How to Manage Material Outgassing in Reflow Oven

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Abstract

In a lead-free reflow process, temperatures are higher, and materials use outgasses more than in a leaded reflow process. The trends toward higher density populated boards and more pin-in-paste technology also increase solder paste use. More components and more solder paste result in more outgassing of chemistry during the reflow process. Some assemblies report condensation of vapors when the cold printed circuit board enters the oven. Little is known about the interaction between these condensed materials in terms of the interaction between these condensed materials and the reliability of the assembly. Apart from the question of reliability, a printed circuit board contaminated with a small film of residues after reflow soldering is not desirable.

This study investigates the evaporation of chemicals during the reflow process from preheating until cooling. Different solder pastes are compared with respect to outgassing. Residues collected in the reflow process were submitted to Thermal Desorption-Gas Chromatography-Mass Spectrometry (TDGMS) to determine which volatile and semi-volatile substances the residues contained. A test vehicle was made to investigate if these gasses could be eliminated using a catalyst. After a successful investigation, these catalysts were installed in reflow ovens on individual zones and in those areas where the most outgassing was determined. Different catalysts and solder pastes, chain lubricants, and other materials were part of the study.

Solder paste composition

Solder paste is a mixture of flux and solder spheres. What makes this product unique is that it combines chemistry with metals. This complex combination requires certain properties to be successful. One potential risk is that the chemistry starts to react in the jar before it is used because oxidized metal reacts with solder paste activators when the temperature increases. The solder paste must be thixotropic that is, viscous when printed on the assembly and solid after component placement. The solder paste must also retain a certain tackiness to keep the components in place during reflow soldering.

Solder paste undergoes multiple handling and production processes before it is soldered. After transportation, solder paste is stored, laid on a stencil, printed, and then transported over the Surface Mount Device (SMD) line before it is preheated in the reflow process. The reflow process itself contains four sub-processes: preheating, soak, reflow, and cooling. During different phases of this process, the chemistry composition changes due to evaporation and the melting of the alloy. The IPC J-STD-004 standard divides solder paste fluxes into classes depending on the chemical composition and activation system. In general, fluxes that require cleaning after soldering have much stronger activators than no-clean flux systems. No-clean flux systems are mild because their residues are inert. The requirements for the alloys are defined in the IPC J-STD-006.

The identification designator for the flux in the solder paste is defined in IPC STD-004. This designator has four characters. The first two define the base material. Rosin (RO), Resin (RE), and Organic (OR) are the most common for reflow solder pastes. The other two characters define the activation level (Low (L), High (H), or Medium (M)) and indicate the absence or presence of halides. All these different types and compositions of chemistry can be used in a reflow. Some users mix lead and lead-free solder paste technologies in production, which results in two completely different chemical compositions heated in the same oven. A reflow oven should be flexible enough to handle recipes at different temperatures. A reflow oven should also be capable of processing different flux chemistries that will evaporate and condensate at different temperatures and spots in the oven.

Identification of Volatile Components

Fumes generated in a reflow process are influenced by the chemistry of the materials heated in the reflow oven. Solder pastes, solder masks, and machine components contain chemistries that outgas in the oven. For example, the chain in the oven is lubricated with grease. The grease contains volatiles that fume in the oven after being heated.

Since flux typically contains a variety in chemistries, we investigated three different compositions. The flux of the solder paste in the next experiment was not mixed with the solder spheres to make it easier to define the composition. The method used to define the volatile components was by Gas Chromatography/Mass Spectrometry (GC/MS). The flux paste was held at 185 °C for 30 minutes in a sealed vial and the sample was injected into GC/MS. In total, 42 different ingredients were identified in the three solder pastes. The table lists ingredient names, CAS numbers, and boiling points.

Table 1 –Identified ingredients in solder paste

Name	**CAS number**	**Boiling point**
Terpineol and isomers of	7299-40-3	214-217
	562-74-3	212
	98-55-5	213-218
Higher terpene compounds	2221-95-6	235-236
Cyclohexanone	108-94-1	155
1-ethyoxy-2-methyl-propane	627-02-1	81
Butylated hydroxtoluene	128-37-0	265
Hexaoxaoctadecane	1191-87-3	335
Tripropylene glycol	1638-16-0	360
Tripropylene glycol monomethyl ether	20324-33-8	243
Hexylene glycol	107-41-5	197
1-Methyl-2-pyrrolidinone	872-50-4	202
Isolongipholene	1135-66-6	197
Muurolene	30021-74-0	298

The ingredients included five types of rosin (rosin ester, modified rosin, and hydrogenated rosin). The three solders paste chemistries were a mixture of lead-free, tin-leaded, no-clean, and washable solder paste. Most of today’s applications (worldwide) are lead-free, no-clean rosin or resin-based flux chemistries. It was not possible to do a similar analysis for all these fluxes, but with the solder samples, it was possible to investigate how much volatiles are evaporated, at specific temperatures, for popular lead-free solder pastes.

Thermogravimetric Analyzer studies of solder paste

A small solder paste sample (10 ± 2 mg) was put into a Thermogravimetric Analyzer (TGA) for a reflow analysis. A small gas flow of 25 ml/min was purged into the analyzer during the experiment. The paste was stabilized for one minute at 40 °C. After that, the solder paste was heated with a slope of 60 °C/min from 40 °C to 245 °C. During this heating, the balance of weight in the solder paste changed. See figure for weight loss as a function of temperature.

A total of nine different commonly used lead-free, no-clean solder pastes from different suppliers were investigated by TGA.

Table 2 - Solder paste properties.

	Alloy	Classification	Spheres	Melting point	Remarks
Paste 1	Sn3.0Ag0.5Cu	ROL0	20-38 micron	217-219	
Paste 2	Sn3.0Ag0.5Cu	ROL0	20-38 micron	217-219	
Paste 3	Sn3.5Ag0.5Bi6.0In	ROL0	20-38 micron	202-204	
Paste 4	Sn3.5Ag0.75Cu	ROL0	25-36 micron	217-219	
Paste 5	Sn3.0Ag0.5Cu	ROL0	20-38 micron	217-219	HF*
Paste 6	Sn3.0Ag0.5Cu	ROL1	20-38 micron	217-219	
Paste 7	Sn3.0Ag0.5Cu	ROL0	20-38 micron	217-219	
Paste 8	Sn3.0Ag0.5Cu	ROL0	20-38 micron	217-219	
Paste 9	Sn3.0Ag0.5Cu	ROL0	20-38 micron	217-219	HF*

HF = Halogen free

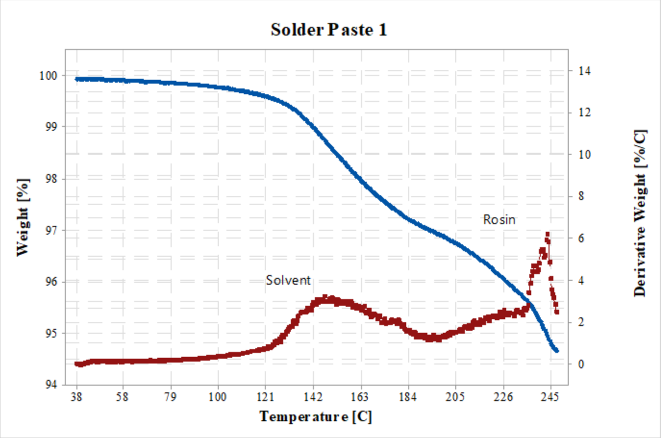

Figure 1 – TGA solder paste 1.

Solder paste loses weight during heating. The percentage weight is recorded in the primary Y-axis of the graph (**Error! Reference source not found.**). The derivative of the weight is the percentage weight loss per degree Celsius. This line indicates the evaporating of chemistry: the higher the value, the more evaporation. It is typical for all pastes to have a high evaporation score in the soak part of the process and in the peak. First, the solvents evaporate, and then, when temperatures rise above the melting point, the activators with rosins evaporate.

A general full factorial Design of Experiment (DoE) was done with the nine solder pastes to investigate the flux evaporation in a reflow process. Different reflow recipes were used to investigate if the reflow profile affects the amount of flux evaporating in the oven. Four different lead-free profiles were run. The Linear and Ramp Soak Spike profiles were part of the experiment. The Time Above Liquidus (TAL) was varied. Four different profiles for nine different solder pastes equaled a total of 36 runs.

The first run was a linear profile with long TAL. The graph shows the result for solder paste 1.

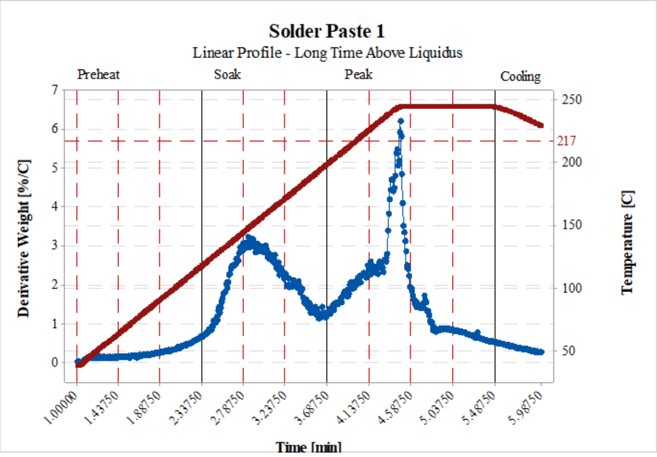

Figure 2 – Linear profile with long TAL

Error! Reference source not found. shows the derivative of the weight of the flux on the primary Y-axis. After one minute of stabilization, the flux was heated with a slope of 60 °C/min to a peak temperature of 245 °C. Before cooling down, the sample was held for one minute at 245 °C. A sample 25 ml/min of nitrogen was purged into the small furnace of the TGA to avoid oxidation. The secondary Y-axis shows the temperature of the sample during the experiment. All the solder pastes except sample 3 have a melting point of 217-219 °C.

The red vertical lines represent the different zones of a reflow oven. In the graph, we assume the reflow oven has 10 heating zones. In a linear reflow profile with a long TAL, the peak zone will typically have four heating zones. The derivative of the weight shows the evaporation of the chemistry. Low scores indicate no or a small amount of flux evaporation, and high values indicate a high amount of flux evaporation. This is typically the case in the first part of the soak zone (solvents) and in the first part of the peak zone. In the first part of the peak zone, the solder paste is starting to melt, and the chemistry must be active to avoid oxidation and stimulate reflow soldering.

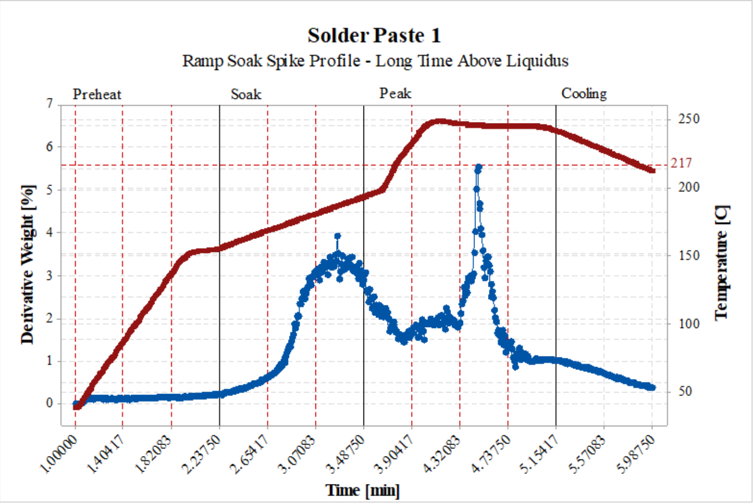

Figure 3 – Ramp Soak Spike profile with long TAL

The second profile has the same long Time Above Liquids (TAL) but a different preheating (**Error! Reference source not found.**). The Ramp Soak Spike type has a slope of 30 °C/min from 150 to 200 °C. **Error! Reference source not found.** shows a ramp soak spike with a short TAL, **Error! Reference source not found.** shows a linear profile with a short TAL.

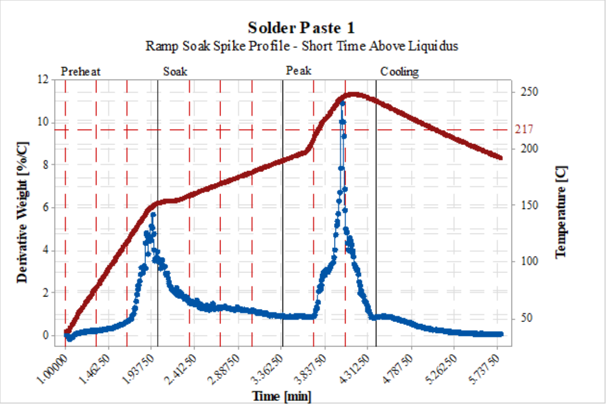

Figure 4 – Ramp Soak Spike with short TAL

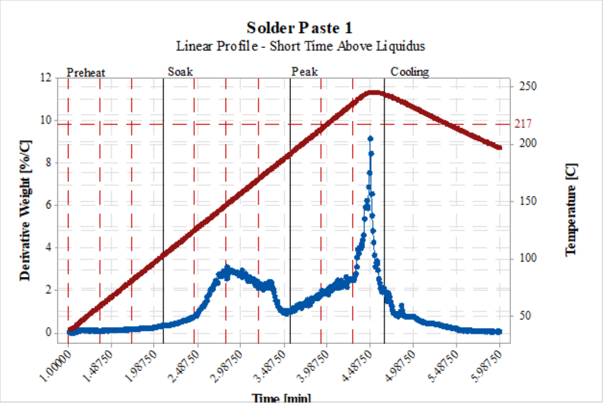

Figure 5 –Linear profile with short TAL

The objective of this thermogravimetric analyzer study of solder paste was to define the parameters and conditions that impact solder paste flux evaporation during reflow soldering. The chemistry that evaporates generates fumes. More chemical components in the solder paste flux will result in more chemicals released in the oven, causing more contamination. Furthermore, the amount of contamination increases if the flux contaminates the faceplates of the zones. More contamination requires maintenance, which will affect both machine downtime and the machine maintenance interval.

The study's first output characteristic is the amount of flux evaporated in the oven.

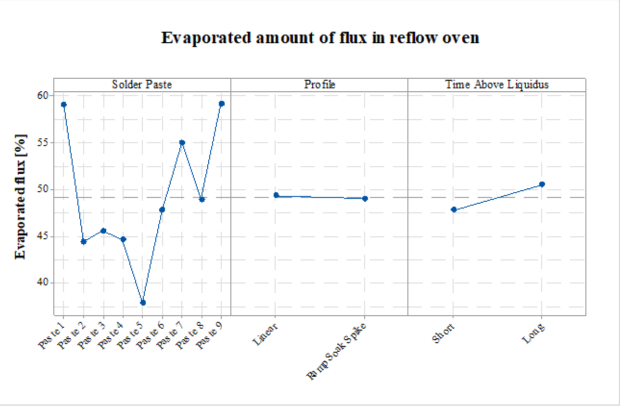

Figure 6 – Evaporated amount of flux

The table provides the results of the evaporated flux analysis.:

Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Model	27	1782.26	66.010	63.67	0.000
Linear	10	1748.91	174.891	168.70	0.000
Solder Paste	8	1679.33	209.916	202.48	0.000
Profile	1	0.89	0.886	0.85	0.382
Time Above Liquidus	1	68.70	68.702	66.27	0.000
2-Way Interactions	17	33.34	1.961	1.89	0.181
Solder Paste * Profile	8	11.41	1.426	1.38	0.331
Solder Paste * TAL	8	17.32	2.165	2.09	0.159
Profile * TAL	1	4.62	4.619	4.46	0.068
Error	8	8.29	1.037		
Total	35	1790.55			

R-Sq = 99.54%

The analysis confirms that the Profile (Linear or Ramp Soak Spike) has no significant impact on the evaporation of solder paste flux. Other parameters (TAL and different solder pastes) have a significant impact (**Error! Reference source not found.**). The R-Sq value is almost 100%, indicating the collected data was reliable and the study successful.

The reflow process is divided into four sub-processes which include: preheating, soak, peak, and cooling (**Error! Reference source not found.**). The next part of the study uses the previous experiments to define areas the solder pastes evaporate most.

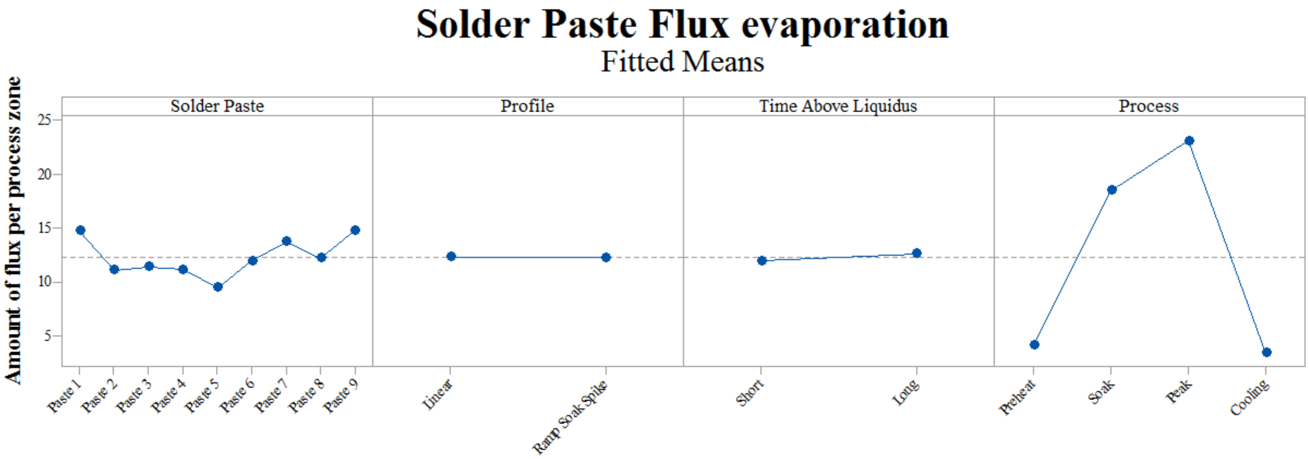

Figure 7 –Significant differences between sub-processes

The preheat and cooling processes have a decreased volume of fumes to handle. Most of the chemistry evaporates when the solder paste is above its liquidus in the peak zone. The composition of the solder paste contains a number of rosins (refer to Identification of Volatile Components) that evaporate in the Soak and Peak parts of the process.

The data shows a small amount of flux evaporation in the cooling zone (**Error! Reference source not found.**). Fumes are more critical in the cooling zone because the cold temperatures of heat exchangers and other cooling zone parts cause the chemistry to condense and contaminate the oven. Additional condensation on critical areas will decrease the maintenance interval and result in machine downtime. The average flux evaporation in the cooling zone is 3.3%. Solder Paste #4, a special composition, shows fewer residues in the cooling zone. Solder Paste #6 contains the most chemistry evaporating (average 5.1%).

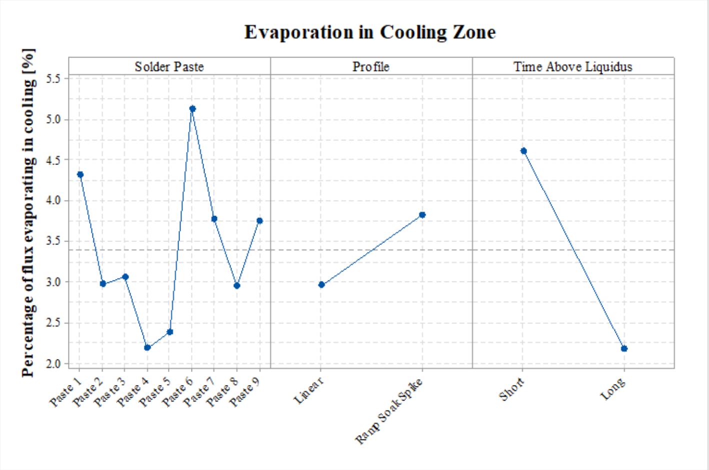

Figure 8 – Percentage flux condensation in cooling zones

Residues in Cool Zones

The previous experiment showed that Solder Paste #4 returns small amounts of residue in the cooling zone. One solder paste user produces double-sided printed circuit boards in a three-shift, Surface Mount Device (SMD) line. Because the board contains one side that is reflowed twice, the reflow in the second run has more chemistry evaporation. During the second reflow run, the solder paste applied in the first reflow run outgasses another 10%. The average solder paste consumption on this line is 3 kilograms per day. With a flux amount of 10.5%, this equals about 300 grams flux in the cooling area every month. This amount only refers to solder paste, so the actual amount will be higher because of the other evaporated materials. No matter how the oven is designed, the flux vapors will condense due to low temperatures at certain places in the oven. This user's oven contains bins that collect residues from the heat exchanger. The first and third zones have residues in the bin, whereas zone two and four are clean. This is most likely related to the temperatures in those zones. The residues were investigated in a laboratory.

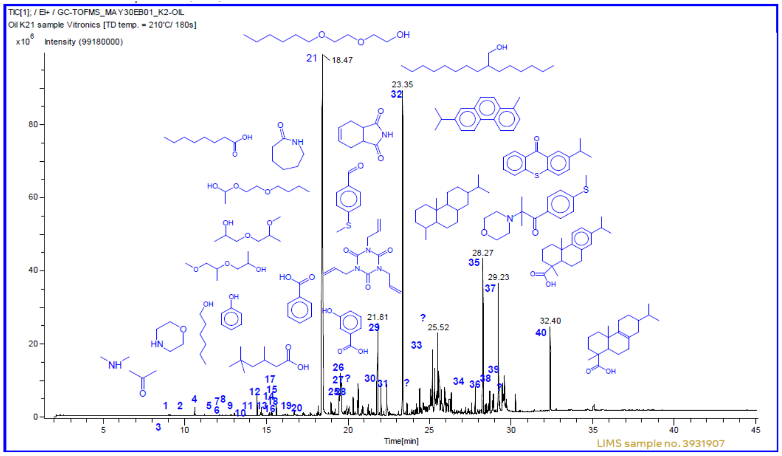

Figure 9 –Sample out of the first cool zone

Table 3 – Identified compounds zone 1

Peak Number:	Identified compound:	Remarks:	Boiling point [°C]

21	Diethylene glycol monohexyl ether	Solvent solder paste	196
29	Triallyl isocyanurate	Radiation promotor	149
32	2-hexyl-1-Decanol	Solder and metal lubricant	220
35	2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone	Soldermask and adhesive	210
37	Quantacureitx	Photoinitiator, jetting ink	
40	Quantacure BMS	Photoinitiator, solder mask	

The method to analyze the composition of this residue is called Gas Chromatography/Mass Spectrometry (GC/MS). Thermal desorption at 210 °C for 3 minutes returns the chromatogram above. The same method was used for the sample from cool zone three (**Error! Reference source not found.**).

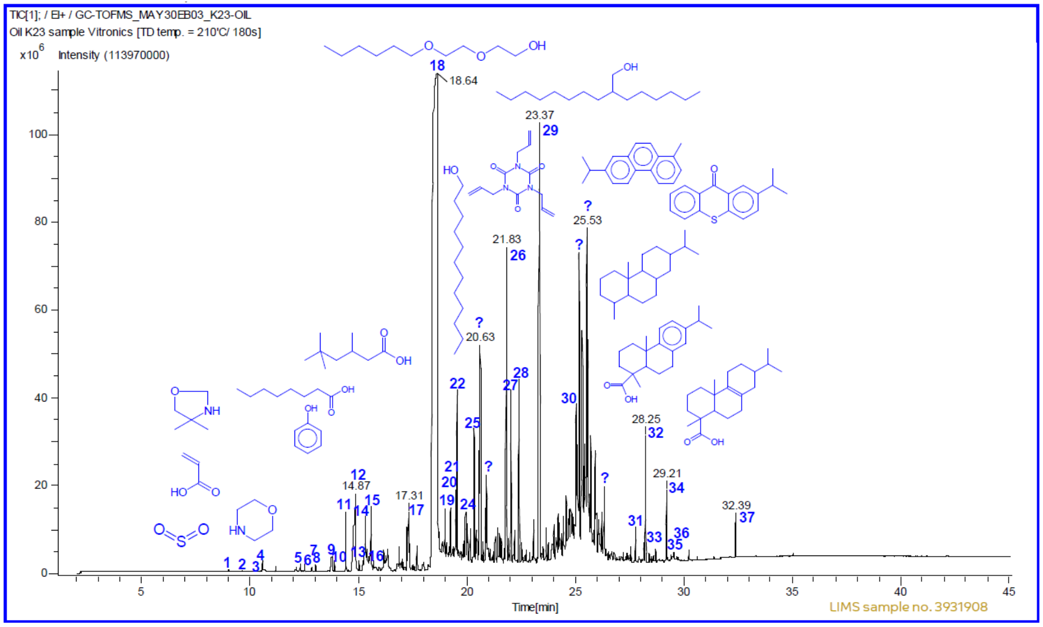

Figure 10 – Sample out of cool zone three

The visual difference between both samples is that the residue from zone one is far more solid. The viscosity of the residue of zone three is much lower.

Table 4 – Identified compounds zone 3

Peak Number:	Identified compound:	Remarks:	Boiling point [°C]
18	Diethylene glycol monohexyl ether	Solvent solder paste	196
26	Triallyl isocyanurate	Radiation promotor	149
29	2-hexyl-1-Decanol	Solder and metal lubricant	220
30	18-Norabietane	Solder paste by-product rosin	
31	1-methyl-7-(1-methylethyl)-phenanthrene	Soldermask and adhesive	210

Although the viscosity is significantly different, the composition of both residues is quite similar. The solder mask outgasses more chemistry than the solder paste residues. Different solder mask related compounds were found in other analyses.

How to handle gasses in the heating zones

Although residues during cooling are critical, they represent only 5% of the overall chemistry evaporating in the oven. The question is what happens to the other 95%. For this answer, we must differentiate inert ovens and air ovens. In inert ovens, nitrogen gas is recirculated and cleaned. In air ovens, a relatively high amount of air is sucked from outside into the oven and extracted. The gas at higher temperatures will not condense, but once in the exhaust system, it may start to clog. If it does not clog, it will end up in the environment.

Users need to minimize nitrogen consumption in inert ovens, which require a filtration or condensation system to consume the gas. In these systems, hot gas is typically cooled and condenses in a heat exchanger, after which it is sent through filters and reused in the oven. This costs energy and requires cleaning the system. Several years ago, a new cleaning technology was introduced which uses multiple catalysts in the oven. Each heating zone has a catalyst that cracks the residues from the fumes in the zone itself. The process breaks the long carbon molecules into carbon, carbon dioxide, and nitrogen. In an air environment, water (H_2O) is an additional output. The nitrogen is now cleaned before it goes into the exhaust system. There are no tubes contaminated and the environment benefits.

Several studies were conducted to verify the catalyst was capable of cracking all types of solder paste. First, experimenters determined the minimum catalyst temperature and maximum gas flow rate and volume necessary to make the catalytic process work. Experimenters set up the test by checking different conditions and solder pastes but struggled with how to measure or quantify the performance of a catalyst. The following test setup was designed to quantify the performance of a catalyst (**Error! Reference source not found.**).

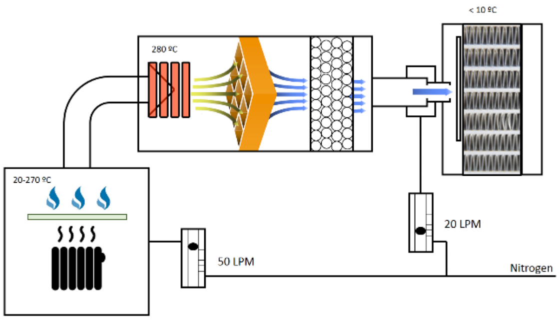

Figure 11 – Test setup

The test setup starts with a glass plate installed behind the catalyst. The glass plate has a heat exchanger behind it that cools the glass and makes the flux condensate (**Error! Reference source not found.**). In the next portion of the test setup, there is a small chamber in which nitrogen or air is purged. In the chamber, the heating element heats up a sample of 5 grams solder paste flux (without powder). The flux is heated to 300 °C and then flows through a catalyst using a venturi to exhaust the gas. The catalyst is heated by a heating element installed in front of it.

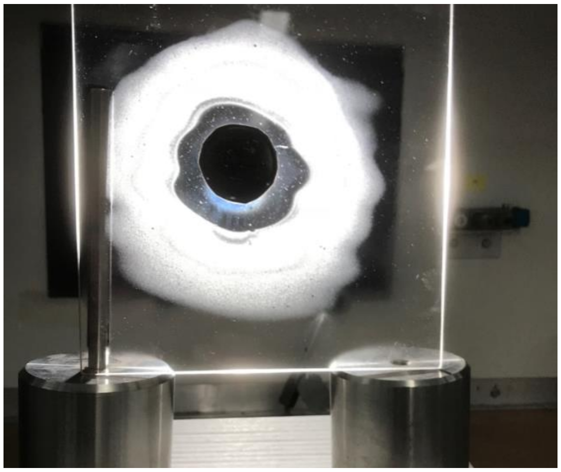

Figure 12 – glass plate with condensate flux residues

Error! Reference source not found. shows the gas exhaust as the dark colored center of the glass plate. More flux condensates toward the outside of the glass, where it is colder. This method shows the presence of residues, but it was challenging to measure and find a repeatable method to quantify the performance. It was difficult to see the condensation because the solder paste included spheres. The studies found that fumes were visible when there was no catalyst installed and that fumes were gone when the catalyst was at a certain temperature (**Error! Reference source not found.**). This turned out to be a better criterion for quantifying the performance of the catalyst. When the solder paste is above 200 °C, heavy fumes will show up. If the catalyst is cracking the molecules, the fumes are gone. The heating slope of the sample was 1 °C/s.

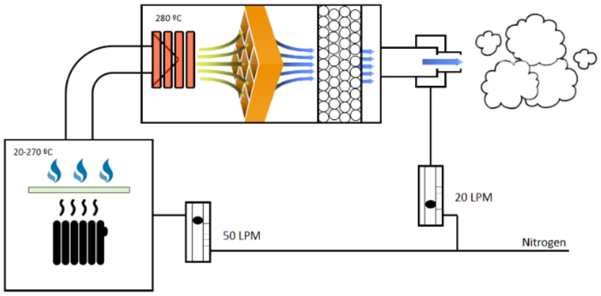

Figure 13 – new test setup with new criterium (fumes)

There are multiple factors that define the catalytic performance:

- Catalyst and gas temperature
- Time the gas is in the catalyst (flow rate versus catalytic area)
- Environment (air or nitrogen oven)
- Catalytic efficiency (thickness/composition, Nano-coated layer)
- Solder materials (paste, solder mask, components)

The sign of failure is the presence of smoke coming out of the venturi. If there is no smoke, there is full catalytic performance. When there is smoke the efficiency of the catalyst is less than 100%. There are two different catalysts used for this application. Catalyst 1 is a frequently-used catalyst in many industrial applications. Catalyst 2 is a palladium group material, Nano-coated catalyst with a thicker layer which should allow it to work at lower operation temperatures.

Most of the tests were done with Flux 1. Flux 1 is the flux of a no-clean solder paste type REL0. A small study with different temperatures was done to define the temperature at which the catalysts work properly. The results are listed in the next table.

Table 5 – Catalyst temperatures in Nitrogen

Temperature	**Catalyst**	
[°C]	**Catalyst 1**	**Catalyst 2**
180 – 200	Fail	Light fumes
200 – 240	Light fumes	Pass
260 – 300	Pass	Pass

Catalytic performance in nitrogen is better due to the lack of oxygen. H_2O also comes out in air environments other than carbon dioxide air environments. In general, higher temperatures are required to be successful.

Table 6 – Catalyst temperatures in Air

Temperature	**Catalyst**	
[°C]	**Catalyst 1**	**Catalyst 2**
260 – 280	Fail	Pass
280 – 300	Pass	Pass

Similar tests were done to define the maximum flow rate of gas through the catalyst. Flow rates up to 22.5 m^3/h at 280 – 300 °C pass the test for both catalysts. These tests were done with three different flux systems, and all showed similar results. The test method makes it possible to check the compatibility of the solder paste with the different catalysts. So far, Catalyst 2 passed all the tests. Catalyst 1 failed for some flux and solder pastes tests.

A slightly different sample method was required for the solder paste to make it repeatable. A small film of solder paste is squeezed on a copper coupon (**Error! Reference source not found.**). The coupon is heated according to the procedure described above.

Figure 14 – Solder paste sample

Table 7 – Compatibility of solder paste type with catalyst

	Baseline	**Catalyst 1**		**Catalyst 2**	
	[no catalyst]	**Air**	**Nitrogen**	**Air**	**Nitrogen**
Paste 2	Heavy fumes	Pass	Pass	Pass	Pass
Paste 4	Heavy fumes	Light fumes	Pass	Pass	Pass
Paste 5	Low fuming	Fail	Pass	Pass	Pass
Paste 6	Low fuming	Pass	Pass	Pass	Pass

The compatibility of solder paste and catalyst should be verified for air applications. Most catalyst applications in air ovens clean air before it is exhausted into the environment. The catalyst removes the fumes in the heating cells, so that when the oven is opened no fumes come out.

The catalyst has a long lifetime, sometimes two years or more in the field without needing to be cleaned. If functioning properly, the catalyst increases slightly in weight (approximately 5 grams per year). These remaining particles in the catalyst are mainly carbon. Catalyst 1 was inspected after one year in an air/nitrogen application of a customer that has pin-in-paste assemblies and consumed 40 kg of solder paste per week (**Error! Reference source not found.**).

Figure 15 – catalyst 1 sample after one-year production

The sample was sent to the lab for inspection. With SEM-EDX (Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy) the metals on the surface of the sample could be determined. The table shows the elements that we found on the catalyst material in percentage.

Table 7 – Elements found on the catalyst

O	C	Al	Si	P	S	Fe	Sn	Pt	Co
41.59	36.33	20.29	0.46	0.38	0.38	0.25	0.16	0.07	0.01

Before the gas flows back into the heating zones it passes a box filled with ceramic balls. The balls are there to collect catalyst and other particles to make sure that the process area remains clean. These balls get contaminated over time. The contamination depends on the solder paste, the heating zone where it is located and the throughput. Two ceramic balls from different companies were investigated and compared to a fresh ceramic ball. This returns information on what passes the catalyst and is not filtered out.

Table 8 – Ceramic balls inspected with the different elements

	O	Al	C	Na	Si	Ca	P	Mg	S
Baseline	53.24	29.74	16.53	0.28	0.09	0.08	0.04	0	0
Nitrogen	52.28	28.54	18.55	0.27	0.05	0.11	0.03	0.04	0.13
Air	24.35	8.9	65.14	0.68	0.12	0.02	0.01	0.01	0.76

The data shows that there is only a small difference between the nitrogen ceramic balls and the baseline (unused ceramic ball). The air ceramic ball is more contaminated with Carbon. Carbon is created from the pyrolysis process in the catalyst. The air oven used more solder paste. The nitrogen ovens typical show less carbon and ceramic balls remain cleaner.

The ceramic ball base material is Al_2O_3. The main concern is the presence of P and S. Further investigation using TDGMS showed that the P and S are present in chemistry that is coming out of the printed circuit board, more specific the solder mask. Both elements are known as a catalyst poison. The concentrations found are small and so far, no catalytic reduction has been observed in over 100 field applications.

Conclusions

- The experiments showed that the solder paste has different chemistries that evaporate primarily in soak and peak zones of the oven. A small part (5% or less) condenses in the cooling and is critical for maintenance. The composition of the residues is a mixture of solder mask and paste materials.
- In the heating zones, catalysts can significantly reduce fumes and chemical contamination by cracking the molecules of solder paste and solder mask.
- Pin-in paste soldering is more often applied and requires significantly more solder paste to have all the barrels filled with solder paste. Assemblies have more solder paste. Applications are observed that contains about 10 times more solder paste for this application. Having all zones fit with a catalyst the fumes in the oven can be minimized.

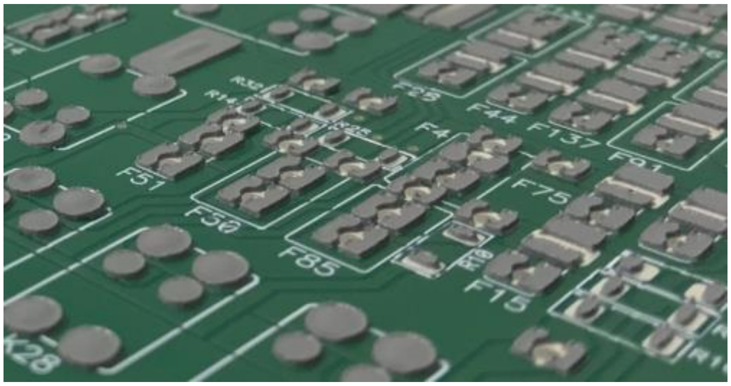

Figure 16 – pin in paste application (solder paste 2 from table 2) ~23 gram paste on one board

Acknowledgements

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References

1. Gerjan Diepstraten, “Effective Methods to Get Volatile Compounds Out of Reflow Process”, APEX 2015.
2. Gerjan Diepstraten, “Reduce Pollution of Process Gasses in an Air Reflow Oven”, APEX 2017.