Smart Chemistry Towards Highly Efficient Solder Material Formulation

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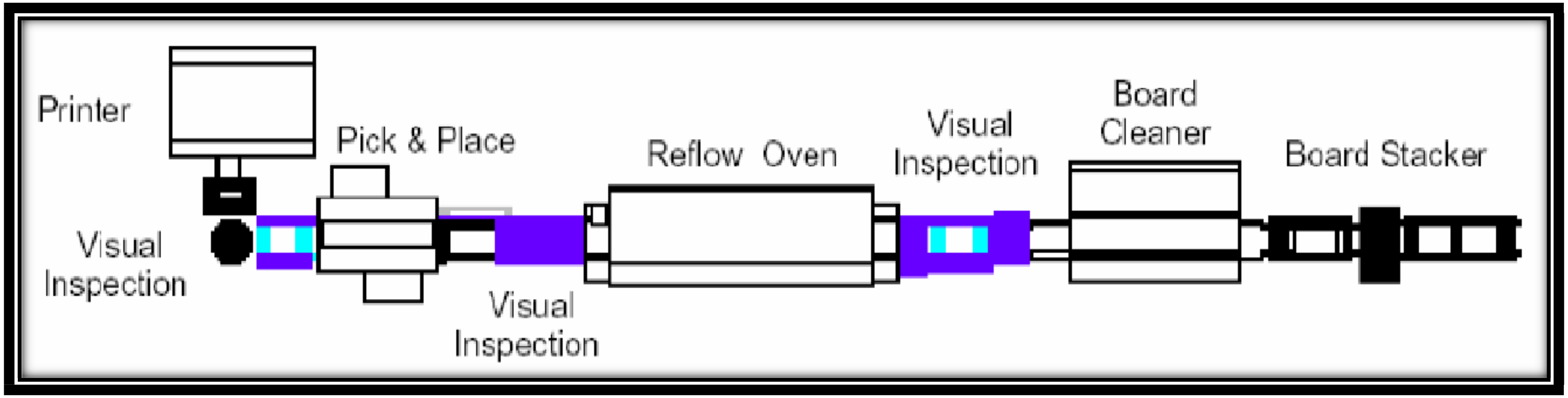
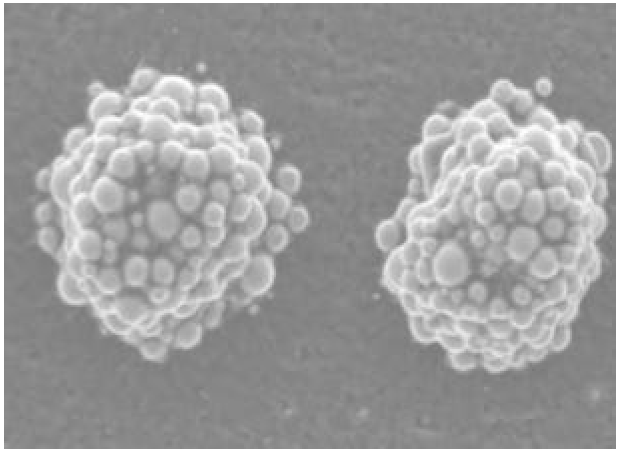
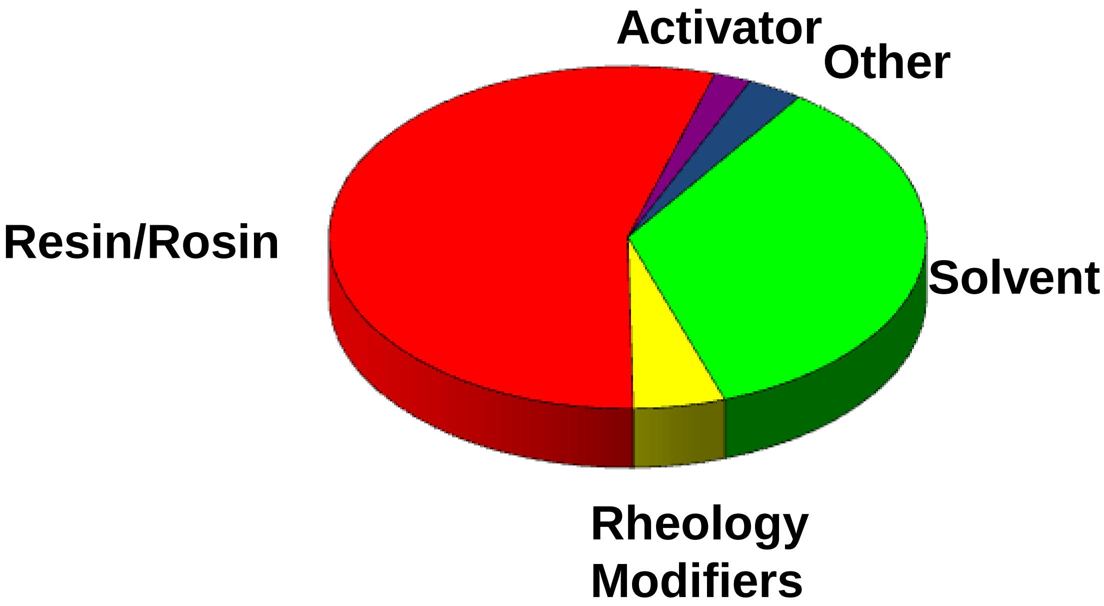
Outline/Agenda

- Introduction of Paste and Fluxing Chemistry
- Activator Properties
- Paste Performance
- Conclusions
- Acknowledgements
- Q & A

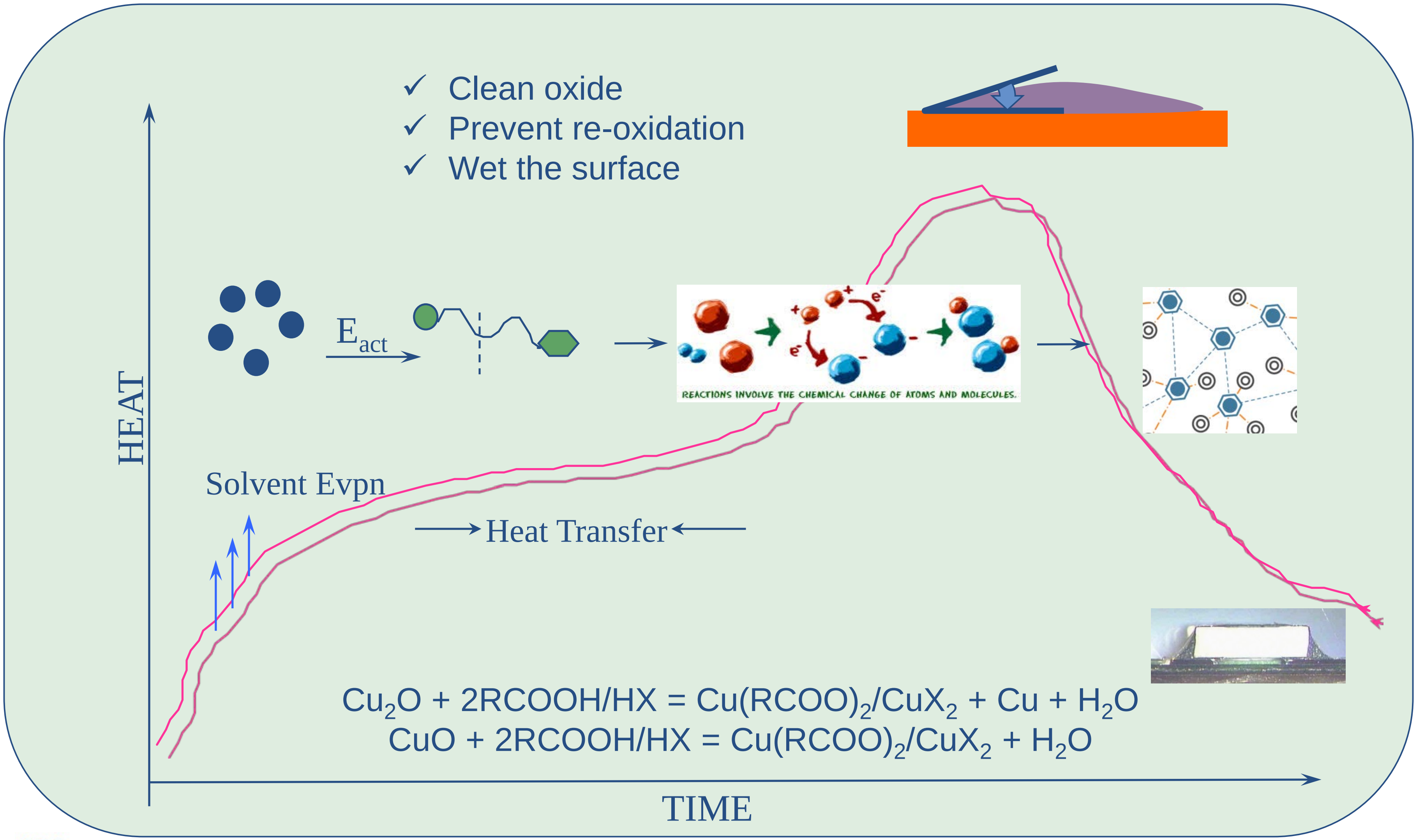
Paste in SMT Process







Fluxing Chemistry



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

$$CuO + 2RCOOH/HX = Cu(RCOO)_2/CuX_2 + H_2O$$

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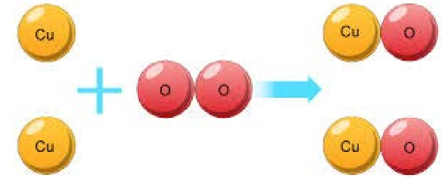
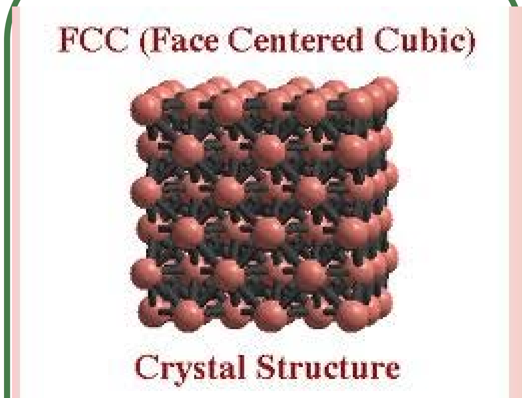
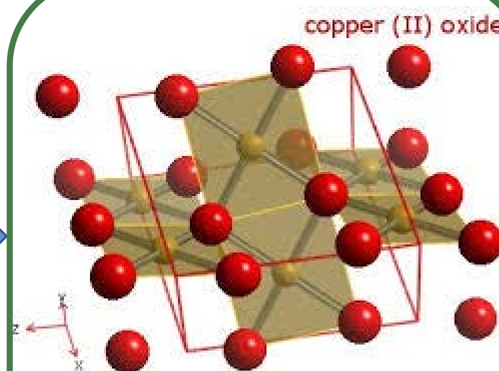
Cu Oxidation

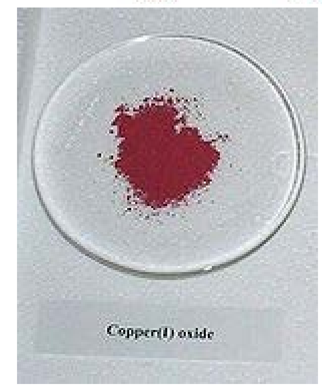




Cu



CuO



Cu_2O

Copper Oxide Removal by Halide

$CuO + 2HCl \rightarrow CuCl_2 + H_2O$

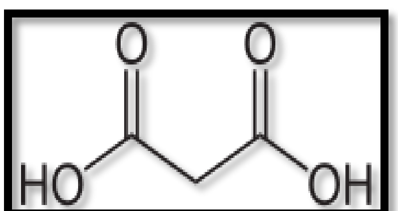
$Cu_2O + 2HCl \rightarrow CuCl_2 + Cu + H_2O$

Aqueous solutions of "copper(II) chloride". Greenish when high in [Cl^-], more blue when lower in [Cl^-].

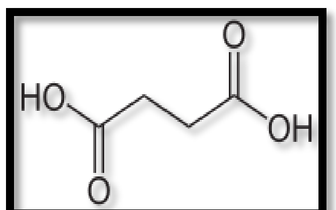
Oxide Removal by Organic Acid

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

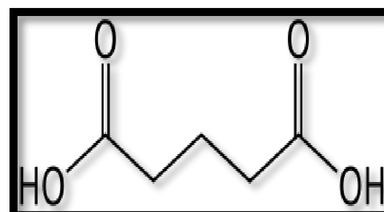
Dicarboxylic acid	Malonic	Succinic	Glutaric	Adipic
Cu complex dissociation constant (pK_{MA})	5.80	3.48	3.00	3.02
Acid dissociation constant (pKa)	2.83, 5.69	4.20, 5.61	4.31, 5.41	4.43, 5.41



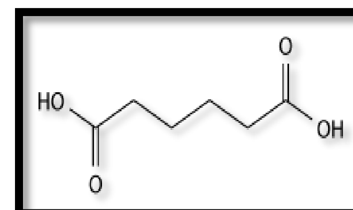
Malonic



Succinic



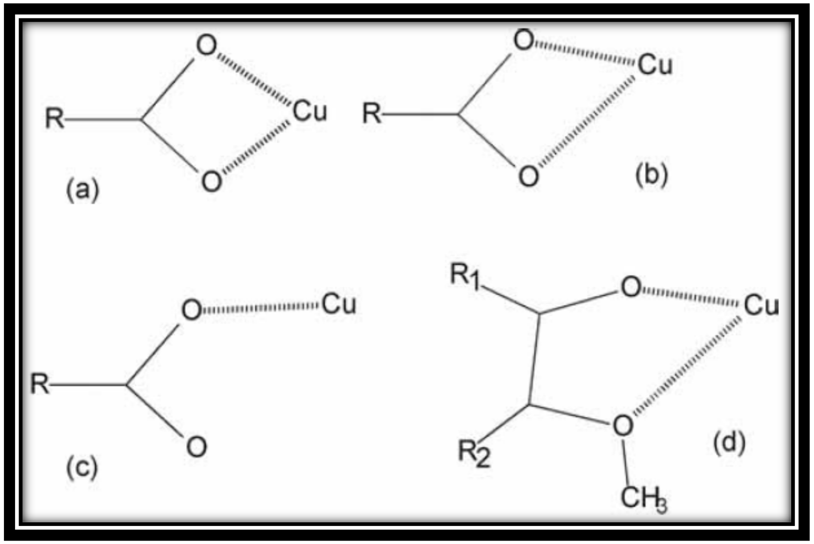
Glutaric

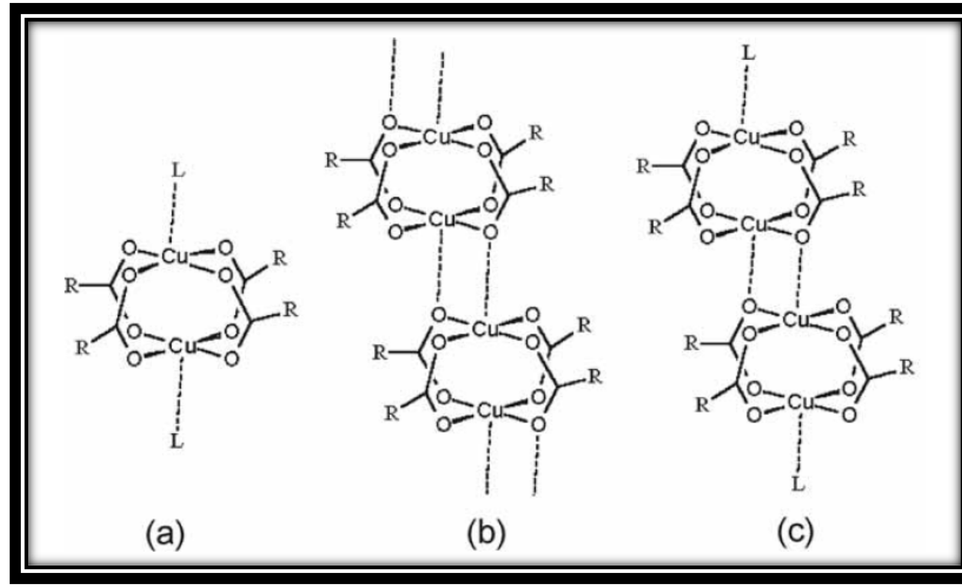


Adipic

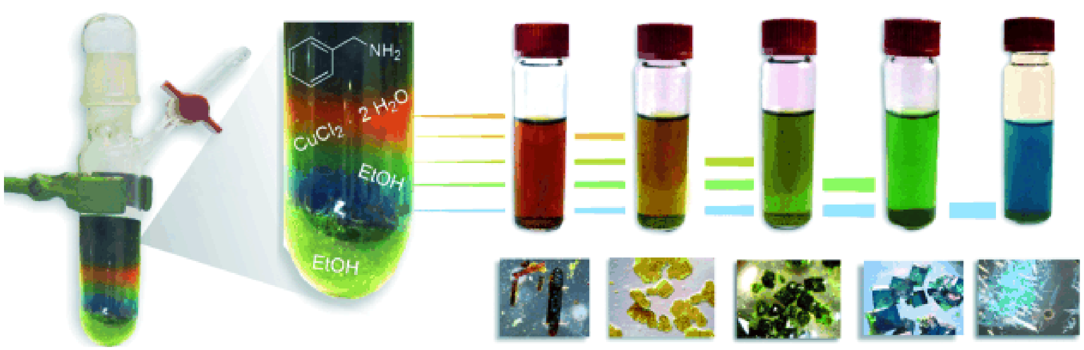
Fluxing reaction byproducts have different stabilities

Copper Coordination





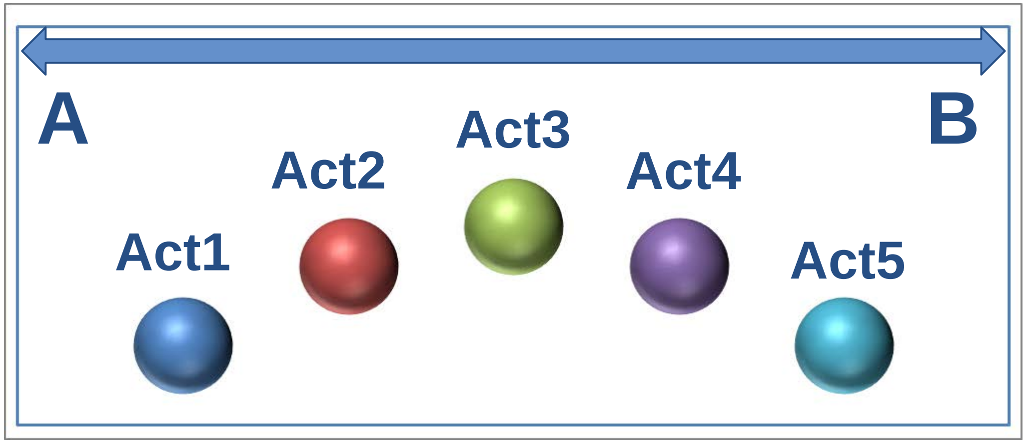
Coordination modes of the carboxylate



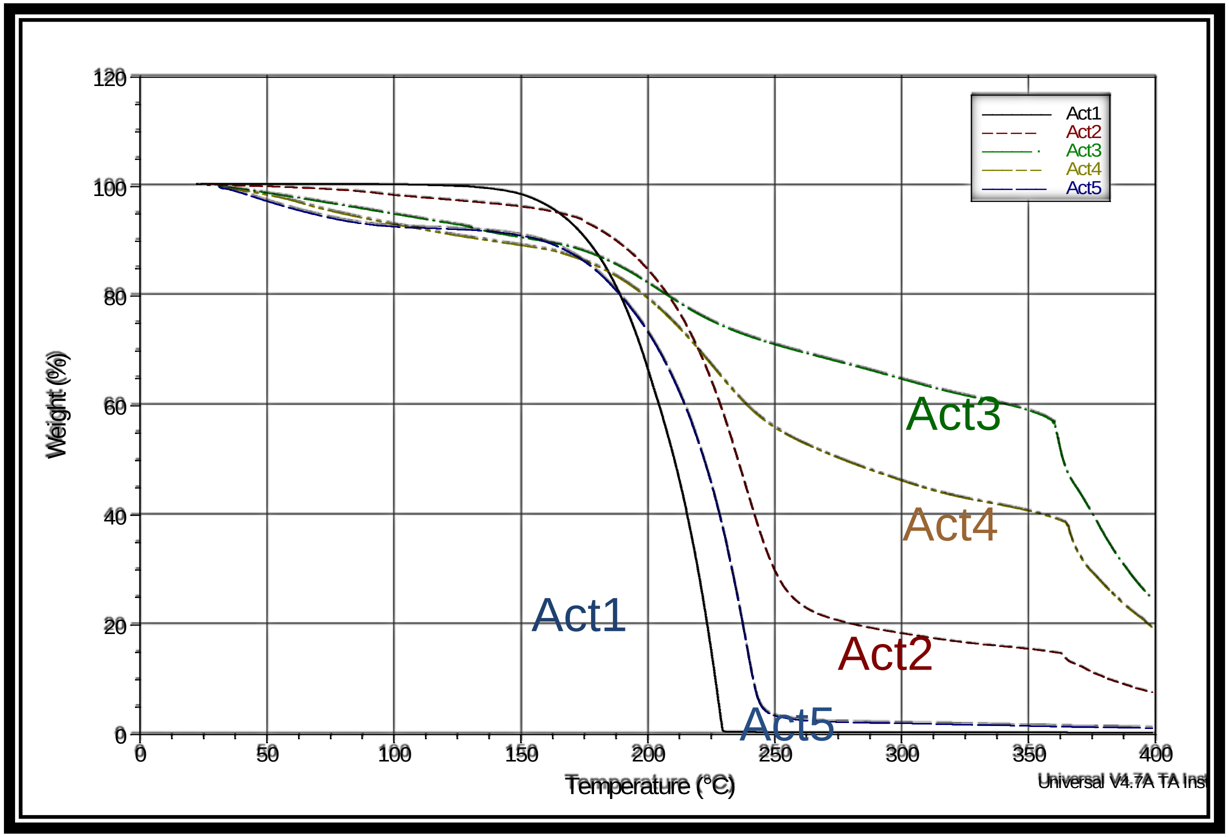
Fluxing reaction byproducts can have distinct structures based on the activator component, board and reflow condition

Activator Study

- Two common activators A&B are chosen
- A & B are combined in different ratios to give activators Act1-5
- Act1-5 are studied for their physical properties and solderability
- Act1-5 are formulated to give Paste P1-5

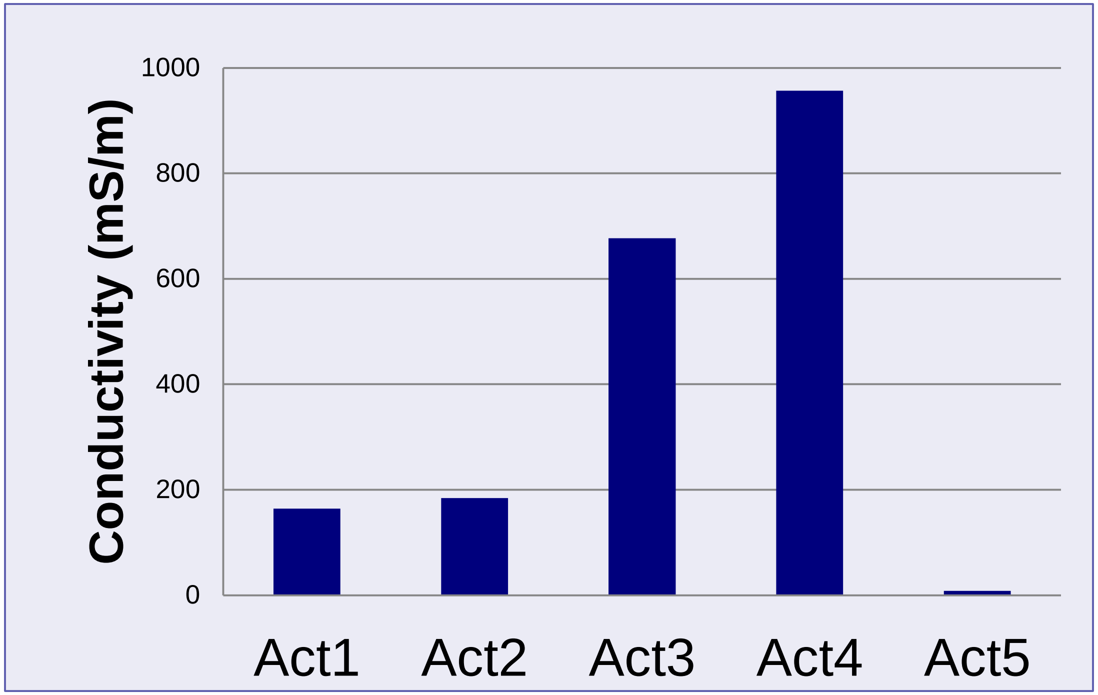


Thermal Stability of Act1-5



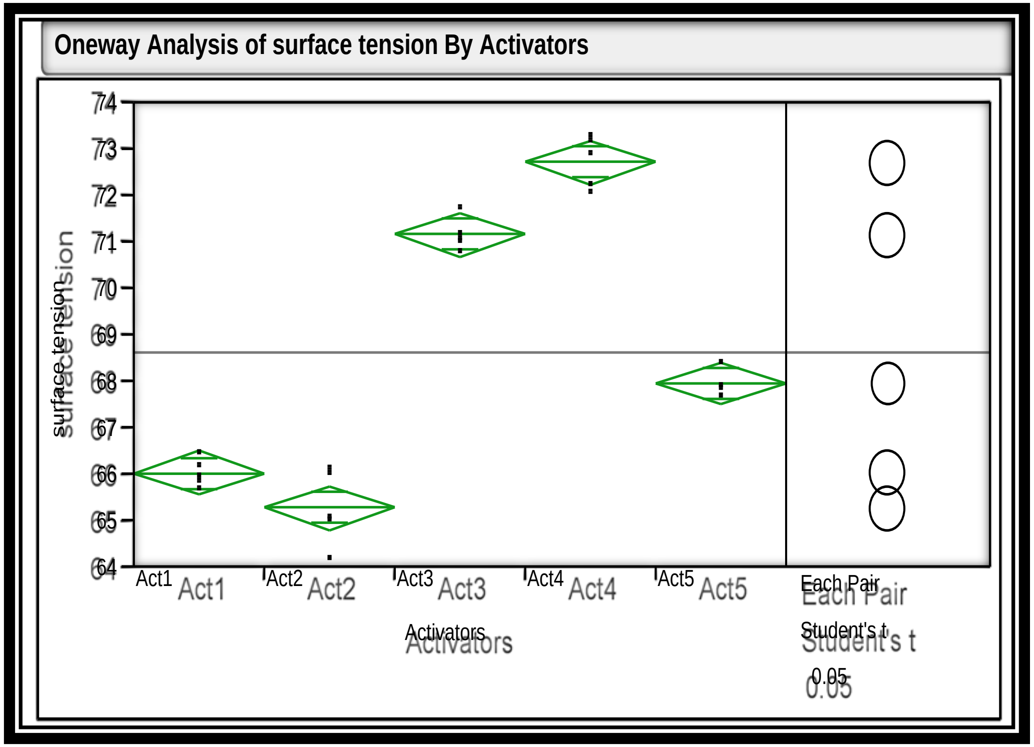
Thermal stability:
Initial stage (preheat and soaking): Act1 > Act2 > Act3 ≈ Act4 ≈ Act5
Second stage (reflow): Act3 > Act4 > Act 2 >Act5 > Act1

Conductivity of Act1-5 Solution1



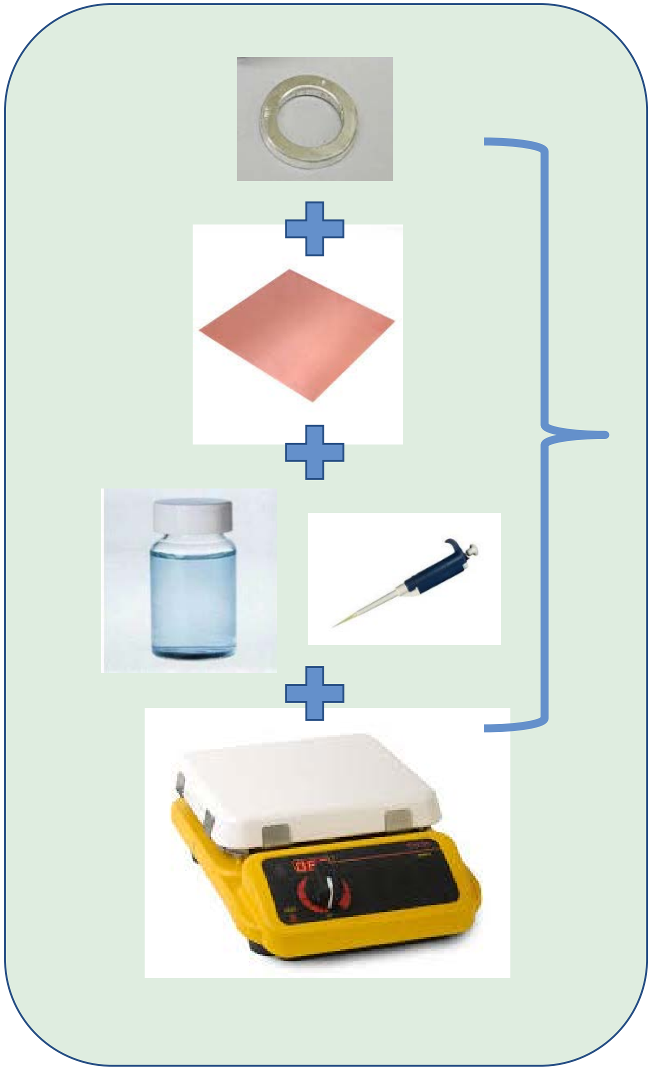
- ❑ Conductivities of Act1-5 change dramatically
- ❑ Act4 shows the strongest ionic mobility

Surface Tension of Act1-5 Solution1

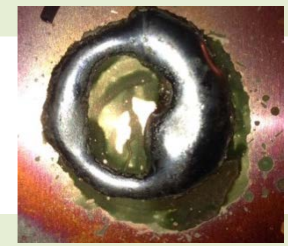


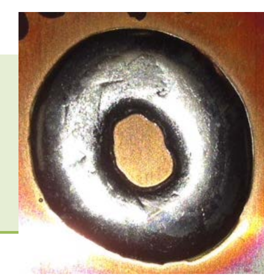
- ❑ Act1-5 changed the surface tension of solvent 1
- ❑ High surface tension limits the flux spread and coverage on PCB, thus may impact wetting

Spread Test of Act1-5

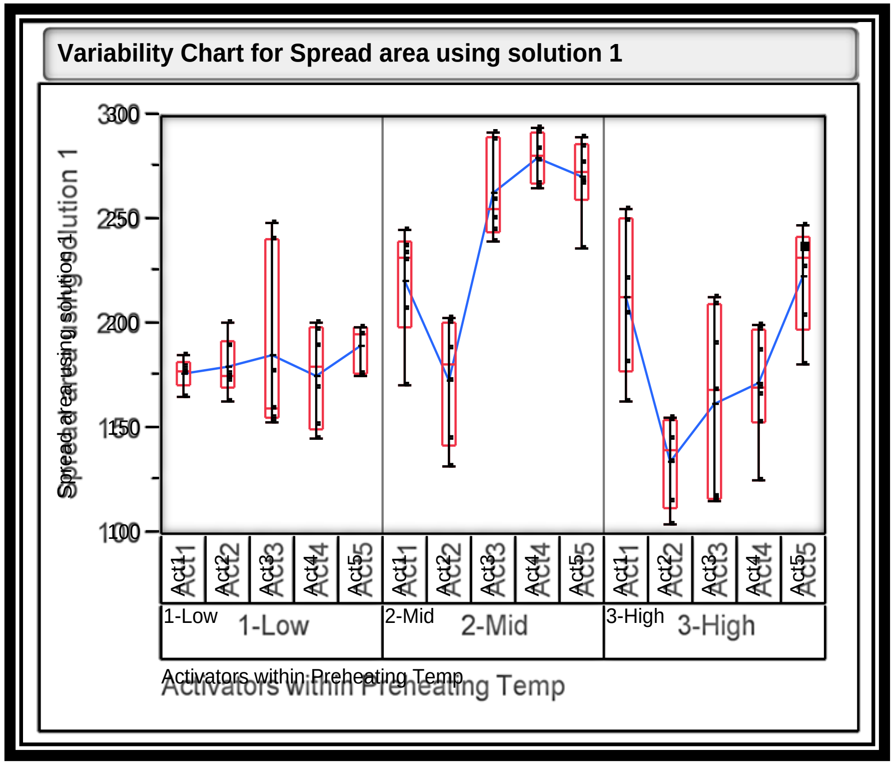


Activator	Residue color
Act1	blue
Act2	green
Act3	black
Act4	black
Act5	clear





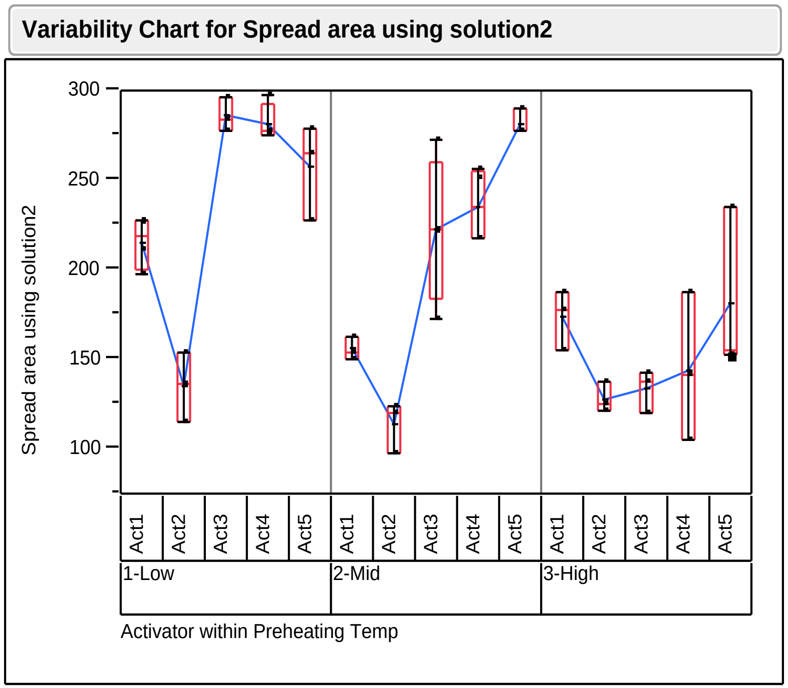
Spread Area of Solution 1



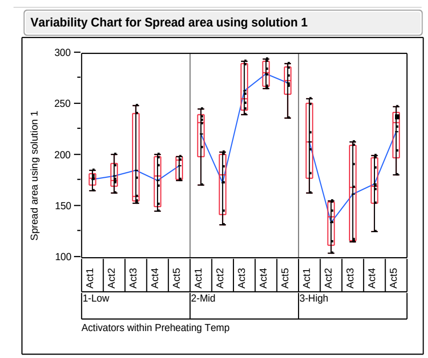
Preheat and soak impact:

- Low: all activators are close
- Mid: Act3-5 spread over more area
- High: Larger spread area of Act1 correlates with its high thermal stability

Solder Spread-Solvent Impact



in solvent 2



in solvent 1

- Act3-5 start to activate at low preheat temperature
- More degradation at high preheating

Formulation solvent is a critical component of performance:

- ✓ mediate chemical reactions during the initial heating stage
- ✓ physical barrier against oxidation and thermal degradation

Model Paste Formulation

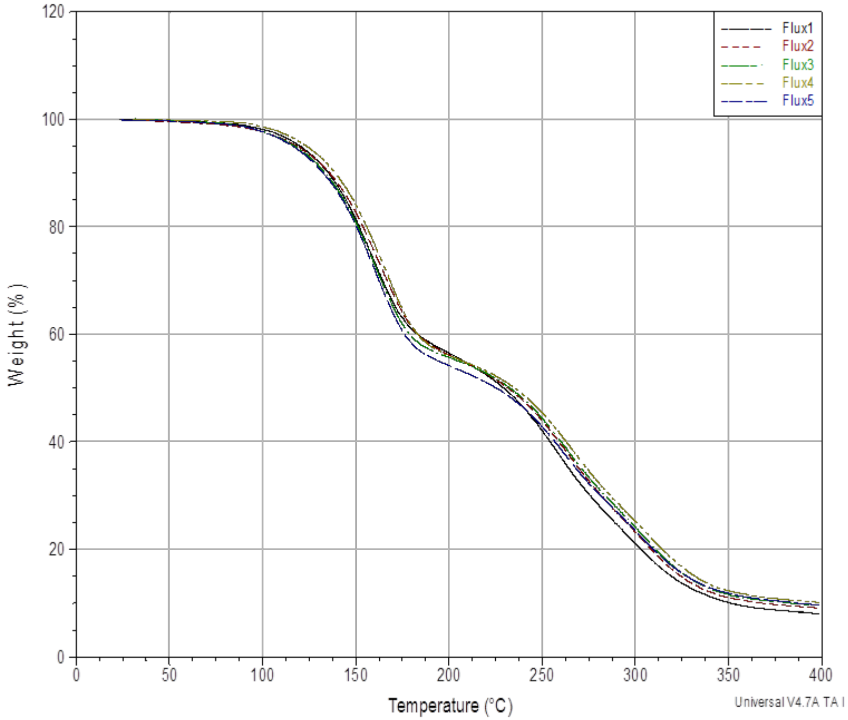
Flux:

Material %	Weight
Solvent	30~60
Rosin	30~60
Activators	5
Rheology modifier	0~10
Additives	0~2

Paste:
SAC305, T4, 88.5%

The formulation was not designed for optimal performance, but to study the activator impacts

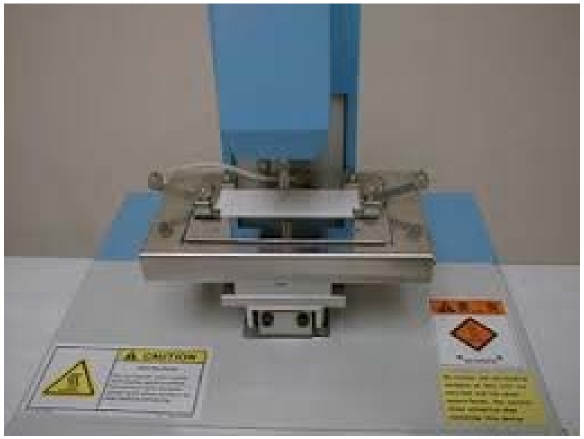
Flux Thermal Stability

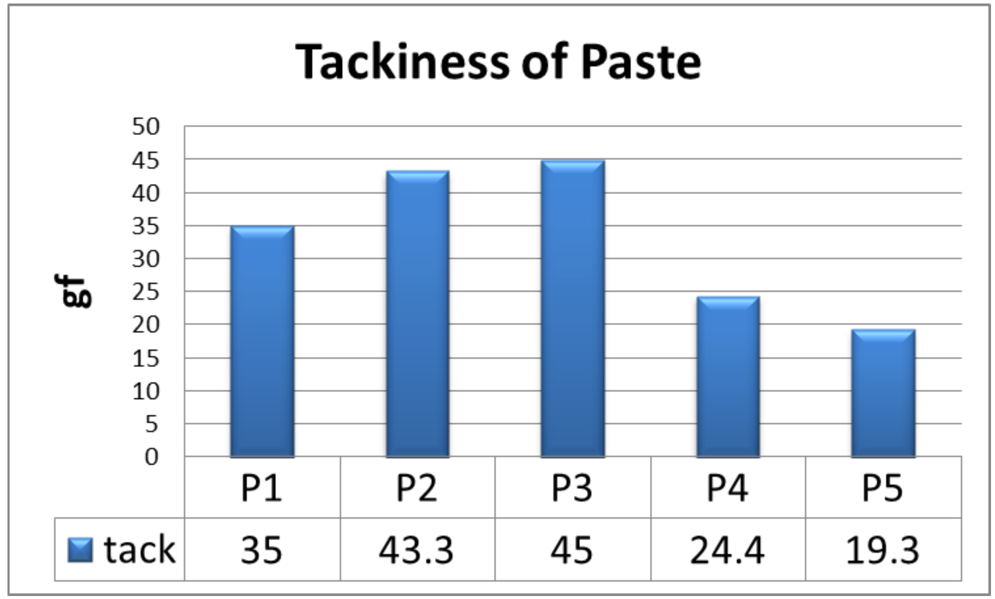


- ❑ Flux1-4 show same level stability
- ❑ Flux5 shows slightly lower thermal stability

Flux	*Flux1*	*Flux2*	*Flux3*	*Flux4*	*Flux5*
Flux weight loss on TGA at 150 ° C	18.7%	17.4%	19.2%	16.0%	19.8%
Flux weight loss on TGA at 217 ° C	46.8%	46.7%	46.7%	46.3%	48.4%

Paste Tackiness





In A&B mix, complex interactions between activators, other flux additives and the solder particles result in byproducts having a strong influence on the rheology of these pastes.

IPC Slump

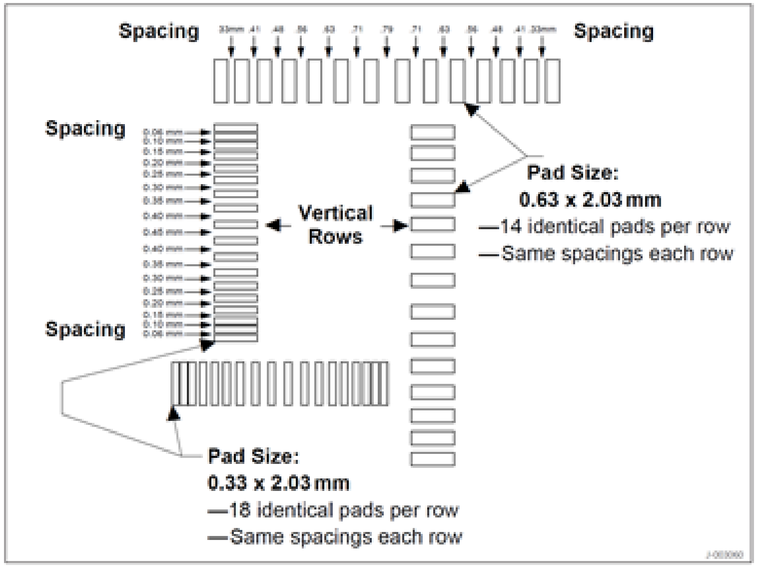


Figure 1 Slump test stencil, IPC-A-21

Paste	Slump IPC-TM-650 2.4.35
P1	0.30, 0.33
P2	0.15, 0.33
P3	0.25, 0.56
P4	0.30, 0.63
P5	0.30, 0.56

- P2 shows the best hot-slump resistance
- Besides rheological impact, the reaction between the activators and the solder alloy at elevated temperature structure the pastes deposit
- Different reaction mechanism at room temp vs. high temp

Paste Shelf-Life

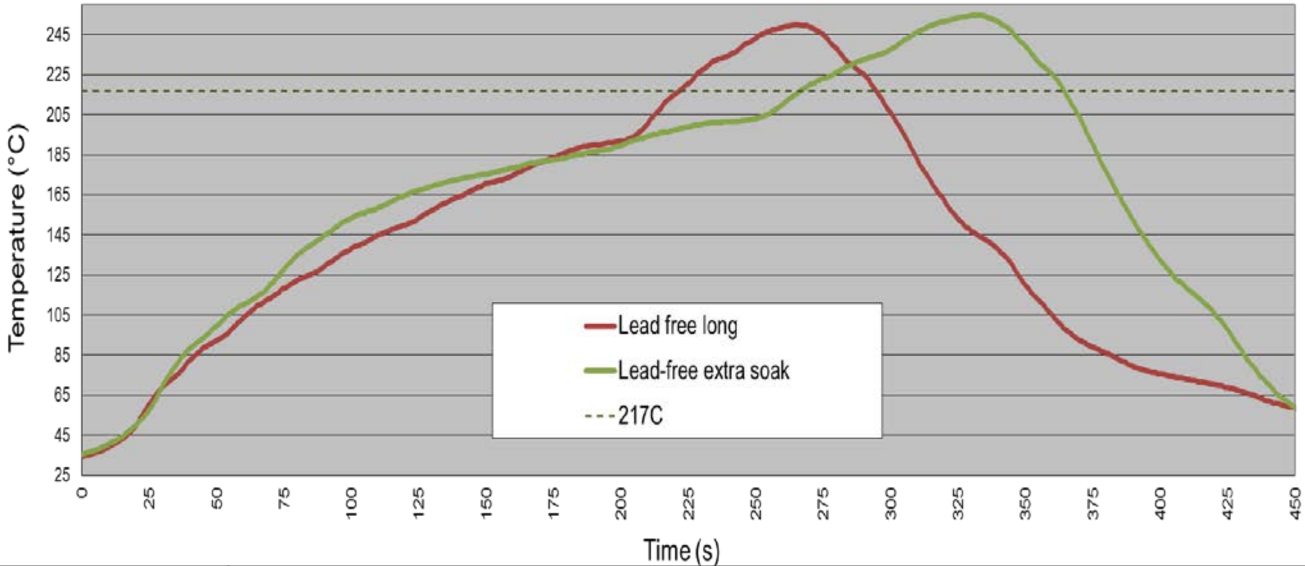
P1, P4 and **P5** are remarkably stable over 3 month storage at room temperature

no separation or viscosity increase, no degradation in solderability

P2 started to dry out after one week followed by **P3** drying out after two weeks

A&B mix in Act2 and Act3 interact much faster with the solder powders under ambient conditions.

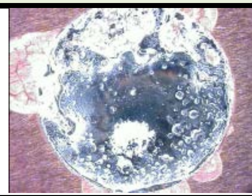
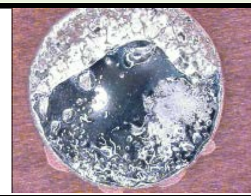
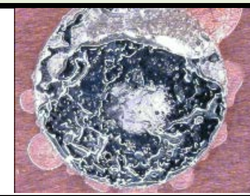
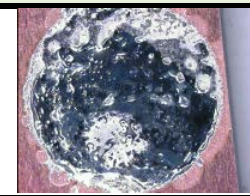
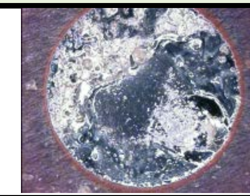
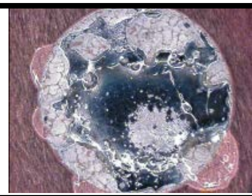
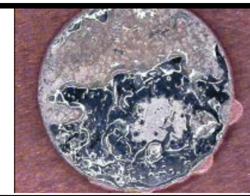
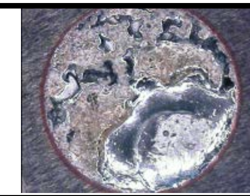
Reflow Profiles



Harsh profile in air to stress the flux chemistry

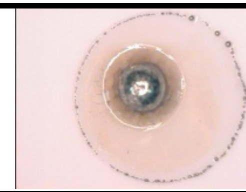
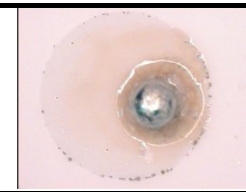
Profiles	*Max(+) slope*	*Max(-) slope*	*Time 50-220° C*	*Time >217° C*	*Peak Temp*	*217° C/ peak*	*Peak/217° C*
Lead-free long	2.03	-2.47	204	73	250.0	0.80	-1.19
Lead-free extra soak	1.14	-1.77	249	99	255.0	0.59	-1.21

Large Pad Dwetting

Profile	*P1*	*P2*	*P3*	*P4*	*P5*
Lead-free long					
	71%	68%	72%	74%	60%
Lead-free extra-soak					
	58%	59%	55%	57%	31%

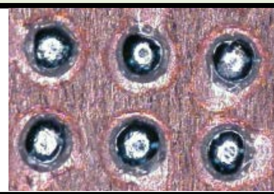
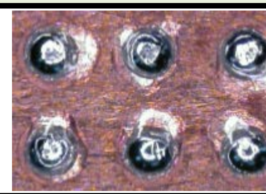
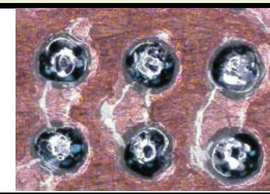
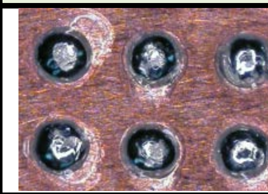
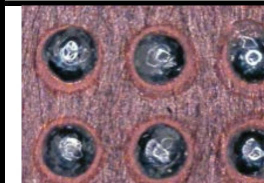
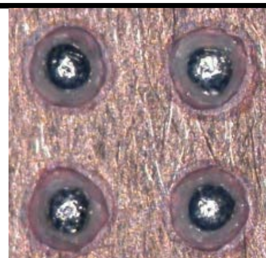
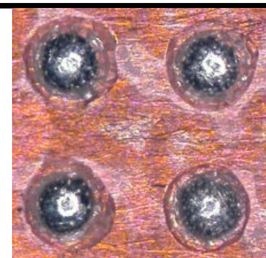
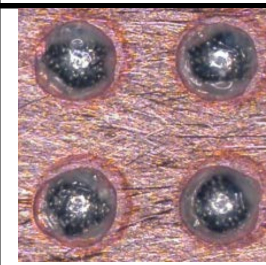
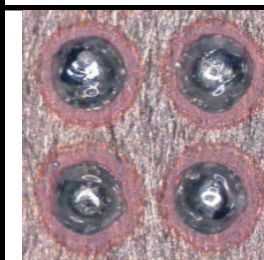
Dewetting performance on 6.5 mm pad:
Lead-free long: P4 ≈ P3 ≈ P1 ≈ P2 > P5
Lead-free extra-soak: P2 ≈ P1 ≈ P4 ≈ P3 > P5

Solderballing

Paste	***P1***	***P2***	***P3***	***P4***	***P5***
Lead-free long					
	L3	L2	L1	L1	L4
Lead-free extra-soak					
	L3	L4	L4	L2	L5

Solderballing performance:
Lead-free long: P3 ≈ P4 > P2 > P1 > P5
Lead-free extra-soak: P4 > P1 ≈ P2 ≈ P3 > P5

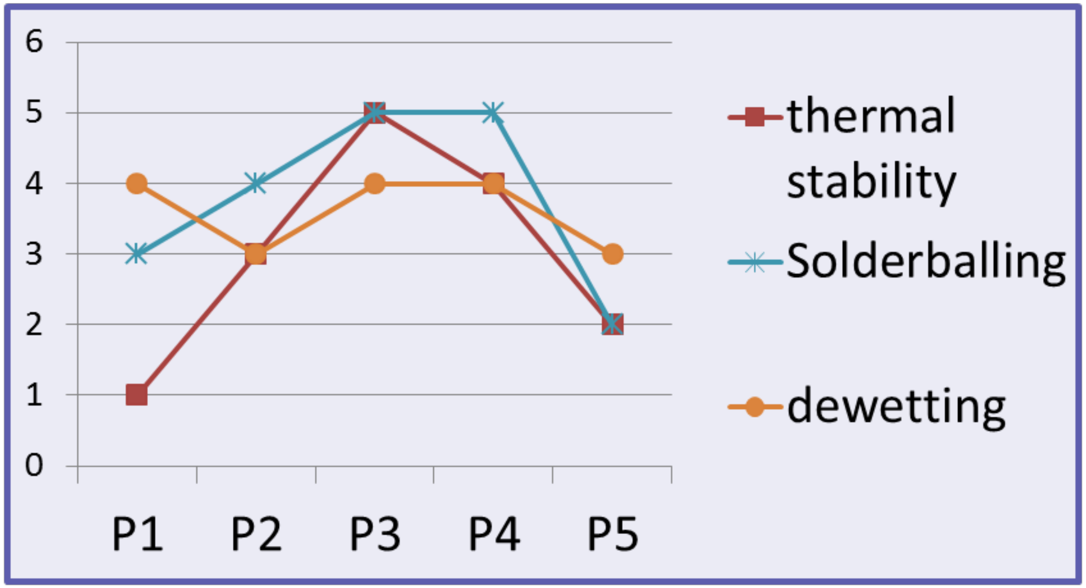
Coalescence

Paste	*P1*	*P2*	*P3*	*P4*	*P5*
Lead-free long					
	0.15mm BGA	0.15mm BGA	0.15mm BGA	0.15mm BGA	0.15mm BGA
Lead-free extra-soak					
	0.30mm BGA	0.45mm BGA	0.45mm BGA	0.45mm BGA	0.40mm BGA

Coalescence performance:
Lead-free long: All pastes have show excellent coalescence
Lead-free extra-soak: P1 > P5 > P2 ≈ P3 ≈ P4

Correlations

Under “lead-free long” profile



*Performance level:
1-5 scale, 5 is the best

Wetting and solderballing performance correlate with the thermal stability of activators during reflow

Paste Summary

Paste	*P1*	*P2*	*P3*	*P4*	*P5*
Tackiness	4	5	5	3	2
IPC slump	3	4	2	1	1
Shelf-life	5	0	1	5	5
Reflow profile1 (lead-free long)					
Solderballing	3	4	5	5	2
Coalescence	5	5	5	5	5
Dewetting	4	3	4	4	3
Reflow profile2 (lead-free extra soak)					
Solderballing	3	2	2	4	0
Coalescence	2	0	0	0	1
Dewetting	3	3	3	3	1
Total	**75**	**47**	**52**	**72**	**53**

*Performance level, 1-5 scale, 5 is the best.

Conclusions

- The physical properties, thermal stability and solderability of these activators can be tuned by adjusting the ratios between activators

- Paste physical properties and performance depend on complex interactions within the formula

- Studies on reliability and the reaction mechanisms are desired to provide further scientific guidance to improve the performance of solder paste formulations

Acknowledgements

Kester R&D team

- Michelle Wilson for her great support to paste preparation and testing
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