

The Role of Organic Amines in Soldering Materials

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Abstract

The transition from eutectic tin-lead to lead-free soldering in electronic assembly, mandated by the RoHS legislation, has brought great pressure and challenge to solder material formulation due to the high soldering temperature and high alloy surface tension. Moreover, the demand for halogen-free materials, which should be transparent to process yields, along with the miniaturization trend in the electronic industry, is triggering a revolution in solder flux and paste formulations.

The chemical and material interactions related to soldering and assembly processes are many and varied. In general, the chemicals have to be stable during handling at mild temperatures to warrant a process-friendly shelf-life. While at preheat and soldering temperatures, the solder flux or the paste have to provide thermal transfer to the joint area and react with the metallization on the printed circuit board (PCB) and component leads to remove oxide and surface contamination in order to prepare the surface for good metallurgical bonding, prevent re-oxidation with the atmosphere until the solder alloy re-solidifies, and promote wetting to form the joint. Residues created by the flux contain metal salts, as well as organic and inorganic byproducts.

A traditional formulation mainly relies on organic-based materials, rosins and carboxylic acids to promote fluxing. Several attempts to understand the reactivity of organic acids and halogenated species have demonstrated the complexity of the chemical systems involved in fluxing mechanisms. Amine based formulations were mostly found in the old days, in the forms of ammonium or ammonium halides. Here, we report a preliminary study aiming at giving some insight into the role of amines in electronic assembly applications. Our work shows that practical tests can be developed to characterize some fundamental properties of the activator packages which directly impact the final performance. The study of interactions between individual components within the system is another key aspect of the design work. From that perspective, we intend to demonstrate that the formulator can develop robust formula based on scientific principles and rational studies rather than empirical knowledge and trial-and-error approaches.

Key words: Lead-free, halogen-free, flux, activator, amines

Introduction

A revolution in the formulation of soldering materials in the electronic assembly industry is carrying forward along with the transition from eutectic tin-lead to lead-free soldering mandated by the RoHS legislation. However, most lead-free solder alloys are associated with higher melting points, poorer wetting ability, and inferior oxidation resistance compared to the eutectic Sn/Pb solder systems.¹⁻³ On the other hand, with the fast development and advances in the electronic industry, such as higher integration and fine pitch components, the fluxing performance in terms of activity, process robustness, and reliability has become paramount. Moreover, the demand for halogen-free soldering materials with equal or superior performance compared to their halogenated predecessors makes the design of interconnecting materials (solder paste, liquid flux, tacky flux, cored wire, etc.) formulations even more challenging. New characteristics of solder material formulation have to be adjusted to promote enhanced thermal stability and higher fluxing activity.

Soldering is defined as the process of joining metallic surfaces mediated by a low melting point alloy without melting of the basis metal. Despite of the application orientated differences in solder paste, chemical flux or other soldering materials, the flux chemistry plays the critical role to promote the formation of a reliable intermetallic bonding between pads/barrels and components. The soldering process is triggered and controlled by a carefully engineered thermal profile, where 3 key aspects of the fluxing mechanism can be highlighted:

- 1) The flux mediates the thermal transfer to the joint area and properly wets the surface
- 2) It removes the passivation layers and the surface contamination from the PCB pads and component leads.
- 3) It protects 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 soldering process.

Most traditional solder formulation are acid-based, relying on rosins, halides and carboxylic acids to perform the fluxing chemistry.⁴ High concentration ammonium or ammonium halides have sometimes been utilized in the past. However, the knowledge base on the fluxing functionality of amines is limited as published studies are scarce.

There are two types of reactions involved in removing the metal oxide or surface contamination layer: the redox reaction and the acid-base reaction. The simplified reaction mechanism can be illustrated through two general chemistry experiments. One evidence is that passing dry ammonia over copper (II) oxide in a heated hard glass tube; the ammonia reduces the black copper (II) oxide to brown copper and is oxidized to nitrogen gas. The reaction can be expressed using the chemical equation below:



This redox type reaction mechanism has been widely studied in ammonia elimination process using copper oxide bimetallic catalysts.⁵ More commonly, acid-base reaction between ammonia and copper (II) ion is often accountable. The blue hydrated Cu(II) ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is formed when the Cu(II) hydroxide, carbonate, sulfate, or nitrate binary compounds are dissolved in water. In the first stage of the reaction, the ammonia acts as a Brønsted-Lowry base,⁶ which is a molecular entity capable of accepting a hydrogen (proton) from an acid (i.e. a 'hydrogen acceptor') or the corresponding chemical species. With a small amount of ammonia solution, hydrogen ions are pulled off two water molecules in the hexaaqua ion (Figure 1). The neutral complex is a pale blue precipitate insoluble in water due to lack of charge. Adding an excess of ammonia re-dissolves the precipitate, resulting in a deep blue solution. In this step, ammonia behaves as a Lewis base [6] owing to its lone pair of electrons. The ammonia uses its lone pair to form a co-ordinate covalent bond with the copper and replaces four of the water molecules around the copper to give a charged tetraamminediaquacopper(II) ions. The color change of reaction is shown in Figure 1.

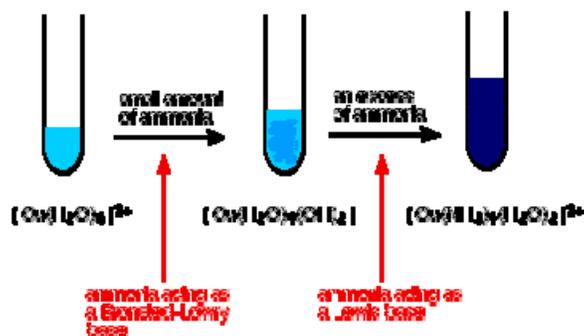


Figure 1. Color change of reaction between ammonia and copper ion.

The definition for amine from International Union of Pure and Applied Chemistry (IUPAC) is “compounds formally derived from ammonia by replacing one, two or three hydrogen atoms by hydrocarbyl groups, and having the general structures RNH_2 (primary amines), R_2NH (secondary amines), R_3N (tertiary amines)” (Figure 2). Similar to ammonia, amines are basic because of a lone pair of electrons on the nitrogen atom as shown in Figure 2. The strength of the base is related to the availability of the lone pair and hence the electron density. Ammonia (an amine with H as R) is a weaker base than primary amines because the alkyl group pushes electrons towards the lone pair. However, aromatic amines are less basic than ammonia, because the delocalized electrons in the benzene ring reduce the electron density.

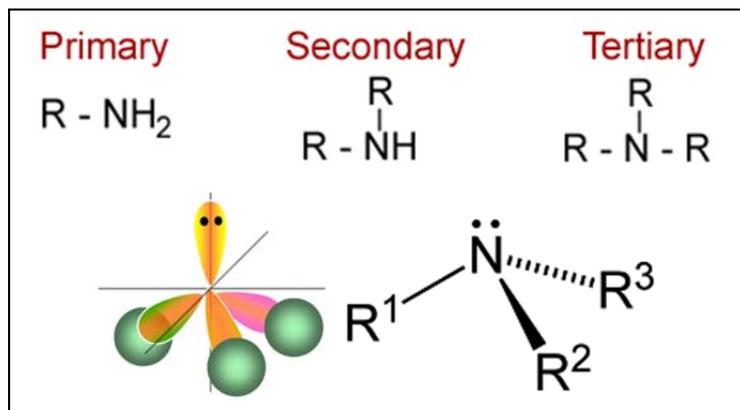


Figure 2. Structures of primary, secondary and tertiary amines and illustration of a lone pair of electrons.

Just like ammonia, amines can react with CuO or Cu(II) ions in similar ways. In the actual soldering process, the reaction mechanism can be extremely complex due to the soldering material formulation complexity, reflow profile differences, board and component variations, and environmental impacts. The chemical reactions and by-products can be greatly altered at elevated temperatures, in different solvent media, and on distinct reaction substrates. Nitrogen- and oxygen-donor ligands are very prevalent in Cu(II) chemistry and cover a wide range of ligand types, for example, N-donor ligands include saturated amines like ammonia and ethylene diamine, azides, nitrogen-bound cyanates, and aromatic amines such as the pyridines and imidazoles. In some cases, these bidentate ligands whose geometry enables them to occupy more than one coordination position on the central Cu ion and tend to form stable complexes. The Cu(II) complex with a N/O-mixed donor ligand and a diamine ligand are shown in Figure 3 as an example.^{7,8}

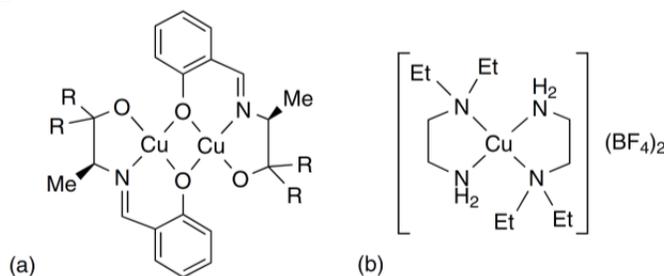


Figure 3. Examples of copper complex with N/O-mixed ligand and diamine ligand.

In order to understand the chemistry of soldering reactions and build up the bridge between amine physical properties and solderability to gain fundamental understanding of the role of organic amines in solder material, four common organic based amines, with variance in basicity, boiling point, and structure complexity were studied as activators in this report. The physical properties, surface tensions, and conductivities of their aqueous solutions were investigated. Their thermal stabilities were assessed through thermogravimetric analysis. The activities of the water based fluxes were evaluated using wetting balance and solder spread tests. The basic chemical models may help to describe the complex reactivity of these species in actual conditions, and build up practical methods and principles to characterize fundamental chemical properties which impact the final formula performance.

Experiments

Amine activator flux

Four simple water based flux formulas were made by dissolving four amines at 5 wt% in deionized (DI) water.

Surface Tension

Surface tension of each amine activator flux was tested using pendant drop method. The results are computed with proprietary software. The averages of five reading are recorded in Figure 3.

Conductivity measurements

Conductivity of each amine activator flux obtained using conductance meter.

TGA

Thermogravimetric analysis of amine activators was performed on TGA using a straight ramp in air atmosphere. 10±1 mg of sample was weighed and loaded in auto-sampler to a sequence run.

Spread tests

Hot plates with controlled temperature setup were used to investigate the impact of various preheating temperatures on soldering by heating a SAC305 (96.5 % tin, 3% silver, and 0.5% copper) preform placed in the center of a copper test coupon. A small aliquot (0.1 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 circle. Four preheating temperatures in increasing sequence, namely Low, Mid, High, and V. High, were used to evaluate the activator heat resistance. Observations of the soldering sequence were documented and the solder spread areas were measured. Three samples of each amine flux at each preheat temperature were tested and the spread areas are shown in the variability chart in Figure 9.

Wetting balance

To evaluate the activity and solderability/wettability of the respective 5 wt% amine activator solutions, wetting balance was utilized. Copper wires with diameter of 0.6 mm and length of 30 mm attached to a 78 mm long spring-loaded chuck were used to test the flux wetting time and force in a solder pot filled with SAC305 alloy. The copper wire filaments were first washed and degreased in isopropyl alcohol by swirling for 1 minute with a stir bar and stirrer. They were then acid washed swirling in 5% hydrochloric acid solutions for 1 minute, followed by deionized water rinsing. The copper wires were finally

cleaned individually using a lint free wipe. Measurements were performed immediately following cleaning and drying. Table 1 describes the parameters used for wetting balance set-up.

Table 1. Wetting balance set-up parameters

Test parameter	Set value
Solder pot temperature	260 °C
Immersion Speed	1 mm/s
Immersion Depth	2.0 mm
Hold Time	10 s

Copper wires were dipped in flux and held for 10 seconds using a chuck and quickly attached to the main unit. The wave was activated by software and the wetting curve was recorded. The corresponding wetting times and forces were exported from the curve and calculated according to the equations shown in Figure 6 and Table 3.

Results

Four common organic-based amines activators (**AA1-AA4**) with various chemical structures are selected in this study. The physical properties of **AA1** to **AA4** are investigated on their 5 wt% aqueous solutions.

i. Surface tension

Surface tension is the force per unit length in the plane of the interface between a liquid and a gas, which resists an increase in the area of that surface.⁸ Higher surface tension holds the materials from spreading, as seen in the case of water beading on a leaf. On the other hand, lower surface tension helps the flux spread over to cover more surface area of the PCBs and component leads, which may enhance wetting. Interacting with water molecule, probably through intermolecular hydrogen bonding and dipole-dipole interaction, these amines bring down the surface tension of DI water to as low as 54.3 dynes/cm for **AA1**, compared to 72 dynes/cm for DI water at 25 °C.

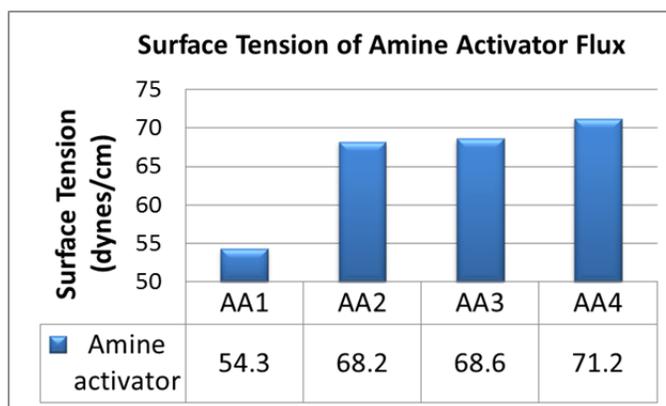
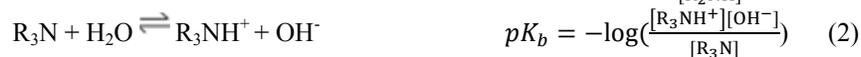


Figure 3. Surface tension of amine activator solutions.

ii. Conductivity

Conductivity measures a material's ability to conduct an electrical current. Upon dissolving in water, amine molecules start to react with water and dissociate to form positively charged ammonium ions and negatively charged hydroxide ions. The electrical conductivity depends on the ion charge, mobility, and concentration. Since hydroxide ion is much smaller than the ammonium ion while carrying the same charge, the conductivity of the amine solutions with the same concentration mostly depends on the availability of hydroxide ions. The basicity of an amine is usually described by the base dissociation constant (pK_b) in which K_b is the equilibrium constant of the reaction between amine and water as shown in equation (1) and (2) below:



The stronger basicity of amine is, the smaller number of pK_b is, the higher concentration of hydroxide ions are presenting in solution. The conductivity of the amine solutions are listed in Figure 4. **AA4** solution has the highest conductivity which is consistent with its highest basicity in nature. It is worth noting that 1) the basicity of amine is strongly depended on solvent and temperature and 2) the strong basicity of amine is not always corresponding to high solderability; many other factors contribute during the solder process.

Hence, properties of the flux in its original state are remotely related to the final performance. However, the conductivity nature of the activator may be an indicator to the solder byproduct physical state which may influence the solder surface tension and residue reliability.

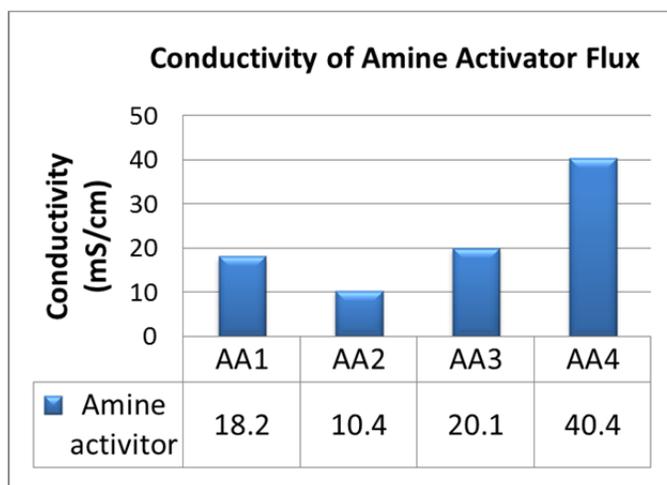


Figure 4. Conductivity of amine activator solutions.

iii. Thermal Stability

The thermal stabilities of the four amines are evaluated by thermogravimetric analysis at a slow ramp in air. The weight change versus temperature curves are shown in Figure 5 and the weight loss rate and temperatures are summarized in Table 2.

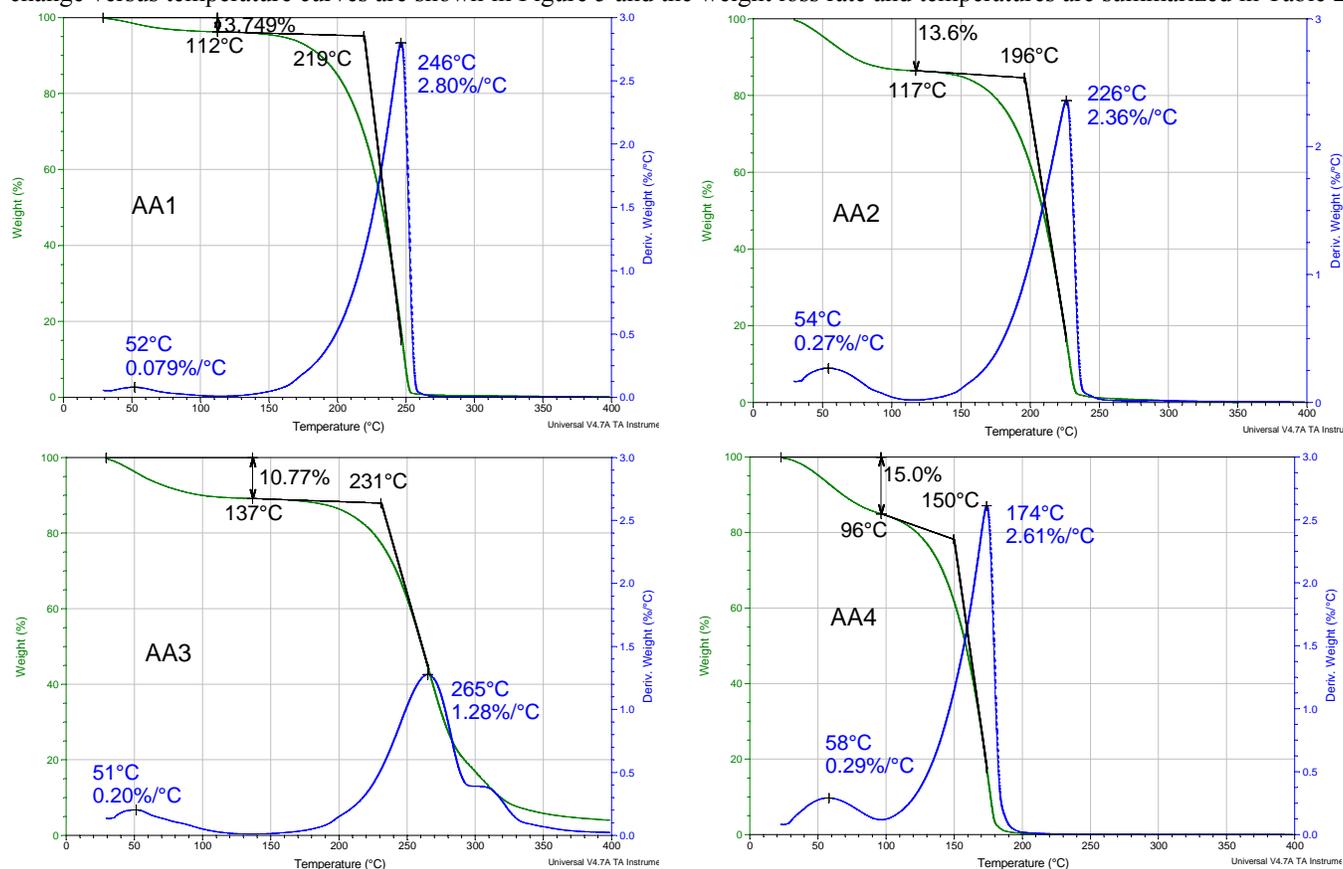


Figure 5. TGA curves of 4 amine activators with straight ramp of 10 °C/min.

There are two stage weight losses observed for all four amines. The initial stage is a slow weight loss from room temperature to a plateau around 100 to 140 °C, corresponding to the evaporation of the amine liquid. **AA1** has the least weight loss with a rate of 0.079%/°C, which is consistent with the lowest vapor pressure of **AA1** among the four amines. **AA1** to **AA4** experienced the major weight loss in the second stage which may relate to thermal oxidation and decomposition. Right after the evaporation stage, **AA4** severely decomposed from an onset temperature of 150 °C, reached the peak rate of 2.61%/°C at

174 °C, and totally burnt out before 200 °C. **AA3** has the highest stability and heat resistance. The weight loss only started above 200 °C at a less than half rate compared to other three amines. There was around 5% left even up to 400 °C. The high thermal stability of **AA3** may help it survive harsher conditions (e.g. high preheat temperature, longer soak reflow profiles) to still maintain the activity reaching the solder temperature; however, the relative high residue level may result in some reliability issues.

Table 2. TGA characteristics of amine activator AA1-AA4.

	<i>AA1</i>	<i>AA2</i>	<i>AA3</i>	<i>AA4</i>
Initial weight loss (%)	3.75	13.6	10.8	15.0
Initial stable temperature (°C)	112	117	137	96
Initial weight loss peak temperature (°C)	52	54	51	58
Initial weight loss peak rate (%/°C)	0.079	0.27	0.20	0.29
Major weight loss onset temperature (°C)	219	196	231	150
Major weight loss peak temperature (°C)	246	226	265	174
Peak weight loss peak rate (%/°C)	2.80	2.36	1.28	2.61

iv. Wetting balance

To quantitatively investigate the solderability of flux, the wetting balance method creates a dynamic process to estimate the kinetics of wetting of the surface under test. In this test, the wetting force and time were collected by carrying on the experiments using dip wetting balance methodology. The flux coated copper wire specimen is suspended from a balance with high sensitivity and immersed to molten solder at a predetermined speed, a controlled depth and time, and a specific temperature. The specimen experiences the vertical buoyancy forces and time-varying surface tension forces through the interaction between the molten solder and the substrate entering the molten solder at t_0 . The wetting forces are pulling the specimen into the molten solder whereas the buoyancy forces are pushing the specimen out. When the wetting forces are equal to the buoyancy force (t_1), the solder contact angle to the test coupon is 90°. The molten solder is continuing to wet the specimen surface and the wetting force reaches two-thirds of its maximum value at t_2 . Flux continues to be consumed when the specimen is held in the molten solder for a certain time before it is taken out to give the final wetting force F_{end} . The whole process is illustrated in Figure 6.^{9,10}

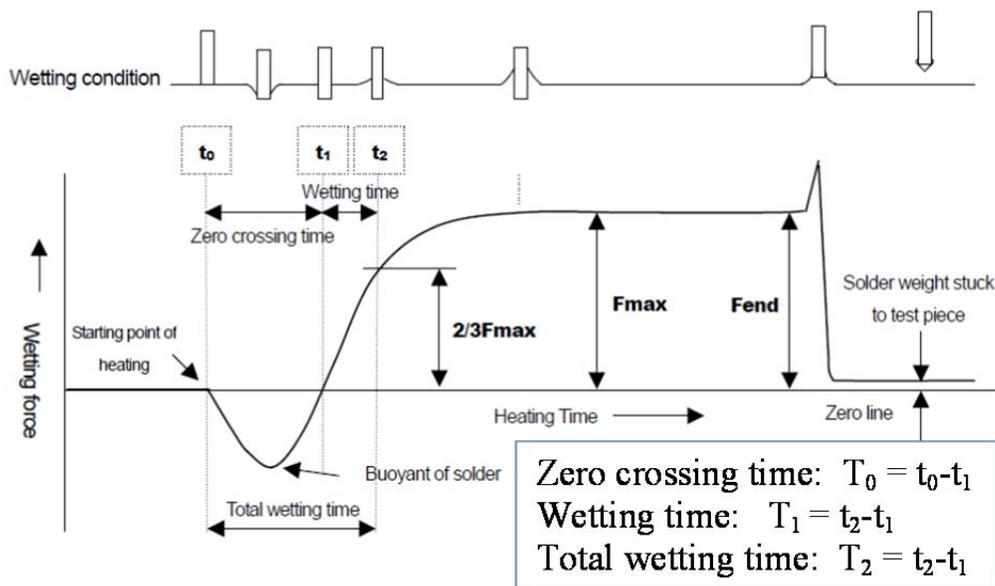


Figure 6. Wetting Curve by wetting balance method.

Wetting time ($T_1 = t_2 - t_1$) and maximum wetting force (F_{max}) are the key parameters measured to estimate the flux solderability. The wetting stability (F_{end}/F_{max}) gives some indication of sustainability of flux activity. The recorded data and wetting curves of **AA1** to **AA4** are listed in Table 3 and Figure 7. One can clearly see that **AA4** shows no wetting when in contact with the solder. **AA1** promoted the solder to quickly wet the copper wire within 0.15 s and reached a maximum wetting force of 0.41 mN, which slowly decreased to 70% of its original value after 10 s holding in molten solder. **AA2** and

AA3 exhibited excellent wettability with an extremely fast wetting speed to reach 2/3 of the maximum wetting force within 0.05 s. Although **AA2** has slightly higher max wetting force, **AA3** stands out by being able to maintain the high wetting force even after 10 s immersing in molten solder. This is consistent with the highest thermal resistance observed for **AA3** through thermogravimetric analysis, as discussed earlier.

Table 3. Wetting balance test summary.

		<i>AA1</i>	<i>AA2</i>	<i>AA3</i>	<i>AA4</i>
Zero crossing Time	T0 (s)	1.93	1.06	0.94	Non-wetting
Wetting Time	T1 (s)	0.15	0.04	0.05	Non-wetting
Total Wetting Time	T2 (s)	2.08	1.10	0.98	Non-wetting
Max Wetting Force	F _{max} (mN)	0.41	0.62	0.58	Non-wetting
End Force	F _{end} (mN)	0.29	0.46	0.49	Non-wetting
Stability (F _{end} /F _{max})	F _{end} /F _{max}	0.70	0.74	0.85	Non-wetting

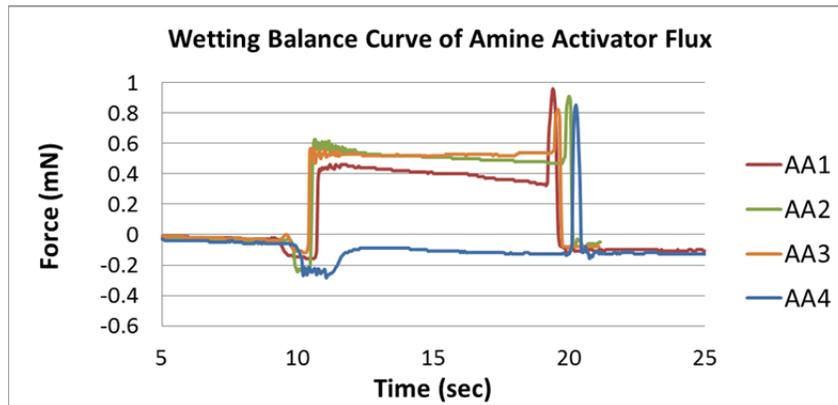


Figure 7. Wetting curves of amine activator solutions.

v. Spread test

Spread test is an intuitive way to quantitatively estimate the solderability of activator and flux. The experiments designed in this study were to mimic different preheat conditions and evaluate the wettability of the amine activators by measuring the spread area under each profile. The typical pictures of the SAC305 preform after soldering with each amine activator flux and the variability charts of the spread areas at four preheating temperatures are shown in Figure 8 and Figure 9, respectively.

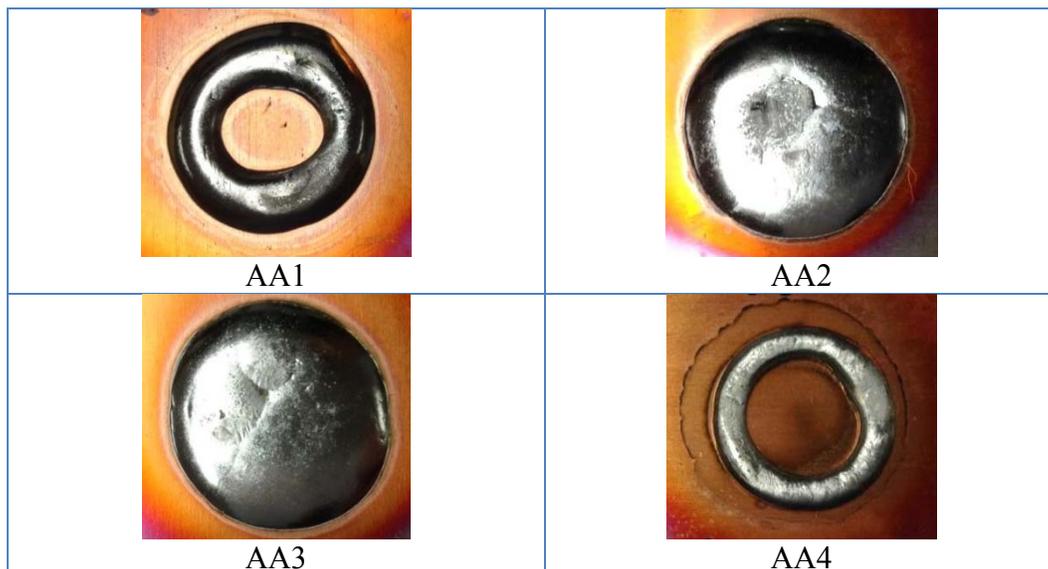


Figure 8. Spread test sample pictures.

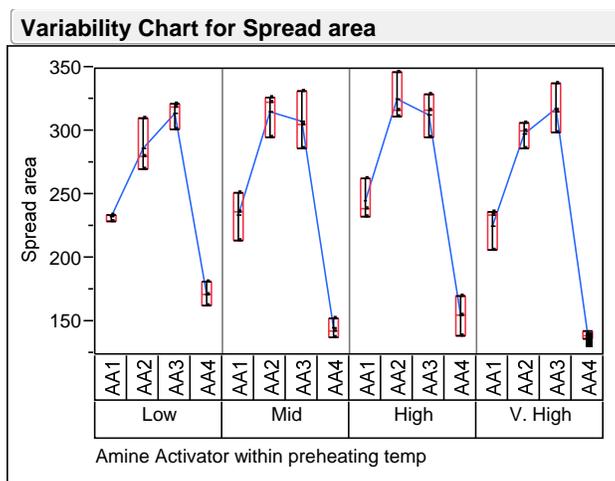


Figure 9. Variability Chart for spread area of amine activator fluxes.

It can be clearly seen from the picture and the variability charts that **AA2** and **AA3** fluxes provided excellent wettability. The solder preform spread out quickly after molten to wet the surface; the contact angle of which is much smaller" with "the contact angle of these preforms is much smaller compared to the preform soldered by **AA1** and **AA4** fluxes. The sustained activity of **AA2** and **AA3** is revealed by the consistent spreading performance over a wide preheat profile range where no degradation was seen even under "V. High" preheating. This could be attributed to the high thermal stability of **AA2** and **AA3** as described in the TGA study. On the other hand, although **AA4** has relatively strong basicity, the high volatile nature and low thermal stability make it easily lose activity even at low preheat temperature. Also, the solderability observed from this spread test is consistent with the wetting balance study.

Conclusions

The selection of activator for solder material formulation needs to take multiple factors into consideration. The activator must be suitable for thermodynamically favorable and kinetically accessible reactions to remove metal oxides; hence, solderability is a combined outcome of the overall physical and chemical properties. More importantly, the activators also need to be compatible with other ingredients in the formulation to provide adequate shelf-life at mild temperature and activated synergistically during reflow to perform the fluxing chemistry. Further studies are ongoing to gain a comprehensive understanding of the reliability aspects associated with this class of chemicals.

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