Vapor phase and Convection Reflow:

Comparison of Solder Paste Residue Chemical Reliability

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Abstract

Convection soldering remains the most common reflow process in electronic assembly, mostly in air, but sometimes using a nitrogen atmosphere to reduce oxidation.

On the other hand, vapor phase soldering remains a niche market: it has been dedicated for years for use on complex boards with heavy mass and/or a large mix of component sizes. Despite its excellent heat transfer capabilities and high wetting performance, this process suffered from weaknesses that prevented it from being used on a large scale: high fluid consumption (CFCs), high tombstoning effect, long process time, and the inability to integrate it into a production line.

In the last few years, vapor phase reflow technology has been improved: New fluids, with boiling temperatures up to 240°C, have been developed, the consumptions have been greatly reduced and the control of preheat and peak ramp rate has been improved, lowering the tombstoning effect.

With lead-free implementation, some limitations are observed on complex boards with convection ovens: the thermal reflow process window is reduced due to the higher temperatures required for SAC alloys, the maximum temperature allowed for fragile components, and the wide range of component sizes.

Vapor phase reflow might be an option to consider.

However, because of the relatively low peak temperatures and the elimination of oxidation with this process, a question may arise about the reliability of the paste residue. More unburned activators might remain on the board, which could cause some corrosion to develop, even when using no-clean solder pastes.

The purpose of this paper is to assess the reliability of several lead-free, no-clean paste residues after vapor phase reflow in comparison to convection reflow. We will use Surface Insulation Resistance (SIR) and Electrochemical Migration (ECM) according to IPC standards, in addition to the Bono test which has been proven to better differentiate the nature of solder pastes residues.

Introduction

In the eighties, when surface mount technology (SMT) processes became more commonplace, two reflow methods were being used, infrared and vapor phase, both of them having advantages and disadvantages. In infrared ovens, several ceramic heaters transferred the heat to the assemblies, moving through the oven on a conveyor belt, by radiation: the limitation was the risk of oxidation and overheating. Nevertheless, the use of fans to help the transfer efficiency by convection minimized highly this issue. Nowadays, the reflow ovens are called "convection ovens" because the heat is mostly transferred by forced air circulation; nitrogen may be used to help wettability. On the other hand, vapor phase soldering technology is based on the thermal energy transfer emitted by the phase change of a heat transfer fluid condensing on the board: the fluid's boiling point is chosen just above the alloy's melting point to avoid overheating. Thus, the soldering takes place in a perfectly inert atmosphere. Despite these advantages, vapor phase reflow suffered from major drawbacks. At that time, fluid consumption was high and these fluids were CFCs. The thermal profile could not be mastered, leading to tombstoning during the extremely rapid melting of the alloy. It was impossible to integrate vapor phase reflow ovens into a production line since all available equipments were batch type. So this technology remained limited to special applications with complex boards with large mix of components sizes produced in low volumes (e.g. defense, aerospace).

The solder pastes developed in the eighties were made of tin-lead or tin-lead-silver (Sn63Pb37, Sn62Pb36Ag2) using an aggressive flux designed to be cleaned after reflow. With the ban of CFCs and the need to reduce the cost of assembly by eliminating a manufacturing step, chemists developed no-clean solder pastes. The success of no-clean solder pastes was huge as they now comprise at least 90% of the market. The RoHS European Directive [1], restricting the use of six hazardous substances in electronics, including lead (Pb), took effect on July 1, 2006. Tin-lead-silver (SAC) alloys with various levels of silver and copper replaced leaded alloys in many applications. Due to the higher melting temperature of SAC alloys (around 217°C) versus Sn63Pb37 (183°C), the risk of overheating temperature sensitive components increases, reducing the thermal profile window. Additionally, the increased level of integration required on PCBs leads to the mix of different thermal mass components on the same board such as BGA's (Ball Grid Arrays), alone or stacked with POP (package on package) technology, small chips and power components, which again raises temperature homogeneity and potential wetting problems in convection ovens.

Recent improvements in vapor phase reflow were made. New vapor phase fluids do not contain CFCs; they are now based on perfluoropolyethers. New developments allow for mastering the thermal profile to drastically reduce the tombstoning phenomenon [2]. Finally, some vapor phase ovens can be integrated in an assembly line with acceptable cycle times. The energy consumption is reduced compared to a standard convection oven. All of these reasons make this technology interesting to reconsider.

During a vapor phase reflow, the solder paste, the terminations of the components and the board are not exposed to oxidation. The peak temperature is lower and the required time above liquidus (TAL) is reduced because of the higher wetting speed in such an environment. Theoretically, a no-clean solder paste designed for use in air convection, where "long and high" profiles are needed, could leave more residue and especially some unburned activators on the PCB when exposed to vapor phase reflow. On the other hand, the residue spreads better in this inert atmosphere, leading to a thinner and more homogeneous residue layer. The purpose of this study is to compare the chemical reliability of several no-clean solder pastes reflowed in air convection versus reflowed in vapor phase by using Surface Insulation Resistance (SIR) and Electrochemical Migration (ECM) according to IPC standards. Then, the pastes will be evaluated using the Bono test which has been found to better differentiate the nature of solder pastes residues [3].

Experiment

Surface insulation resistance description

The selected SAC305 solder pastes are printed onto IPC B25A coupons (figure 1), which comprises two B24 patterns and one B25 pattern and which dimensions are specified in table 1.

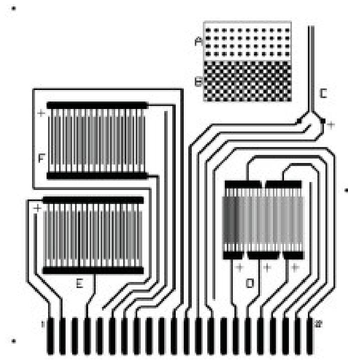


Figure 1: IPC B25A test coupon

Table 1: IPC B24 and B25 dimension

	IPC B24	IPC B25 (D)
Track width (mm)	0.4	0.3175
Space width (mm)	0.5	0.3175

Some SIR boards are reflowed in a 5-zone convection oven under air. A standard profile with linear preheat is used (figure 2).

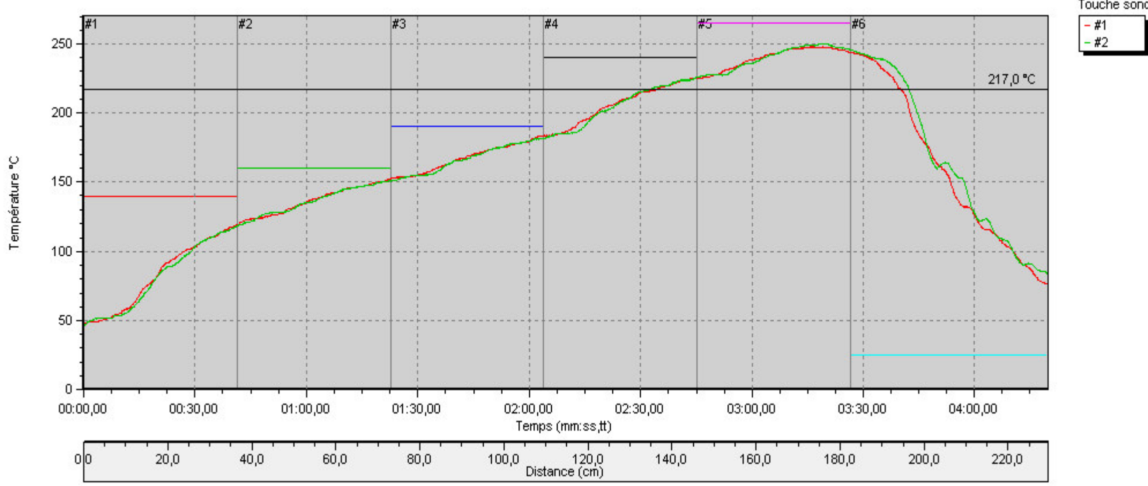


Figure 2: Convection thermal profile

The other boards are reflowed in a vapor phase oven using a fluid with a 240°C boiling point. This oven is able to produce the profile in Figure 3, especially the ramp rate through the liquidus range.

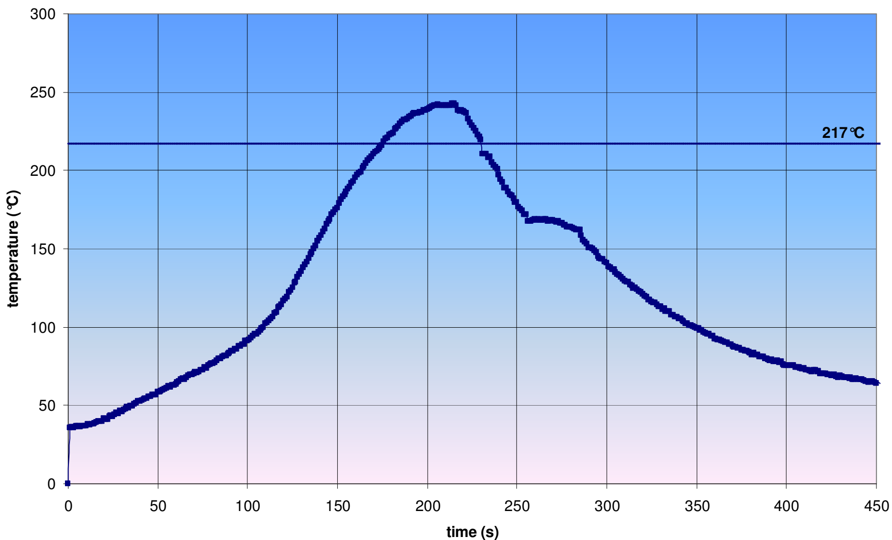


Figure 3: Vapor phase thermal profile

The thermal profiles characteristics are summarized in Table 2. The convection profile is linear between 100 and 200°C with a ramp rate of approximately 1°C/s while the vapor phase profile has a ramp of 1.8°C/s: this higher value was chosen to better approximate the actual conditions of a vapor phase oven where the temperature homogeneity on the board is achieved more quickly. The time above liquidus is shorter in the vapor phase than the one in convection because of the higher wetting speed.

Table 2: Thermal profile characteristics

	Convection reflow profile		Vapor phase reflow profile	
	Time (s)	Ramp rate (°C/s)	Time (s)	Ramp rate (°C/s)
Preheat 1 (50-100°C)	25	2.0	73	0.7
Preheat 2 (100-150°C)	52	1.0	27	1.8
Preheat 3 (150-200°C)	58	0.9	27	1.8
Reflow (200°C to peak)	57	0.8	50	0.8
Total time to peak	192		177	
Time above 217°C (TAL)	65		45	
Peak temperature	248°C		240°C	

The SIR test according to IPC-TM 650 method 2.6.3.3, Revision A [4] is performed: the boards are placed in a vertical position in the climatic chamber according to the temperature/humidity curve below (Figure 4) in order to avoid any water condensation on the boards.

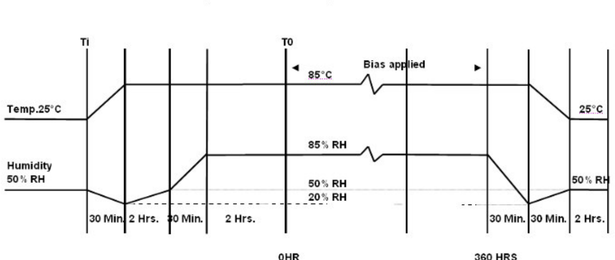


Figure 4: Temperature-Humidity curve

The test conditions are summarized in the table below.

Table 3: SIR test method 2.6.3.3 conditions

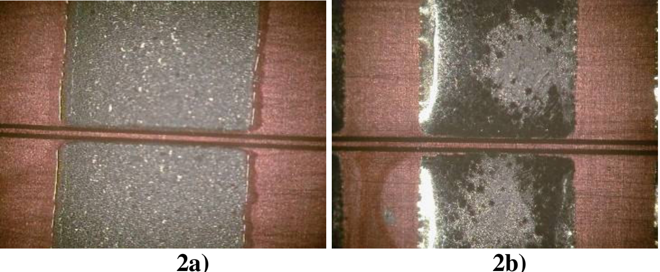
Standard	Test Method	Temperature (°C)	Humidity (%RH)	Test Voltage (V)	Bias Voltage (V)	Test Duration (hrs)	Board
IPC J-STD-004B	IPC.TM.650, 2.6.3.3	85	85	-100	50	168	IPC B24

Bono Test description

This method is based on an existing test which assesses the liquid soldering flux residue corrosivity after wave soldering. The test board has been modified to measure the solder paste residue corrosivity [4] (Figure 5) and is different from the one used in the SIR and ECM tests. It is composed of 10 electrolytic cells and is made of an FR4 epoxy substrate with a single copper layer, having a very thin anode between two cathodes.

figure 5: Bono Test Board

The solder paste is printed on cathodes through a 120µm thickness stencil and reflowed under convection or in vapor phase according to the profiles described above (figures 2,3, table 2).



2a) 2b)

Figure 6: Solder Paste a) after printing and b) after reflow

The samples are conditioned for 16 hours 85°C/85% RH. Initial measurements (T0) are then taken. All measurements are made under temperature/humidity exposure, at a test potential of 12 VDC. The chamber is set at 85°C/85% RH for a total exposure time of 360 hours (15 days), with 20 VDC bias voltage applied to all samples. Resistance measurements of the anode are taken daily and the corrosion factor (Fc) is calculated according to the equation below:

$$Fc = \frac{R_d - R_0}{R_0} \times 100$$

where R_d is the resistance value at day “d” and R_0 is the resistance value at day “0”. Fc is given in percentage (%).

Solder Pastes

Six lead-free no-clean solder pastes are tested: they are made of Sn96.5Ag3Cu0.5 alloy with 25/45 microns particle size and contain 88% alloy and 12% flux. Five solder pastes are halide-free and are classified as ROL0 according to the J-STD-004 IPC standard while the sixth contains halide and is ROL1. Their main characteristics are summarized in the table below (table 4): non volatile residue, acid index and presence of halogen.

Table 4: Solder pastes characteristics

Paste	NVR (%)	Acid index	Halogen	Test performed
1	63	110	No	SIR / Bono
2	50	110	No	SIR / Bono
3	65	125	Yes	SIR / Bono
4	60	120	No	SIR / Bono
5	50	100	No	Bono
6	60	120	Yes (halide)	SIR

SIR Results

The geometric average of SIR measurements is calculated and reported in the tables below. The results are expressed in gigohms (Go). Table 5 summarizes the B24 results and Table 6 the B25 results. After 168 hours, as a visual inspection of the boards did not reveal any dendrites, we decided to continue to 500 hours to maximize the probability of developing dendrites. The observations in the table below are made after 500 hours.

Table 5: B24 SIR results

Paste	Condition C convection V vapor	Ti 25°C/50%	T0 85°C/85%	24h 85°C/85%	96h 85°C/85%	168h 85°C/85%	Dendrites	Status
1	C	1000	5.00	10.49	8.75	10.00	No	Pass
	V	1000	1.22	2.09	3.46	4.18	No	Pass
2	C	1000	6.12	6.88	8.00	8.55	No	Pass
	V	1000	1.50	5.00	5.00	5.00	No	Pass
3	C	1000	1.35	5.70	6.06	6.48	No	Pass
	V	1000	0.42	0.91	1.26	2.28	No	Pass
4	C	1000	5.24	7.30	7.95	8.32	No	Pass
	V	1000	2.00	2.00	3.50	4.50	No	Pass
6	C	1000	0.95	4.47	4.78	5.40	No	Pass
	V	1000	0.18	3.74	4.47	6.32	No	Pass
Ref	V	1000	10.30	21.89	23.00	23.54	No	Pass
Limit		0.1	0.1	0.1	0.1	0.1		

Table 6: B25 SIR results

Paste	Condition C convection V vapor	Ti 25°C/50%	T0 85°C/85%	24h 85°C/85%	96h 85°C/85%	168h 85°C/85%	observation	Status
1	C	1000	6.33	8.66	9.17	10.24	No	Pass
	V	1000	3.03	6.62	6.92	7.42	No	Pass
2	C	1000	1.92	5.14	6.96	8.39	No	Pass
	V	1000	1.25	4.38	6.12	8.05	No	Pass
3	C	1000	1.10	2.35	4.55	4.82	No	Pass
	V	1000	0.77	1.80	2.34	3.78	No	Pass
4	C	1000	2.15	4.54	5.12	7.14	No	Pass
	V	1000	1.57	3.56	5.42	5.92	No	Pass
6	C	1000	0.50	1.72	5.03	6.68	No	Pass
	V	1000	0.10	1.84	4.88	7.70	No	Pass
Ref	V	1000	12.24	13.74	20.00	20.00	No	Pass
Limit		0.1	0.1	0.1	0.1	0.1		

Bono Results

Solder pastes 1, 2, 3, 4 and 5 are evaluated. The corrosion factor (average value from the 9 electrolytic cells), the potential shorts, the visual corrosion and potential mousebites are reported in the table 7. Pictures of some boards are attached in the table.

Table 7: Bono Test results

Paste	Condition C convection V vapor	Fc %	Shorts	Corrosion Visual	Mousebite	Discoloration	Picture after test (light table)	Status
1	C	9.1	No	No	No	Yes	X	Fail
	V	8.5	No	No	No	Yes	X	Fail
2	C	2.5	No	No	No	No	X	Pass
	V	2.0	No	No	No	No	X	Pass
3	C	10	2	Yes	Yes	No		Fail
	V	37	3	Yes	Yes	Yes		Fail
4	C	1.5	No	No	No	No		Pass
	V	2.3	No	No	No	No		Pass
5	C	3.8	No	No	No	Yes		Pass
	V	5.0	No	No	No	Yes		Pass
6	C	100	9	Yes	Yes	Yes		Fail
Ref	C	0.23					X	
	V	0.18					X	
Limit		8%		No	No	Accepted		

Discussion
All the no-clean solder pastes (1, 2, 3, 4 and 6) passed the SIR test. The results obtained with the B25 pattern are similar to the B24 values as is the case with vapor and convection reflow. No dendrites were observed after 500 hours. The SIR values are slightly lower after vapor reflow compared to convection although they remain in the same decade for most of the measurements. On the other hand, some differences are observed between the pastes, whatever the reflow process. This is remarkable at the beginning of the test, at T0 and T0+24hours but it is not the case after 168 hours. Paste 6 has the lowest SIR at T0 (below 1 gigohm); it is even at the limit with vapor phase for the B25 pattern (0.18 for B24 and 0.10 for B25). Paste 6 contains halide. Paste 3, which contains halogen. Both pastes exhibit low values at T0 after vapor reflow, respectively 0.42 Go and 0.77 Go for B24 and B25. Pastes 1, 2 and 4 have higher values and do not contain any halogen. As the other characteristics (non volatile residue and acid index) are in the same range, this difference could be due to these kinds of activators.

Pastes 2, 4 and 5 pass the Bono test after convection reflow and after vapor phase reflow. The corrosion factor is slightly higher with vapor for pastes 4 and 5 and slightly lower for paste 2: this difference is not significant. A paste which passes Bono in convection passes the test in vapor phase. Paste 1 fails with 9.1% corrosion factor for convection and 8.5% in vapor phase: the reflow conditions do not affect the results.
Paste 6 fails in convection with all anodes corroded, creating shorts, so it was not tested in vapor reflow. This paste contains halide, its acid index is 120 and NVR is 60%. Paste 3 fails the Bono test with 10% of corrosion factor for convection and 37% for vapor phase. This paste has the highest acid index (125), the highest NVR (65%) and contains halogen. If we look at the corrosion factor of pastes 2, 4 and 5, which do not contain any halogen, the small differences are explained neither by acid index nor by NVR. According to the previous work on Bono made by Puechagut and al. [3] and according to these new results, both halides and halogens drastically affect the Bono results. The large amount of corrosion observed after vapor phase reflow with paste 3 can be attributed to the inert atmosphere: the activators (halogens) are not eliminated from the board because there is not enough oxidation to remove.

Conclusion
The purpose of this study was to compare the chemical reliability of several no-clean solder pastes reflowed in air convection versus reflowed in vapor phase with two methods: SIR test IPC-TM 650 method 2.6.3.3, Revision A and the Bono test. In SIR, the values are slightly lower after vapor phase reflow compared to air convection reflow. The difference is observed within the first 24 hours of the test. The pastes which contain halide or halogen have the lowest values and are close to the limit especially when vapor phase reflow is used. This method shows its limit due to the lack of measurement in at the beginning of the test. The SIR test using IPC-TM 650 method 2.6.3.7, with a recording of the values every twenty minutes, should be interesting to consider.
The Bono test does not reveal any significant difference. The solder pastes able to pass the test in convection also passed after vapor phase reflow. The quantity of residue (non volatile residue) and the quantity of activator (acid index) do not affect the results. Halide and halogen drastically deteriorate the performance of a paste when reflow under air is used. But additionally, both halide and halogen become unacceptable when the reflow takes place in a vapor phase oven if a high reliability of the residue is required. It means the nature of the residue is important: some activators or some decomposition products can affect its reliability.
A “no-clean” solder paste or solder flux has a different meaning depending on how the board is used after assembly. Bono is an efficient test method to select the highly chemically reliable no-clean solder products. This method is already used by a few companies whose expectations in terms of reliability are very high.
In this context it is important to note that many PCB assemblers want soldering products with higher activation to either compensate for lower quality components and boards finishes or to enlarge the thermal profile window, which decreases the product reliability. Vapor phase reflow, however, provides better wetting performance and allows for the use of lower activated solder pastes even with “less than ideal” conditions.

Acknowledgments
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