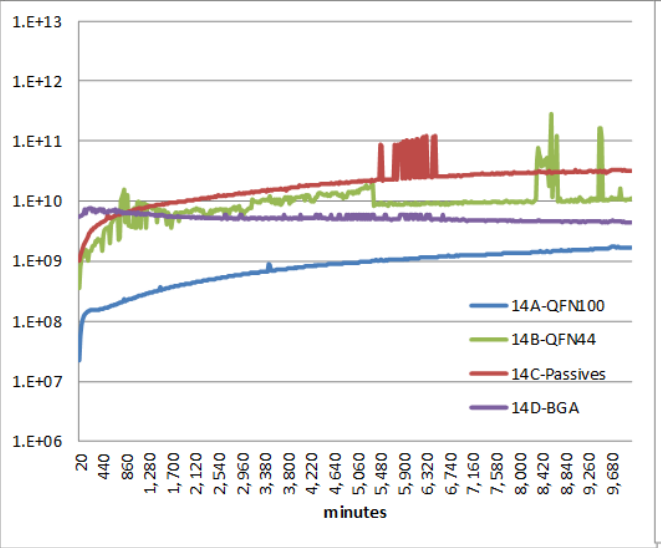
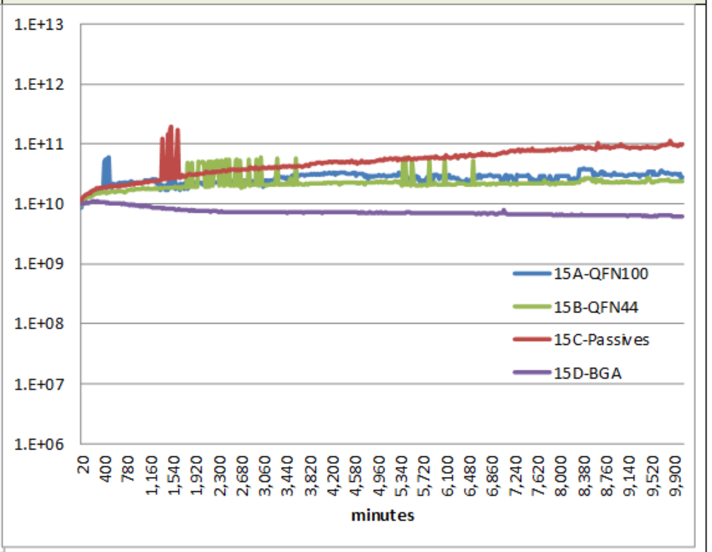
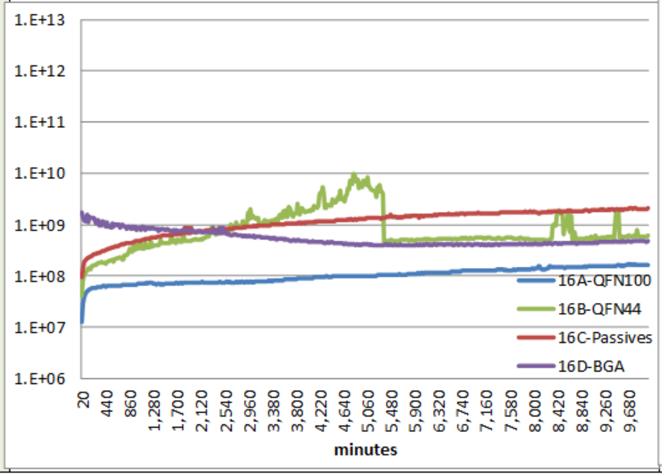
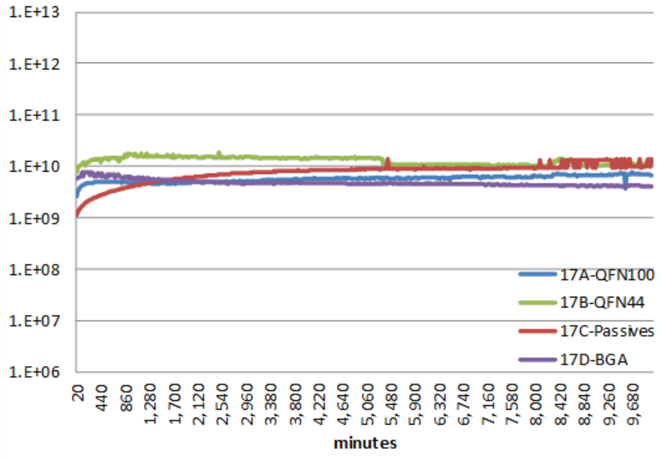
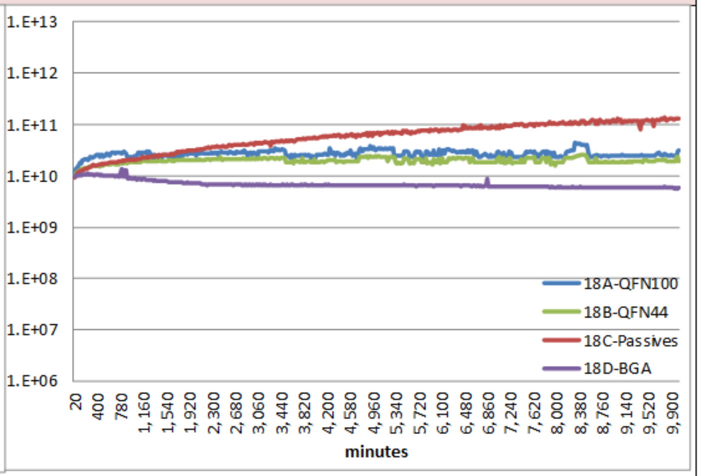
- Fundamental differences
  - Lower ionicity
  - Halogens are “trapped” in a covalent bond
    - Inert species when unreacted

  - Brominated organic species have much lower heat stability

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

Activator #3

Processing impacts

	NoCleaning	Cleaning 2 FPM / 3min	Cleaning 0.5 FPM / 10 min
Activator 3 Ramp to Spike			
Activator 3 Soak			

Activator #2

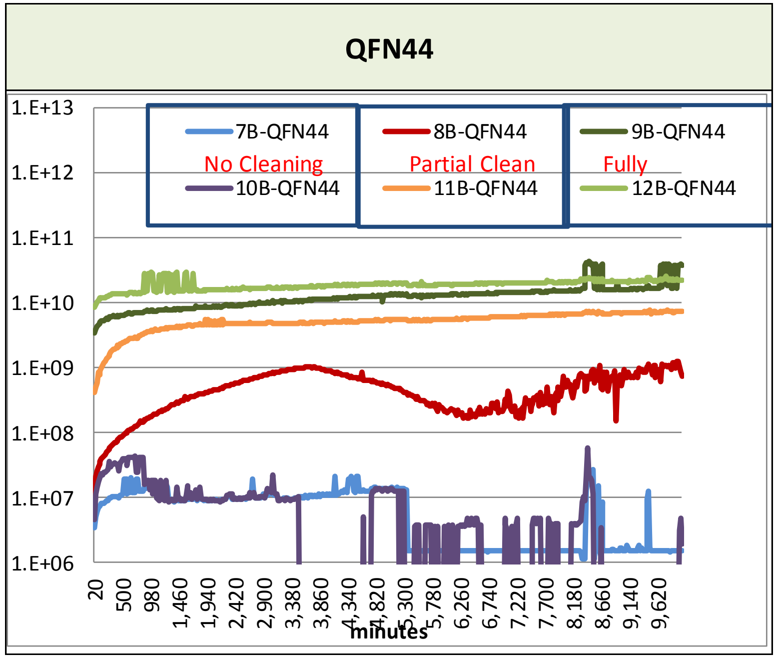
$$CuO + 2RCOOH = Cu(RCOO)_2 + H_2O$$

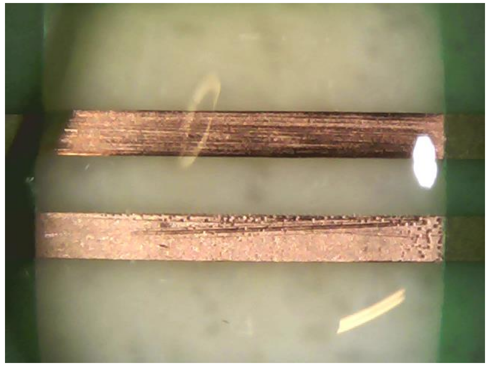
$$Cu_2O + 2RCOOH = Cu(RCOO)_2 + Cu + H_2O$$

- Zero-halogen Solder Paste
  - Substitution of the halogenated activators by a blend of
    - Weak organic acids (RCOOH)
    - Organic amines (RNH_2, RR'NH, RR'R"N)

- This solder paste had the
  - Worst reliability of the four solder pastes tested in uncleaned conditions

Zero-halogen activator packages can be a source of electrochemical migration





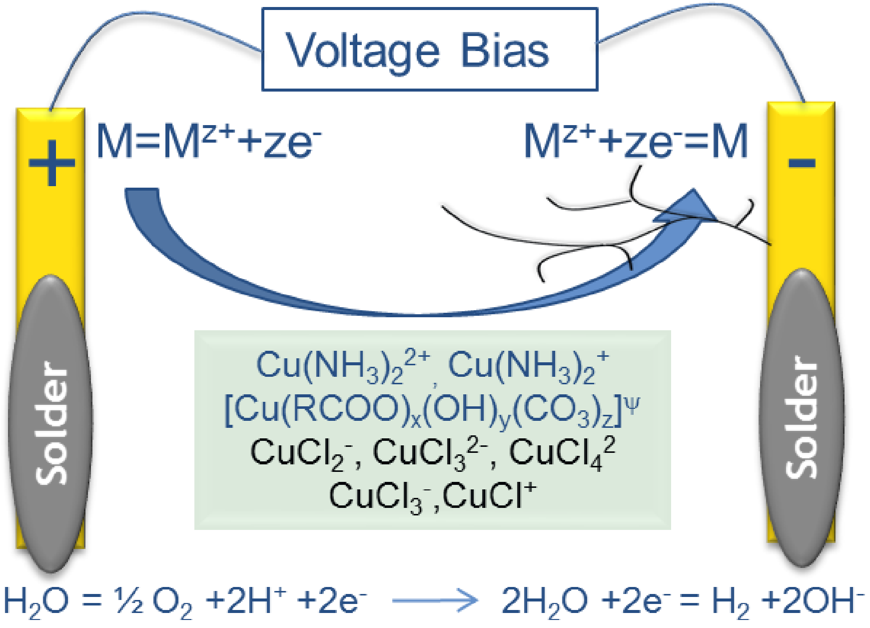
Reliability Fundamentals

- Chemical Impacts on Electrochemical Migration – Zero-Halogen

1. Electrolytic Path formation
   - Residue hygroscopicity and ionicity
2. Electrodissolution
   - Flux corrosiveness
3. Ion Transport
   - Stabilization of charged complexes
4. Electrodeposition
   - Complex reduction at the cathode
5. Dendritic Growth
   - Diffusion-driven from complex supply

$Cu(RCOO)_2 + xH_2O + yCO_2$
$= Cu(RCOOH)_{2-x}(OH)_y(CO_3)_z + xRCOOH$

$Cu + 2RCOO^- \rightarrow Cu(RCOO)_2 + 2e^-$



Voltage Bias

$M = M^{z+} + ze^-$

$M^{z+} + ze^- = M$

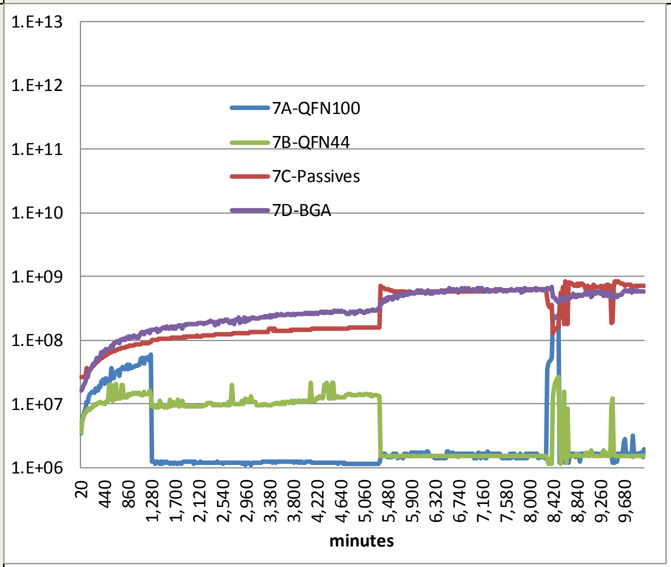
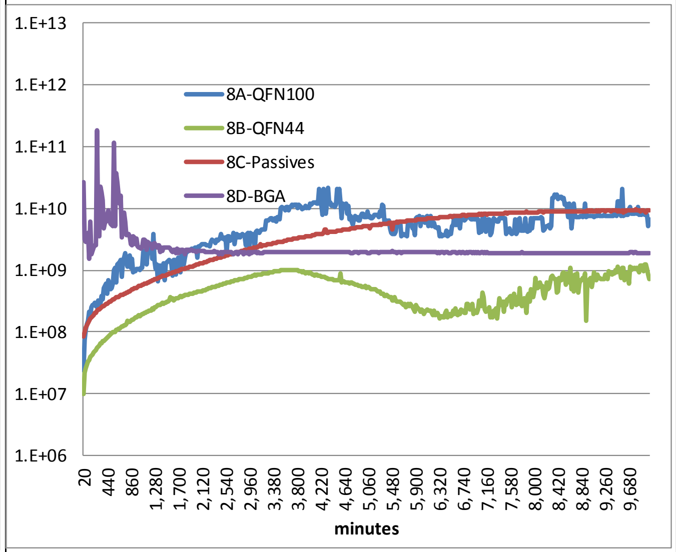
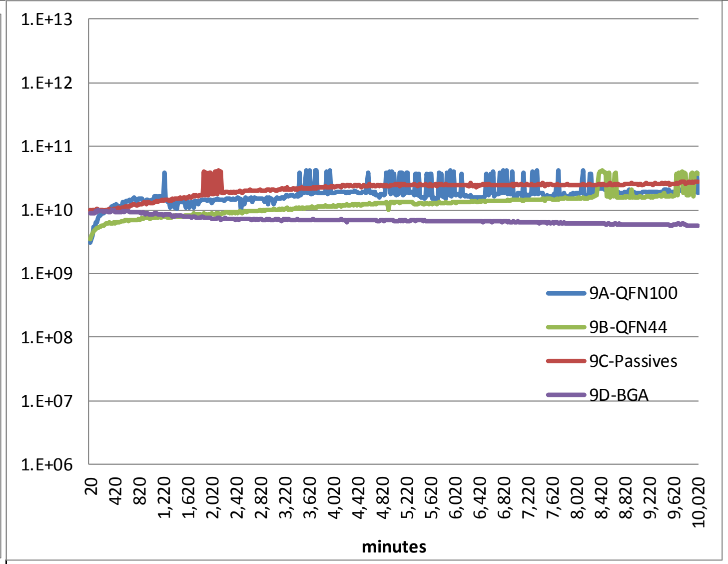
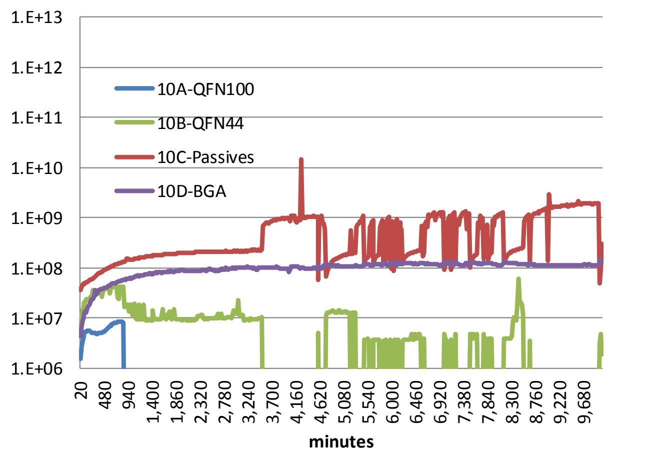
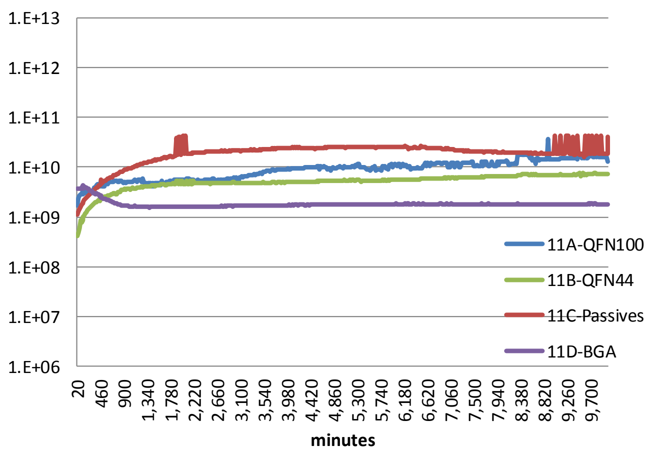
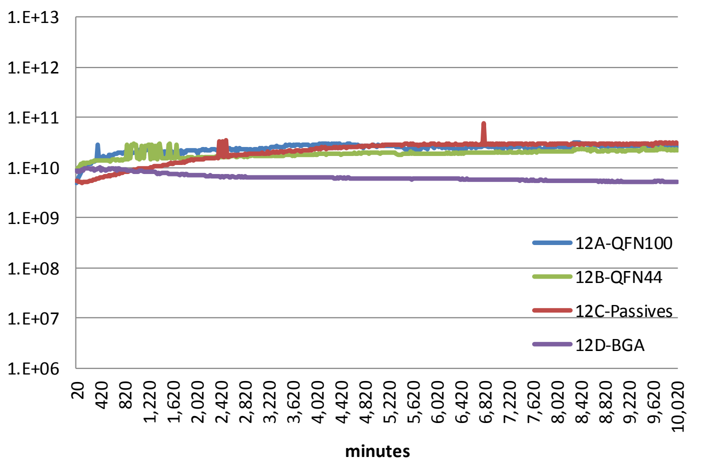
$Cu(NH_3)_2^{2+}, Cu(NH_3)_2^+$
$[Cu(RCOO)_x(OH)_y(CO_3)_z]^\psi$
$CuCl_2^-, CuCl_3^{2-}, CuCl_4^2$
$CuCl_3^-, CuCl^+$

$H_2O = ½ O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O + 2e^- = H_2 + 2OH^-$

3 Basic ingredients : Moisture, Voltage bias, Ions

Activator #2

Processing impacts

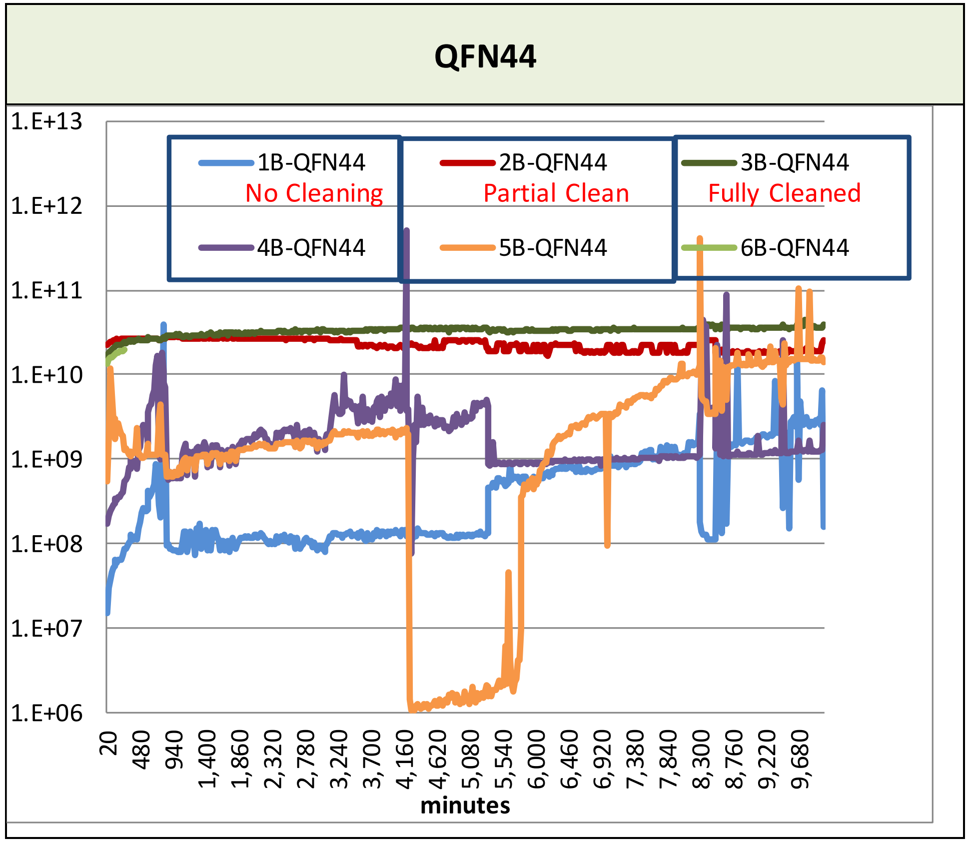
	NoCleaning	Cleaning 2 FPM / 3min	Cleaning 0.5 FPM / 10 min
Activator 2 Ramp to Spike			
Activator 2 Soak			

Activator #1

$$\mathrm{CuO + 2RCOOH = Cu(RCOO)_2 + H_2O}$$

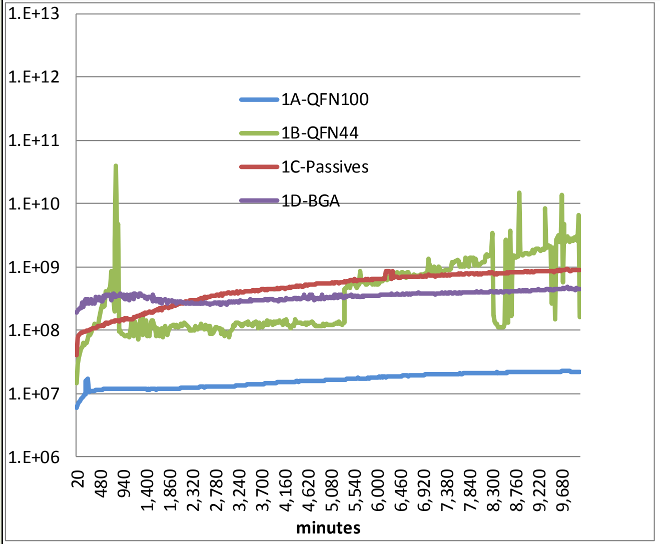
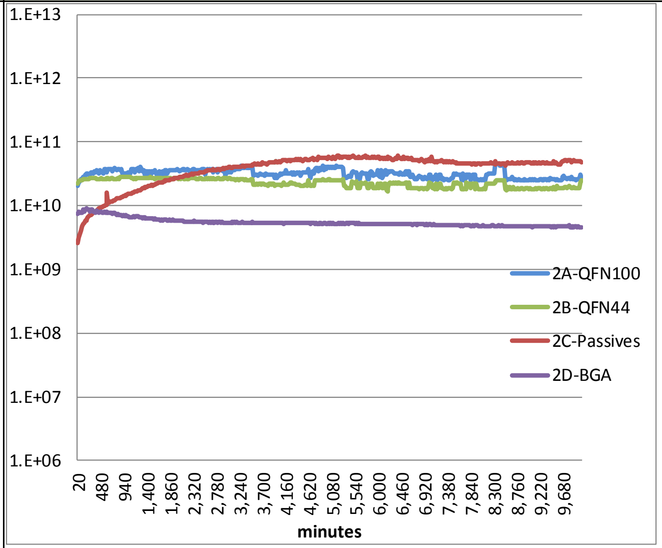
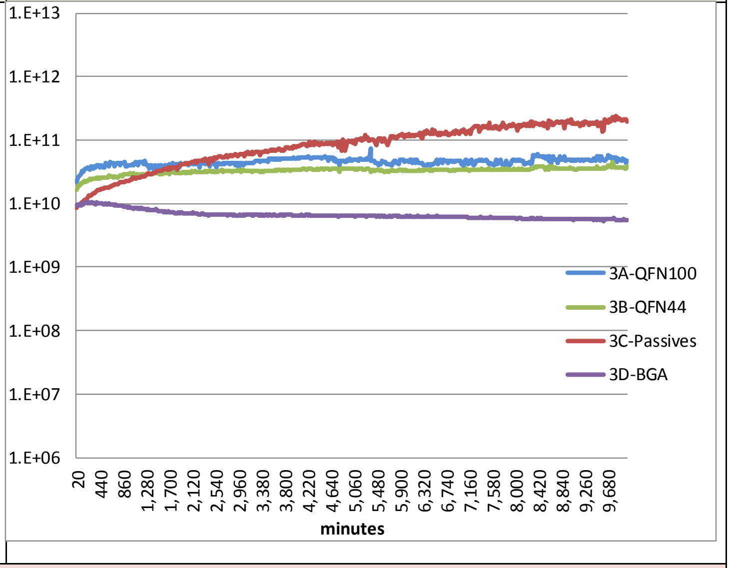
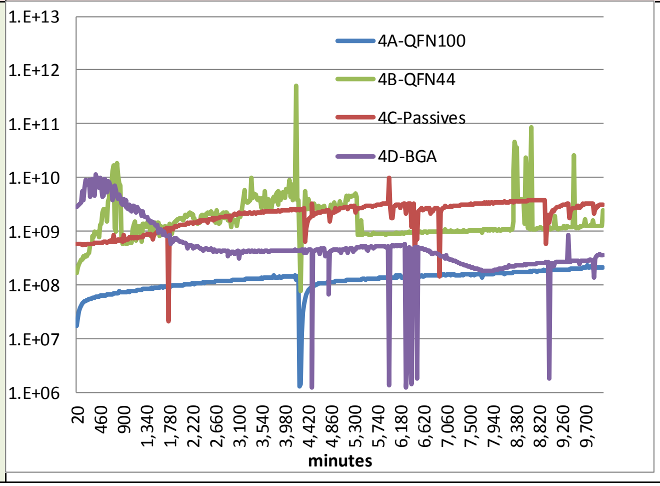
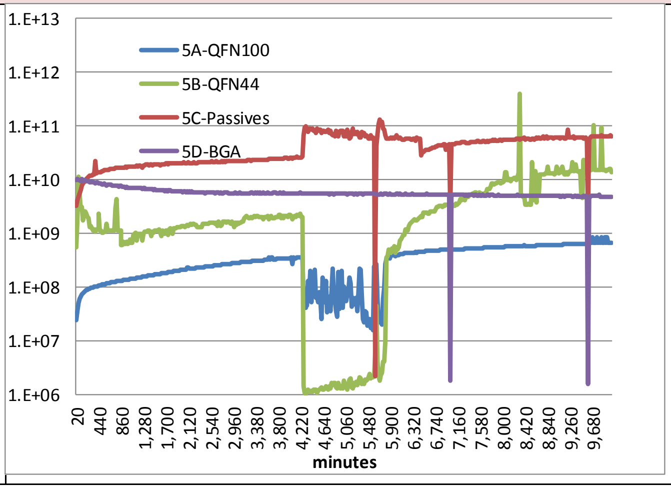
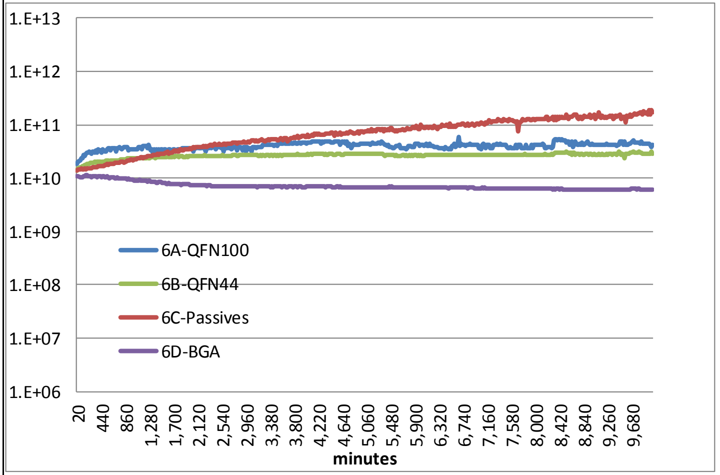
$$\mathrm{Cu_2O + 2RCOOH = Cu(RCOO)_2 + Cu + H_2O}$$

- Zero-Halogen solder paste
  - Optimized blend of:
    - Weak organic acids (RCOOH)
    - Organic amines (RNH_2, RR’NH, RR’R”N)
    - Corrosion inhibitors / antioxidants
- Significant reliability performance improvement under components compared to Zero-Halogen Activator #2
  - Interplay between processing conditions and end use environments



Activator #1

Processing impacts

	NoCleaning	Cleaning 2 FPM / 3min	Cleaning 0.5 FPM / 10 min
Activator 1 Ramp to Spike			
Activator 1 Soak			

CONCLUSIONS

Flux Activators effects

- Activator types can influence the effect on resistance and current leakage
  - Activator packages are designed to react with metallic oxides but can also induce corrosion and electrochemical migration
- Safe residues requires
  - Hydrophobicity ~ do not attract moisture
  - The “right” chemistry: metal complexation effects
    - A zero-halogen activator package is not a guarantee for reliability
  - Volatilization or decomposition at peak reflow temperatures
    - Eliminate as much as possible active residues

Components effects

- Four component types tested
  - BGAs showed the highest reliability when residue was present
    - Higher standoff height allowed flux residue to outgas
  - Passive components exhibited some resistivity spikes but for the most part where reliability when residue was present
  - QFNs were not reliable when residue was present
- Outgassing channel
  - A no-clean flux can be active when there is no channel for the flux to outgas

Reflow Profile

- Most believe that a hotter profile is better for outgassing under low standoff components
  - The data from this study did not show evidence of this effect
- The reflow effect provided interesting findings
  - Zero-halogen activators appear to be more sensitive to reflow conditions
    - Attributed to the thermal instability of activators
  - Halogenated activators
    - Brominated activator showed higher potential to volatilize and outgas
    - Chlorine activator showed electrochemical activity for both soak and ramp-to-spike due to their inherent heat stability

Cleaning effects

- Partial Cleaning
  - Residue left under the component can be detrimental
  - Some activator types are more problematic than others
  - **Similar to partial activation of fluxes: Either you or clean well or you don’t**

- Total cleaning
  - Improves resistivity values systematically, regardless of the components/chemistries
  - Totally cleaned parts showed good results independent of the activator package
  - **Cleaning well can solve the problems of highly active fluxes**