"Thermal Residue Fingerprinting: A Revolutionary Approach to Develop a Selective Cleaning Solution"

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ABSTRACT:

During the last 5 years, the processes to remove flux residues especially for lead-free and challenging geometries have demonstrated new cleaning obstacles which have to be overcome.[i] A new methodology has been recently developed to further increase the propensity for successful cleaning.[ii] At the core of this method is the thermal identification of the residue matrix. Thermal energy changes the physical state, i.e. transitions between liquid, solid and gas phases. By taking advantage of such specific information during phase transitions, the cleaning process can be tailored to such settings, which in turn increases the cleaning success significantly.

Thermodynamic data from differential scanning calorimetry (DSC)[iii] will be presented in conjunction with experimental data obtained from subsequent cleaning trials in spray-in-air batch cleaning systems. Flux systems that were investigated during this initial study including rosin-based and No-Clean fluxes. A correlation between phase transition temperatures of reflowed flux residues and optimized cleaning parameters for each flux will be presented.

This approach is revolutionary in that it offers completely new, previously untapped avenues to clean challenging electronic assemblies. It also offers insight to previously set process limitations on process temperatures that might have to be reconsidered.

INTRODUCTION:

The Thermodynamic Nature of Flux

Experience indicates that softer residues are easier to clean than hard residues. What makes a residue hard is inherent in its make-up and history. The thermal history of a flux residue is important. The number of solder reflow cycles, the peak temperature, time after reflow and duration of the heating and cooling cycle will influence the hardness and thus, the cleanability of the residue.

One other important factor is the chemical make-up of the flux residue. Heating the flux drives out solvents and plasticizers that needed to make the flux/solder paste printable or dispensable in the assembly process. The heating process metamorphosizes the flux from a liquid or gel to a solid plastic like residue. Organic molecules in the solid form can either arrange in a crystalline structure or fold and wrap in an amorphous crystalline matrix (Figure 1a and 1b).

Amorphous and crystalline polymers act differently when softening. Crystalline structures are arranged in nearly perfect lattices and therefore when heat is sufficient to release one molecule from the lattice, they all fall apart.
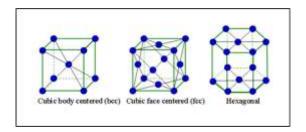
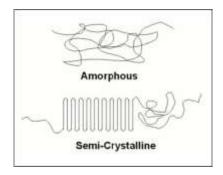**Figure 1a:** Examples for defined crystalline structures

Figure 1b: Examples for amorphous crystalline structures

We refer to this as melting, and the temperature at which this happens is called the melting point (T_m). Amorphous crystalline residues have a glass transition temperature (T_g) not a melting point (Figure 2). Above the T_g the molecules can slip pass one another giving a lower modulus. Most post soldering residues are amorphous, although some are mixtures of both. Amorphous flux solids will therefore soften and continue to soften above its' glass transition temperature.
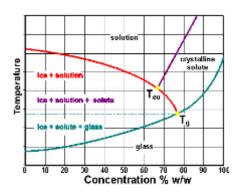

Figure 2: Phase transitions and T_g

Another factor that can influence the softening of the residue for cleaning would be the plasticizers remaining in the residue after reflow. Plasticizers are smaller organic molecules that act as lubricants between the larger polymers in the matrix. They effectively lower the T_g of the residue. This explains the observation that some flux residues become harder to clean if they set for more than a couple hours as the plasticizers evaporate over time. Cleaning solvent molecules can act as plasticizers if they can penetrate the solid residue. The function of the pre-wash in modern inline cleaners is to allow time for the solvent molecules to diffuse into the flux matrix and lower the T_g allowing the wash to act upon a softer residue.

Research Methodology

To cover a range of fluxes, seven common leaded Sn63Pb37 solder pastes and seven lead-free solder pastes were selected for this study. The pastes were screened onto the test substrate; components applied, and reflowed as per guidelines supplied from solder paste suppliers.

The test vehicle used is a standard 2.5" X 3.5" X 0.32" circuit card with solder mask. Each sample was populated with ten, 0603 capacitors as shown in Figure 3 below.
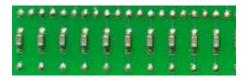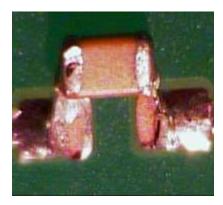

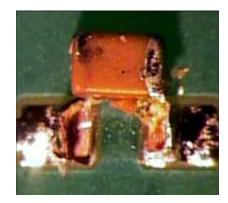**Figure 3:** Test vehicle sequentially populated 0603 capacitors

The smaller resistors and capacitors used on modern SMT electrical designs are very prone to completely filling the 1-3 mil gap between the component and the substrate. In fact, all the test samples created for this test showed visual evidence of nearly 100% filling of the gaps. Even the No-Clean fluxes show signs of complete filling. All Pads were printed and reflowed, but only 10 sites were populated with 0603's.

Following, reflow samples of the flux residue were scraped from the un-populated pads and sent for DSC analysis.

All cleaning trials were performed in an Austin American Technology high temperature, "dishwasher style" batch cleaner. Cleaning temperatures were then selected to bracket glass transitions and melting temperatures indicated by DSC. Following cleaning, each component was removed by sheering at room temperature for microscopic visual analysis at 40X (Figure 4a and 4b). Visual examination was complemented by a visual flux test experiment to fully confirm the presence and/or absence of any remaining residue.

Figure 4a: Pass - No flux residue remains under component
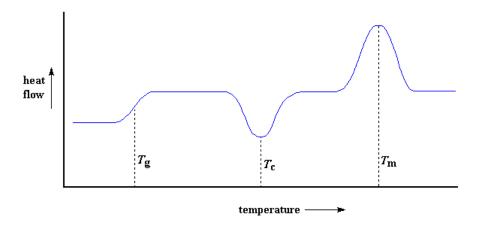

Figure 4b: Fail – Any Flux residue detected at 40X

All of the components were removed for visual analysis. Any residue detected under any of the 10 components on the board constituted failure of the entire board.

DSC Results

The authors chose to employ Differential Scanning Calorimetry (DSC) method to best characterize phase transitions within the flux residue matrix (Figure 5).

Figure 5: Example of a DSC plot

DSC subjects the specimen to a precisely controlled temperature environment while continuously monitoring the heat input and output. Exothermic and endothermic reactions within the specimen cause changes in the heat input and output. For this reason, DSC can be used to assess the thermal stability of a material. The specimen and a thermally inert reference material are placed in a Differential Scanning Calorimeter, exposed to an inert gas atmosphere, such as nitrogen, and curves of Temperature vs. Heat Flow are generated. When a reaction occurs within the specimen that involves a change in enthalpy, the curve will deviate from its baseline. Such reactions include melting, glass transition, decomposition, etc. Melting is an endothermic reaction that produces a upward peak in the Temperature vs. Heat Flow curve. For this and other peaks, the extrapolated onset temperatures, the point where the peak begins and peak temperature are generally reported. Glass transition is an endothermic process that produces an increase in the slope of the Temperature vs. Heat Flow curve. The glass transition temperature is the temperature chosen to represent the range over which the glass transition occurs. This temperature (T_g) can either be the point that corresponds to the maximum value of the slope during this change or the approximate midpoint of the temperature range over which the glass transition occurs. Crystallization is an exothermic reaction that produces a downward peak on the curve.

A Perkin Elmer (model DSC-7) DSC was used to determine the T_g's and the melting point of constituents in the fluxes tested. Some fluxes showed no thermal events which indicated the absence of melting or glass transition points in the temperature range tested (131°F/55°C - 554°F/290°C). Others showed thermal events indicating softening of the residue. The most likely explanation of "no event" fluxes is that they were formulated with resins having T_g's lower than room temperature. In other words, they were soft at room temperature and still can get softer with higher temperatures.

Figure 6: DSC graph of flux residue showing typical thermodynamic responses

Figure 6 shows an example of a typical the DSC scan of a flux sample indication both a glass transition and a melting event. The glass transition occurs around 63°C and is indicated by a shift in the slope of the curve. There are two endothermic events; one occurring around 93°C and a more complex endo/exothermic event occurring from 122°C to 137°C. For the purposes of this study we ignored events above our maximum cleaning temperature of 93°C. The y axis of the DSC scan is differential heat flow between the empty control pan and the sample pan. The flux sample size varied from 7 mg to 30 mg.

A summary of the thermal events detected by the DSC scans for all fluxes tested in this study is shown in Table 1.

Table 1: Thermal events indicated by DSC

Flux (Alloy)	T_g in °C	Melting Point Events in °C	Boiling Point in °C	Thermal Events $T_{critical}$ in °C
1. Alpha RMA 390 DHA		141, 163, 192	154	
2. Indium RMA-SMQ 51 AC	**64**	**93**, 130, 242		**64, 93**
3. Indium NC-SMQ 92 J	214	**92**, 191, 210	**88**	**88, 92**
4. Kester EP 256		155		
5. Kester EP 256 HA	111	173	**61**	**61**
6. Kester FL 250 D		133, 178, 205		
7. Multicore MP 218		121		
8. Alpha OM-338 T	**63**	171		**63**
9. Indium 5.1		198, 230		
10. Indium 8.9		67-75, 183		
11. Kester EM 828		92, 135		
12. Kester EM 907		67, 87		
13. Kester R 520 A		113		
14. Multicore LF 318	120	123		

Cleaning Confirmation Trials

Having established the initial thermodynamic events based on DSC analysis, the authors set out to validate the findings, meaning establishing a relationship between the thermal data and a potentially improved cleaning performance. Table 2 outlines the experimental setup chosen during this study. Based on the results of the DSC thermal event study, the following cleaning temperatures and processes were tested.

Table 2: Overall Cleaning Process Parameters

Overall Cleaning Process Parameters			
Chemistry	ATRON AC® 205	Concentration	10%
Wash Temperature	52°C, 66°C, 80°C, 93°C	Exposure Time	15 min at set temp.
Pre-Rinse	up to 1MΩ	Final Rinse	1 min at 57°C
Drying	30min at 68°C	Distance Nozzle-Board	5"-9"
Nozzle	Coherent	Spray angle	45°

The testing was performed in a stainless steel, spray in air, batch cleaner utilizing high impact coherent fluid delivery jets. The cleaning solution was premixed and preheated to the test wash temperature to keep cleaning times constant as temperature varied. The test boards were racked in the cleaner at a 45° angle with the parts facing up. Cleaning time was set at 15 minutes for all tests. All test results were evaluated through a 4 eye principle. A "passing" grade was given only to areas on which all flux residues were fully removed (Figure 7).
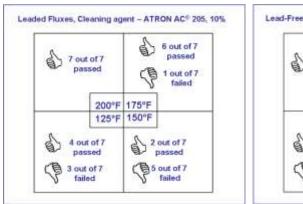
Leaded Fluxes, Cleaning agent – ATRON AC® 205, 10%

7 out of 7 passed | 6 out of 7 passed / 1 out of 7 failed

| 200°F | 175°F |
| 125°F | 150°F |

4 out of 7 passed / 3 out of 7 failed | 2 out of 7 passed / 5 out of 7 failed

Lead-Free Fluxes, Cleaning agent – ATRON AC® 205, 10%

7 out of 7 passed | 5 out of 7 passed / 2 out of 7 failed

| 200°F | 175°F |
| 125°F | 150°F |

2 out of 7 passed / 5 out of 7 failed | 4 out of 7 passed / 3 out of 7 failed

Figure 7: Cleaning results at various operating temperatures

Initial observations showed that there is indeed a tendency for improved cleaning with an increase in cleaning temperature. Especially noteworthy is the fact that at 200°F/93°C all cleaning results were found to be positive. At 175°F/80°C still 78% of the results showed that all flux had been removed from underneath the components. Most spray-in-air type equipment have a temperature limitation to not exceed 160°F/71°C. Therefore these findings might allow to further widen the process window, given that higher cleaning temperatures can be realized in future cleaning equipment. At 150°F/66°C most cleaning results showed partially removed flux residues on the substrates. Similar results were found at 125°F/52°C.

Four of the fourteen fluxes tested show direct correlation to thermal events measured in the Calorimetry tests. Fluxes # 4, 7, 12 and 14 showed a transition from unacceptable cleaning results to acceptable results when cleaned above event temperatures. Interestingly, the authors observed that 3 of the samples got cleaned at all temperatures tested. Two of the three fluxes passing at all temperatures have thermodynamic events around 150°F/66°C. The other did not show any thermal events. It is hypothesized by the authors that those that are cleaned at all temperatures had T_g's less than the 50°C starting temperature used in this study. Flux #4 also demonstrated an endothermic temperature event (i.e. melting) at 67-75°F/19-24°C that matched quite well with the improved cleaning performance at temperatures above 150°F/66°C. However the authors also found that not in every case a direct correlation was possible, and in a number of examples temperature events from DSC spectra were well above 200°F/93°C. Furthermore, the authors believe that for most cases the amorphous crystal structure has a glass transition temperature well below the observed DSC temperature ranges. For example, given a glass transition temperature of 0°C, positive cleaning results should be observed at all cleaning temperatures tested. For fluxes 1, 11 and 13 the authors found that to be the case (Table 3 and 4).

Table 3: Cleaning results showing Thermo events

Leaded Fluxes	200°F	175°F	150°F	125°F	Thermo Events (°F)
1. Alpha RMA 390 DHA*	+	+	+	+	147, 190, 199
2. Indium RMA-SMQ 51 AC	+	+	-	+	190
3. Indium NC-SMQ 92 J	+	+	-	+	none
4. Kester EP 256**	+	+	-	-	153-167
5. Kester EP 256 HA*	+	+	-	-	none
6. Kester FL 250 D*	+	+	+	-	none
7. Multicore MP 218**	+	-	-	+	147, 199
Lead-free Fluxes					
8. Alpha OM-338 T*	+	-	-	-	none
9. Indium 5.1*	+	+	+	-	none
10. Indium 8.9*	+	+	-	-	none
11. Kester EM 828*	+	+	+	+	none
12. Kester EM 907**	+	+	+	-	145
13. Kester R 520 A*	+	+	+	+	145
14. Multicore LF 318**	+	-	-	-	194, 201

+ pass   - fail

* possible correlation to T_g less than 125°F (below range measured in this experiment)
** Direct correlation to thermal events measured

Table 4: Experimental results for Flux # 4

Fix process settings: ATRON® AC 205 at 10% with overall wash time of 1min.				
Cleaning Temperature [°F]	Nozzle Configuration	Flux #	Cleaning Result	Picture
125	Coherent	4	-	
150	Coherent	4	-	
175	Coherent	4	+	
200	Coherent	4	+	

FUTURE EXPERIMENTS:

The initial purpose of this study was defined by the possibility of customizing cleaning processes much more precisely as it was previously thought possible. The authors were able to establish that thermal fingerprint analysis is a viable tool that sets the stage to help customers define needed process improvements. A number of further experiments (i.e. flux sample set, component size and geometry, temperature increments especially below 140°F/60°C, just to name a few) are already in progress to elaborate and more closely define all of the possibilities and limitations with this new technique. Furthermore, other analytical methods such as Thermo Gravimetric Analysis (TGA) are investigated as they may complement the described DSC procedure. Lastly, the authors are interested in comparing the results obtained in the batch type equipment with conveyorized cleaning equipment to better baseline the observed results.

CONCLUSION:

The wash cleaning temperature generally improves the removal of flux residues from under tightly spaced components. There appears to be a considerable improvement in the cleaning efficacy at the higher temperatures. There appears to be a step function increase in the rate between 150°F/66°C and 175°F/80°C respectively for most of the fluxes tested in this study.

There did not seem to be a big significant difference in general in cleaning lead-free vs. leaded. This was an unexpected outcome as it is generally expected that the higher reflow temperatures would make the lead-free flux residue harder to clean.

The DSC scans did identify several thermodynamic events occurring at temperatures of cleaning performance shift. Both glass transition and melting points were observed at these process shift temperatures. It is believed that the three samples cleaned 100% at all temperatures had melting or glass transition events below 122°F/50°C. For future studies, the authors would recommend performing DSC analysis at a lower temperature range of 32°F/0°C – 482°F/250°C to identify these events.

In summary, this study highlighted a new method to analyze the impact of an individual fluxes used on the cleaning process parameters. The results obtained truly open new opportunities for current and potential users to investigate customized cleaning process optimizations. The authors provided evidence that thermal fingerprint analysis is a viable tool to correlate physical flux characteristics to the ease of its removal. The expectation is that this methodology will lay the groundwork for a new, individualized cleaning qualification approach that will provide a more stable cleaning process to current and potential customers.

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REFERENCES:

i Stach, Steve & Wack, Harald (2008) Key to low standoff cleaning in SMT Magazine

ii Wack, Harald Ph.D., Aleksic, Sinisa Ph.D, Becht, Joachim Ph.D., Tosun, Umut (SMTAI 2008) Fluid Flow Mechanics: New Advances in Low Standoff Cleaning.

iii Dean, John A. The Analytical Chemistry Handbook. New York. McGraw Hill, Inc. 1995. pp. 15.1–15.5