SMART CHEMISTRY TOWARDS HIGHLY EFFICIENT SOLDERING MATERIAL FORMULATION

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ABSTRACT
Driven by environmental and health concerns, the RoHS legislation has mandated the electronic assembly industry to transition from eutectic tin-lead to lead-free soldering, which carries forward a revolution in the formulation of soldering materials. Meanwhile, the fluxing performance has become paramount because of the increasing development and advances in the electronic industry, such as high integration and fine pitch components. Moreover, the demand for halogen-free soldering materials with equal or superior performance compared to their halogenated predecessors makes the design of solder paste, tacky flux and liquid flux formulations even more challenging.

Activator choices are critical parameters in the design of paste and flux formula in order to achieve outstanding performance in lead-free and halogen-free soldering processes. For an efficient printed circuit boards (PCBs) soldering operation, the fluxing mechanism requires the right chemistry coupled with a proper initial heat cycle to remove the oxide and surface contamination. A synergetic combination between chemistry and processing will promote a clean and solder-wettable metal surface, which is a prerequisite to achieve good metallurgical bonding. Meanwhile, the activator itself has to remain inert at mild temperatures to guarantee an acceptable shelf-life while leaving non-corrosive and non-conductive residues to ensure a high-reliability in the no-clean categories.

Here, we report a systematic study of a series of innovative activator systems applied in new solder paste and liquid flux platforms. Analytical methods such as thermogravimetric analysis (TGA) are applied to characterize the thermal behavior of these activators. Solder pastes are formulated using these activator packages. The solderabilities, physical properties and stabilities of the pastes and fluxes are evaluated. This fundamental understanding may provide some scientific guidance for future formulation work.

Key words: Lead-free, halogen-free, formulation, activator, fluxing chemistry

INTRODUCTION
As the RoHS legislation and other regulations have driven the electronic assembly industry from eutectic tin-lead to lead free soldering, new demands have been placed on materials and process of assembly printed circuit boards (PCBs) in surface mount technology (SMT). Solder pastes are key materials, which interconnect the copper tracks on PCBs and the components.[1,2] To achieve satisfactory functionality and process yields, especially with the advances in high integration and fine pitch components, it is critically important to understand the performance of solder pastes at the fundamental level.

A solder paste consists of an homogeneous dispersion of solder alloy powder in a stable viscous flux vehicle. Besides the alloy nature, the metal load, the particle size distribution (or powder type per IPC classification), and the solder paste rheology, the flux chemistry plays a key role to mediate the formation of intermetallic bonding between pads and components. A solder paste flux is typically composed of rosin/resin, solvent, rheology modifiers, and activators. In general, the flux chemistry has to present a minimal reactivity towards metals at mild temperature to reach an acceptable shelf-life (refrigerated) and pot life (room-temperature). On the other hand, the fluxing mechanisms need to be activated instantly when the product is heated at a series of preheat, soak and soldering sequences. The fluxing mechanisms are quite complex, but 3 key functions can be highlighted 1) the flux mediates the thermal transfer to the joint area and properly wet the surface; 2) it removes the passivation layers and the surface contamination from the PCB pads and component leads; 3) it protect the highly reactive molten metals from re-oxidation with the atmosphere until the solder alloy re-solidifies to form the joint during rest of the reflow process[3,4] It is important to realize that soldering peformance also depends on the physical state of the byproducts during soldering (e.g. ionic liquid). Hence the flux properties in its original state are remotely related to the final performance.

Multiple reactions are potentially involved in removing the metal passivation layer, including reduction, disproportionation, and complexation. The most common fluxing reaction is an acid-base reaction mediated by inorganic acids such as hydrogen halides and ammonium halides, or organic acids such as carboxylic acids, shown in the equations below:[5-7]

$$Cu_2O + 2RCOOH/HX = Cu(RCOO)_2/CuX_2 + Cu + H_2O$$
$$CuO + 2RCOOH/HX = Cu(RCOO)_2/CuX_2 + H_2O$$
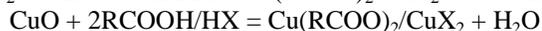
The wettability of the solder depends on the surface energy, which will be directed by the metal oxidation level and the presence and nature of various soldering residues. It is therefore strongly affected by the chemical equilibria above, the thermodynamics and kinetics of which are related to the

acid strengths, stability of the metal complex intermediates, and solubility of the byproduct in molten solder. Due to their high acidity and coordination constant to metal ion which translates to high reactivity towards metal oxide, halogen based fluxing materials generally achieve high solderabilities. Unfortunately, the industry tends to phase-out halogens from fluxes for environmental reasons as well as increased reliability requirements, which makes the design of new formulations even more challenging.[3,4] In searching for the next generation activators, the advanced chemistry in organic acids are attracting more and more attentions. These chemicals can form a structural diversity of copper (II) complexes, largely related to a Cu(II) d^9 system.[8] Divalent copper is found in a large variety of coordination polyhedra with various geometries, like the mononuclear, binuclear, and polynuclear species shown in Figure 1 and 2.[8-11]
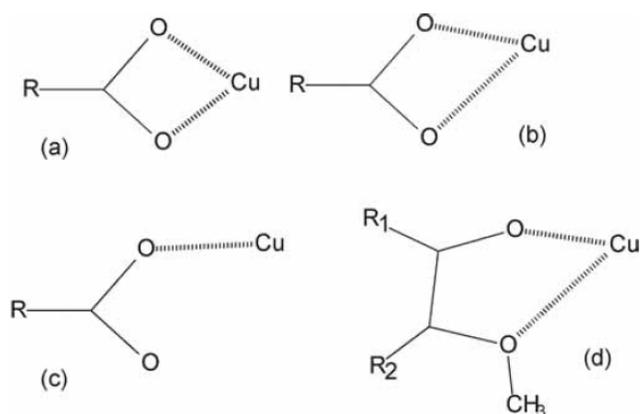

Figure 1. Coordination modes of the carboxylate ((a) symmetric chelate, (b) asymmetric chelate, and (c) monodentate) and the phenol type of ligands ((d) asymmetric chelate).[10]
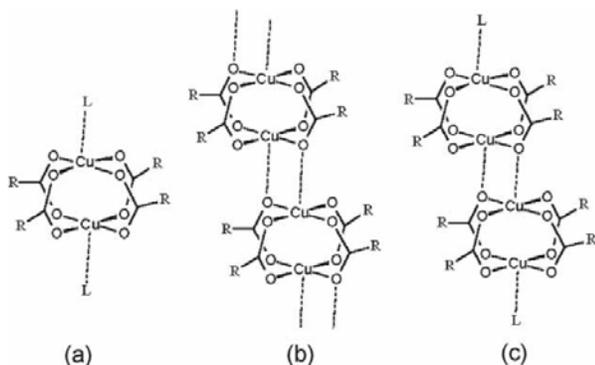

Figure 2. Various structural types in dicopper (II) tetracarboxylates by dimeric building blocks and terminal ligand L: (a) isolated dinuclear; (b) polynuclear; (c) tetranuclear.[11]

The organics, especially dicarboxylic acids are mostly bidentate ligands, whose geometry enables them to occupy more than one coordination position on the central Cu ion as chelating agents and tend to form extremely stable complexes. These complexes are commonly found with

Cu(II) d^9 ion in a tetragonal coordination environment, with four shorter equatorial bonds and another one or two longer axial bonds or less frequently with two shorter axial bonds and four longer equatorial bonds.[8] The structure and stability of the complex depend on the nature of the coordination ligands, as well as the environmental conditions during its formation. The acid and complex dissociation constants of common dicarboxylic acid and copper dicarboxylates are listed in table 1.[12,13]

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

Table 1. Dissociation constants of copper dicarboxyaltes (expressed as pK_{MA})

Due to the complexity of solder paste formulations, the reactions between activators involving acids and amines are much more complicated than a simple dissolution of the copper oxide layer by a conventional acid. In order to understand and optimize the activator systems used in fluxes, not only the acidity of carboxylic acids needs to be taken into consideration, but also many other aspects such as the combination of activators into intermediates with various ratios, the thermal and structural stability of these species, and their impact on paste rheology, physical properties, reliability and shelf-life. Here we report a systematic study of the thermal characteristic of a series of activator packages using thermogravimetric analysis (TGA). The evaluation of solderability is realized on raw activators and their formulations, and includes wetting, coalescence and solderballing. The activator impact on many other pastes performance such as IPC tackiness hot slump, residue appearance, and paste stability is also evaluated.

EXPERIMENTAL
Synthesis and characterization of activators:
Activators **1-5** combine two chemicals (named A and B) in different ratios varying from A predominant in **Act1** to B predominant in **Act5.** Surface tensions of the respective 5 wt% activator solutions are tested using a VCA-Optima system using the pendant drop method. The results are computed with a proprietary software. The averages of five reading are recorded in Table 3. Conductivities of these solutions were obtained using a YSI MODEL 32 Conductance Meter equipped with a YSI 3402 cell.

Spread test:
Hot plates with controlled temperature setup were used to investigate the impact of various preheating temperatures on soldering by heating a SAC305 preform placed in the center of a Cu test coupon. A small aliquot (0.05 ml) of the activator solution was dispensed in the center of the preform using a micropipette to make sure all the flux remains in the solder cirle. Three preheating temperatures, namely "Low" "Mid" and "High", were used to evaluate the activator heat

resistence. Observations of the soldering sequence were documented and the solder spread area was measured.

TGA:
Thermogravimetric analysis of activators and fluxes were performed on TA-Instruments TGA Q5000 using a straight ramp of 10 ℃/min from 25 ℃ to 400 ℃ in air atmosphere.

Flux and paste preparation:
The fluxes were formulated using materials and amounts corresponding to the current state of the art. Five flux formulas were made by testing our activator combinations (**Act1**-**5**) while keeping all the other ingredients the same. The pastes **P1**-**P5** were blended with SAC305, type 4 powder at 88.5 wt% metal load.

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

Table 2. Paste formulation

Paste evaluation methods:
The paste tackiness was recorded on a Malcom TK-1 tester. The samples are stencil printed (5 holes pattern design per IPC-TM-650) on a smooth glass slide . The paste hot slump resistance was tested according to IPC/ANSI J-STD-005 IPC-TM-650, Method 2.4.35.

To evaluate the solderability of these activators, the pastes were printed on copper OSP boards using a 5-mil stencil. Each board contains two 6.5 mm diameter wetting circles and 0.15 to 0.45 mm BGA circles and squares, with 100 pads for each pattern. Two boards are reflowed in a Speedline OmniExcel 7 Reflow Oven for coalescence and dewetting analyses. Two lead-free reflow profiles, "lead-free long" and "lead-free extra soak" (Figure 6), were used in air. IPC-TM-650, Method 2.4.35 was modified to evaluate solderballing performance using stencil-printed ceramic coupons with five 6.5 mm diameter solder circles.

RESULTS
Activator testing :
Chemicals A and B are typical activators widely used in conventional liquid flux and solder paste formulas. They were combined in different ratios as the base component to build-up the activator matrix in this study.

First, the physical properties of **Act1-5** solutions were investigated in a common solvent 1. **Act1** and **Act5** solutions have significantly lower surface tensions than that of solvent 1 (Figure 4a). By slightly increasing B content in **Act2**, the solution surface tension further decreases. However, the new intermediates formed in **Act3** and **Act4** solutions raise the surface tension compared to **Act1** and **Act5**. The high surface tension of these solutions might limit the flux spread on the PCB surface, and thus impact the wetting performance. **Act1** and **Act5** solutions also have relatively low conductivities, indicating the low dissociation constants in solvent 1 (Figure 4b). The conductivity dramatically increases from **Act2** to **Act4**, the **Act4** solution displaying a 6 fold increase compared to **Act1.** It then drops by more than 2 decades in **Act5**. One can observe that this trend is far from continuous, which implies that discrete species with specific properties are stabilized in the A-B system. The high conductivity of the **Act4** solution can be attributed to the strong ionic character of the mixture from A and B.
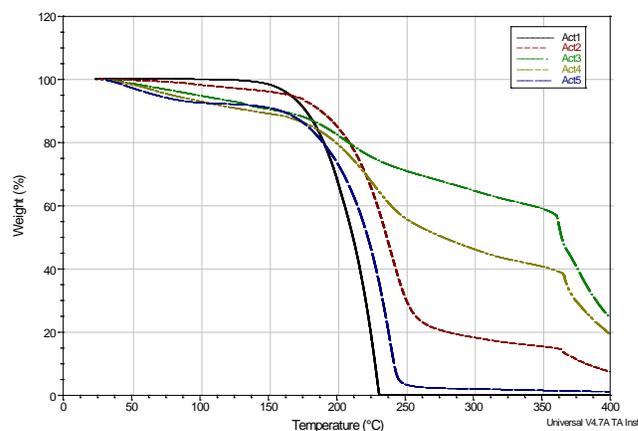

Figure 3. TGA curves of activators 1-5.

The thermal stabilities of the activators are estimated using thermogravimetric analysis as shown in Figure 3. The overall weight loss can be divided into two stages: the initial desorption range below 150 °C and the decomposition of organic compounds between 150 and 300 °C. **Act1** is a fairly dry compound, as only 1.7% weight loss was observed at 150 °C in open conditions. On the other hand, **Act2-4** release volatile species, with a 3.9% weight loss for **Act2** and around 10% weight loss for the others. The slopes of the initial TGA curves of **Act3-5** are comparable. The decomposition of **Act1** and **Act5** starts abruptly shortly after the initial stage, and significant weight loss were recorded before reaching the typical lead-free solder liquidus temperature. Only trace amounts of **Act1** were left above 230 °C. A similar trend was seen with **Act5**, which lost more than 40% of its weight below 217 °C, with only 2% left at 250 °C. Thermal stability towards further heating is remarkably improved in **Act2**, with 30% residue left at 250 °C. Different patterns were observed on **Act3** and **Act4**, where much slower decompositions were achieved in the 150-350 °C range. **Act3** showed the highest stability in this activator series, with more than 70% weight left at 250 °C. From these initial data, one can observe that multiple species with variable physicochemical properties can result from the combination of A and B. The production of either one of these intermediates can depend on a lot of parameters, including interactions with other formulation components and processing conditions. Therefore, the performance of the final formula will be very sensitive to a large array of fundamental and engineering parameters. The careful design of the formulation, process and quality

systems for these complex materials is paramount in delivering a robust product to customers.

The performance of these activators was evaluated by the spread test described in the experimental section. The variability charts of the spread areas of SAC305 solder preforms at three preheating temperatures are shown in Figure 4c and 4d using **Act1-5** 5 wt% solutions in two solvents (solution 1 and solution 2). With solution 1, the solder preform spread areas are at the same level across the whole series at "Low" preheating temperature. One starts to discriminate the wettability of these fluxes when raising the preheating temperature to a "Mid" range. With further increase to "High" setting, the spread areas of all the fluxes shrunk, except for **Act1**. The higher heat resistance of the flux made with **Act1** is consistent with the TGA

observations indicating that this activator presents the highest thermal stability below 150 °C. Somewhat different trends were observed using the activator solution 2. **Act3**, **4** and **5** reach peak performance at "Low" preheating in solvent 2, while preheat at "Mid" temperature is necessary in solvent 1. The formulation solvent is therefore a critical component of performance. It fullfills multiple functions, from a physical barrier against oxidation and thermal degradation of the activators to mediating the chemical reactions during the initial heating stage. We believe the mechanism in the lower temperature range is highly related to the surface tension of the flux, which physically confines the flux. On the other hand, the solvent 1-based fluxes show less activity degradation at high preheating temperature, probably due to the less volatile nature of solvent1, and other solvent effects then start to play a significant role.

Activator	Act1	Act2	Act3	Act4	Act5
Residue color	blue	green	black	black	clear
Surface tension of solution 1 (dyne/cm)	66.02	65.27	71.15	72.71	67.94
Conductivity of solution 1 (milliS/m)	164.3	184.1	677	957	8.52
Weight loss on TGA at 150 °C (%)	1.7	3.9	9.5	10.8	9.0
Weight loss on TGA at 217 °C (%)	63.9	27.3	22.6	28.3	42.6

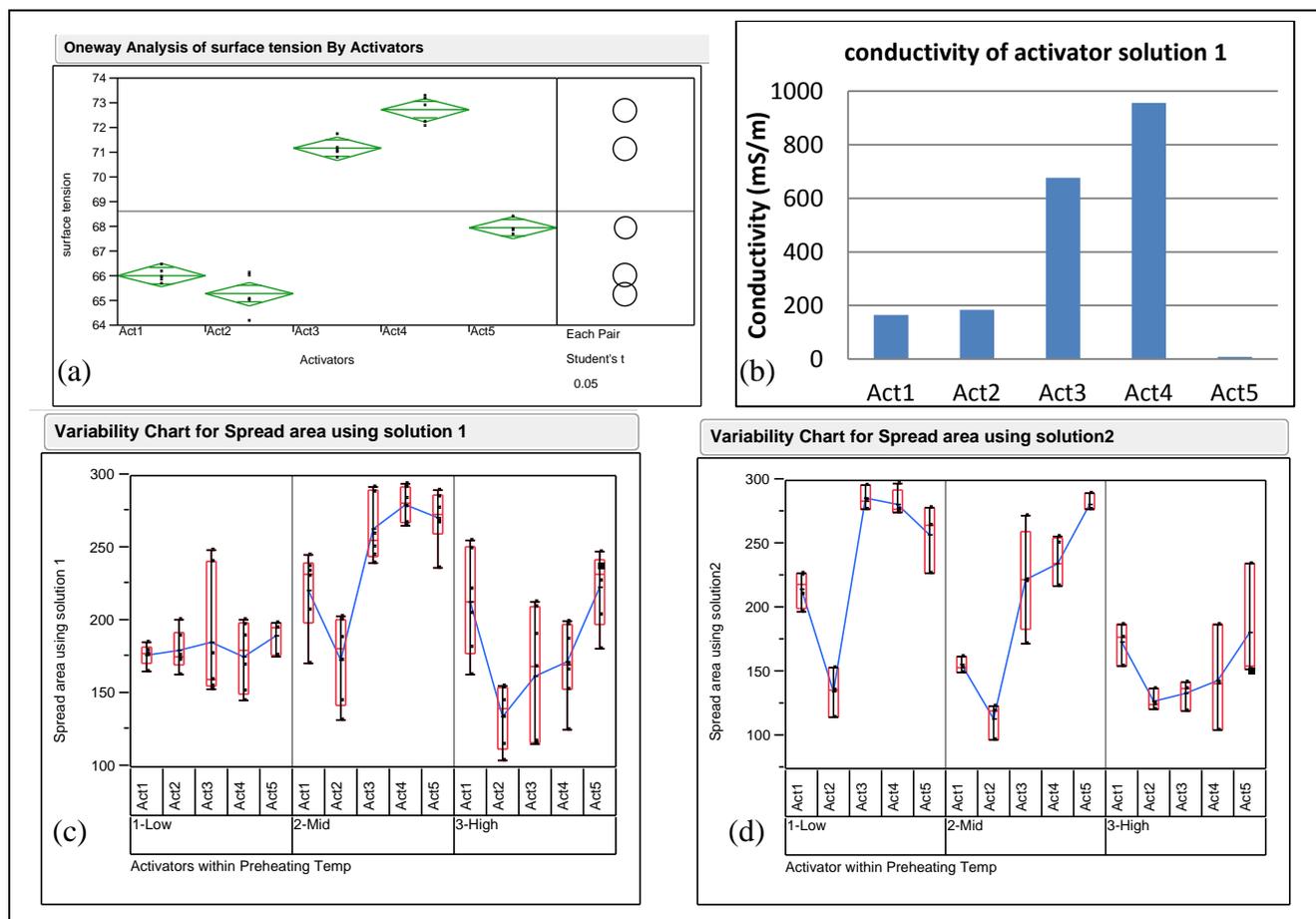**Table 3**. Summary of activator properties.

Figure 4. (a) Surface tension of 5 wt% activator solution 1 at 20 ℃; (b) conductivities of 5 wt% activator solution 2; (c) spread test of 5 wt% activator solution 1 at various preheating temperature; (d) spread test of 5 wt% activator solution 2 at various preheating temperature.

Act1 and **Act2** left blue and green colored residues respectively after reflow on hotplates. This coloration is sometimes attributed to a corrosion effect, while other harmless mechanisms can also explain this behavior. Beside corrosion, the coloration of a coupon can simply be due to the stabilization of chemical byproducts whose shade results from transitions between various electronic states of the copper complex, mainly metal to ligand charge transfer, according to the ligand field theory. **Act3** and **Act4** left brown to black color residues and **Act5** left minimal clear residues. The color difference demonstrates that with different ratios of A and B, the coordination complexes formed between these activators and copper have distinct geometries as discussed earlier. The stability and color of these copper complexes mainly depends on the chelating ligands, which are the activators in this case.

Paste testing:
Act1-5 were dissolved in the paste flux formulation at 5wt% level, together with other basic components commonly combined in lead-free no clean pastes. The formulation was not designed for optimal performance but as a screening template to shed a light on the activator impacts on various aspects of paste properties. All the fluxes present a pale yellow to light brown color with similar body textures. Thermal stabilities of these fluxes are very similar to each other as shown in the TGA curves in Figure 5. Weight losses ranging between 16% and 20% were recorded at 150 °C, the differences being not statistically significant. Continuous weight losses reach 47% at SAC305 liquidus temperature (217 °C). The much smaller difference between the flux thermal stabilities is probably due to the fact that these activators only represent 5% of the total weight, the rest of the formulation being identical.
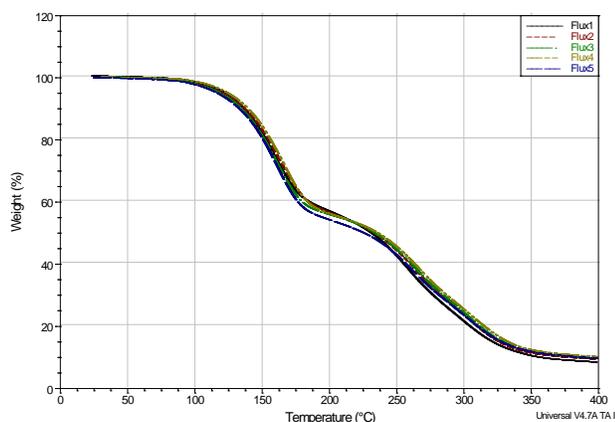

Figure 5. TGA curves of fluxes 1-5.

Five pastes were blended with the SAC305 T4 powder following a consistent procedure. It is surprising to see that with activator levels of only 5% in a flux formulation representing 11.5 wt% of the paste formula, the tackiness of these pastes ranges broadly from 20 to 45 gf. From **P1** to **P5**, the tackiness first increases as the mixing of A and B becomes more balanced in ratios, and then decreases with

excessed of B. **P5** ends-up having the lowest tackiness. This could be attributed to the complex interactions between activators, other flux additives and the solder particles, which result in byproducts having a strong influence on the rheology of these pastes.

P1 showed a moderate hot-slump resistance. **Act2** improves the slump performance of **P2**, however, as B concentration becomes more significant in **Act3** to **Act5**, **P3**-**P5** is more likely to slump during heating in the oven. Given the relatively low amounts of activators, the large variations observed in these slump tests indicates that beyond a purely rheological impact, the reaction between the activators and the solder alloy at elevated temperature create viscous byproducts which structure the pastes deposit.

As shown in Figure 6, two reflow profiles designed for lead-free solders were employed to have long preheating and soaking zone to stress the flux chemistry. The long profiles, especially the one with extra soak, are quite challenging for halogen-free pastes, since the flux activity degrades with heating time and oxidation rates increase dramatically in air at high temperature as well. Solderballing on ceramic coupon, dewetting of 6.5 mm circle and coalescence performance of 0.15-0.45 mm BGAs are evaluated under both profiles.

i. *Solderballing*
When reflowed under the "lead-free long" profile, pastes **P1** to **P5** showed a pronounced variation in their solderballing tendency. **P1** and **P2** left pale yellow to colorless residues on the ceramic coupons with 25 to 40 and 10 to 15 small solderballs in the peripheral area around the center solder sphere, respectively. **P3** and **P4** pastes withdrew to form a large shiny solder sphere and left a light yellow residue after reflow. Large solder clusters trapped in the dark brown color residue were observed on **P5** coupons. The extra soak in the second profile, which is 45 seconds longer in the 50-220 °C range, induces severe solderballing defects for all the pastes except **P4**. The outstanding performance in reducing solderballing defects of **P3** and **P4** could be attributed to the high thermal stabilities of **Act3** and **Act4** as shown in Figure 4, which reduce the activator degradation in challenging reflow conditions. It is therefore demonstrated that the mixture stabilized in the A-B system have a critical influence on the final performance.

ii. *Coalescence*
All pastes showed good coalescence under the "lead-free long" profile with BGAs down to 0.15 mm (circles and squares). Pastes **P1** to **P4** formed shiny solder joints, while the joint obtained with **P5** was somewhat dull when investigated under 20× magnification. However, with the harsh extra soak, serious graping defects were observed with all 5 pastes even up to 0.45 mm BGAs, but with less degradation in performance for **P1**.
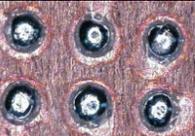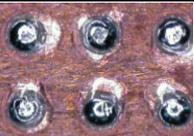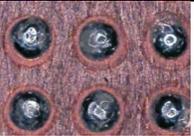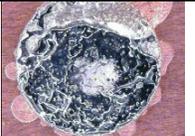
Paste	P1	P2	P3	P4	P5
Tackiness	35	43.3	45	24.4	19.3
IPC slump	0.30,0.33	0.15,0.33	0.25,0.56	0.30,0.63	0.30,0.56
Shelf-life	Stable after 3 month at room temperature	Start to dry out after one week	Start to dry out after two weeks	Stable after 3 month at room temperature	Stable after 3 month at room temperature
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%
Reflow profile1 (lead-free long)					
Solderballing	L3	L2	L1	L1	L4
Coalescence	0.15mm BGA	0.15mm BGA	0.15mm BGA	0.15mm BGA	0.15mm BGA
Dewetting on 6.5 mm pad	71%	68%	72%	74%	60%
Reflow profile2 (lead-free extra soak)					
Solderballing	L3	L4	L4	L2	L5
Coalescence	0.30mm BGA	0.45mm BGA	0.45mm BGA	0.45mm BGA	0.40mm BGA
Dewetting on 6.5 mm pad	58%	59%	55%	57%	31%
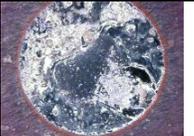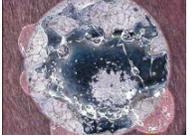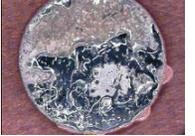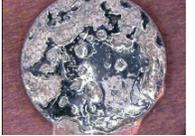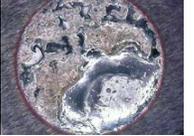
Table 4. Summary of paste properties and reflow performance.

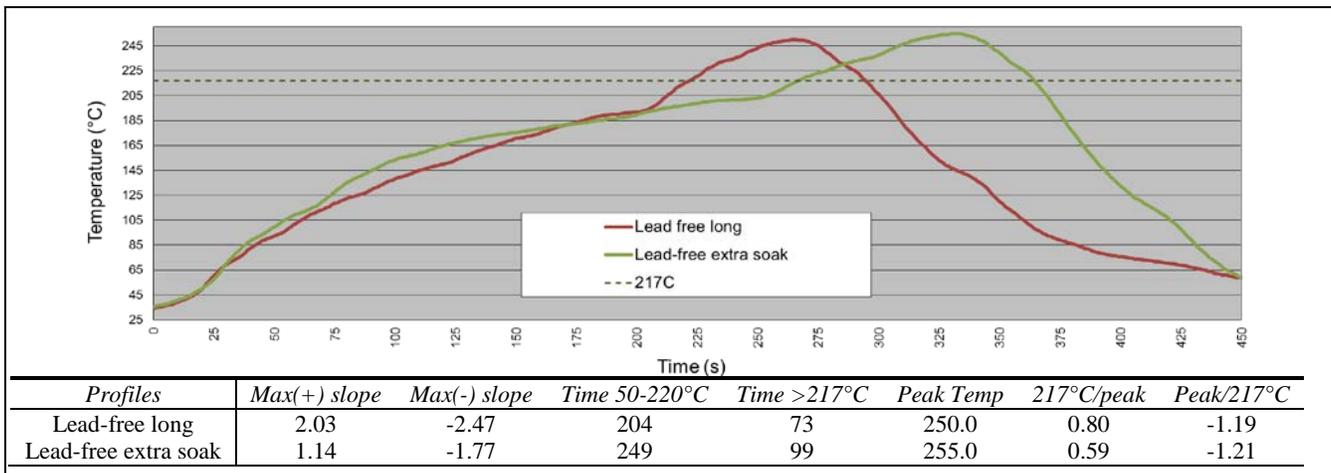| Profiles	Max(+) slope	Max(-) slope	Time 50-220°C	Time >217°C	Peak Temp	217°C/peak	Peak/217°C
Lead-free long	2.03	-2.47	204	73	250.0	0.80	-1.19
Lead-free extra soak	1.14	-1.77	249	99	255.0	0.59	-1.21

Figure 6. Reflow profiles.

iii. *Dewetting*

The dewetting study follows the procedure modified from IPC-TM-650, method 2.4.45, discribed in the experimental section. **P5** did not wet the 6.5 mm circle well, with only 60% of the area covered with solder. The wetting area almost shrunk to half with the extra soak. Paste **P1** showed a much stronger wettability as the solder covered 71% of the 6.5 mm circle area when the "lead-free long" profile was used, and the areas only reduced to 58% when reflowed with the extra soak. It is worth noting that although **P5** could not sustain good wetting, comparable results to **P1** were obtained when B is becoming more predominant in **P2** to **P4**. From this perspective, the far-from-linear evolution of wetting performance with the A/B ratio demonstrates that discrete species drive the performance of the final formula rather than simple mixes.

iv. *Stability*

Pastes **P1**, **P4** and **P5** are remarkably stable with no separation or viscosity increase after 3 month storage at room temperature. Also, no degradation in solderability was noticeable with these three pastes. On the other hand **P2** started to dry out after one week followed by **P3** drying out after two weeks. The compounds created in **Act2** and **Act3** are therefore unstable in the paste environment, and they interact much faster with the solder powders under ambient conditions.

CONCLUSION

In summary, five activators were created from standard chemicals A and B commonly used in solder paste formulation. The physical properties, thermal stability and solderability of these activators can be tuned by adjusting the ratios between A and B. We demonstrated that specific entities govern the product performance. The production of these will depend on complex interactions within the formula and will be dependent on formulation and processing parameters. As an example, the tackiness, hot slump resistance and shelf-life of our pastes varied in a non-linear fashion with the activator stoichiometry. The deviation from linear correlation was also observed in solderability evaluations. In spite that A and B are quite similar in certain aspects, combining them in different ratios may remarkably alter the pastes performance from head to toe. Additional studies on the reaction mechanisms during reflow between these activators and other flux components, solder alloy powders, and surface metal oxide layers areis desired to provide further scientific guidance to improve the performance of solder paste formulations.

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