

# Estimating Stencil Life and Ideal Heating Profile of Solder Paste Using Advanced Thermo-Gravimetric Analysis

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## Abstract

Thermo-gravimetric Analysis (TGA) measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. This technique is currently used in the design phase of lead-free solder paste. In this study, the same technique is used to predict how long solder paste can be left on the stencil before it dries out and is no longer suitable for further use.

In many SMT production lines, the solder paste lies exposed on the stencil for an extended period without being used. This can be due to many reasons: product change-over, machine downtime in the SMT line or just not enough production volume for the line to run continuously. Some chemistry in the paste slowly evaporates even at room temperature. This affects the rheological properties of the solder paste and may result in poor printing, or aperture clogging of the stencil.

Advanced TGA instruments have the ability to simulate a reflow process under different atmospheres. A solder paste can be heated in nitrogen or air with different gas flow speeds over the sample. The TGA shows that the chemistry of a solder paste responds differently when the atmospheric conditions change. Knowing this, an optimal heating profile under nitrogen may be different from one when soldering in air. Heating solder paste and determining its characteristics will help reduce the number of solder defects in SMT production.

## Introduction

Before discussing the stencil life of solder paste, one must understand the flux vehicle of a solder paste. The flux chemistry contains multiple functional groups that define its characteristics. During printing of a solder paste, its rheological performance is critical.

Rheology is the science that defines the flow behavior and deformation of matter. Solder paste is a complex composition of metal particles and multiple polymer species ranging from relatively simple, slightly modified wood rosins to larger molecular-weight resin systems, solvent(s), activator(s), rheological and numerous other property modifying additives. Rheological additives alone do not determine the overall rheology of a solder paste. All constituents make their contribution to the flow properties of a product.

After printing the solder paste, the second process for the solder paste is component placement. The printed circuit board is transferred to the pick and place machine where the solder paste should not slump, and should allow the components to be placed. During placement the paste should stay where it has been printed to avoid solder beading, bridging and other defects. In this part of the SMT assembly process, solder paste cold slump and tackiness are the characteristics that need attention.

A sufficient tack force is required to hold components in place during transport and reflow soldering. In the third process, reflow soldering, different characteristics of the chemistry become of interest. During heating, the viscosity will change. The hot slump of the solder paste should be such that the paste will not touch the paste of the next pad, in order to prevent bridging. The chemistry should protect metal surfaces from oxidation and assists the solder during melting. During solder joint cooling, the flux should conduct the heat to facilitate controlled cooling of the solder.

The fourth process occurs after soldering. This is where the residues of the flux chemistry should be clean, safe and not pollute test pins. Solder paste residues that are not cosmetically clear can cause difficulty during visual inspection.

Summarizing the flux system functions:

- Provide a homogeneous suspension of the powder
- Prevent oxidation of the powder and surfaces
- Provide flow properties in printing
- Hold powder in place after printing
- Provide tack to hold components in position
- Provide self-alignment of components during reflow
- Inhibit re-oxidation of powder and surfaces to be joined during the reflow process
- Provide controlled cooling of the joint

This big list of property requirements contains a number of contradictions. Optimal performance can only be achieved with a number of different additives at defined concentrations. Due to evaporation of solvents already at room temperatures, this may destroy the structure, resulting in decreased performance with regard to some properties. The effect of this will be examined by a number of different experiments related to evaporation of the solvent's stencil life.

### **Solder paste life prior to printing**

Before the solder paste is put on the printer it should have survived a critical part of its life cycle. After the moment the paste is produced, handling, storage, humidity and temperature are critical. In this paper, we assume that the solder paste arrives on the printer in an optimal condition. This means that transportation and storage conditions were according the supplier's user guidelines and that the paste has been removed from the refrigerator 24 hours prior to production. Handling the solder paste is most critical. Prior to use in the printer, the paste must be well stirred with a slow, folding action. Do not stir vigorously, as this will damage the paste. Allow the jar/cartridge to reach ambient temperature naturally. Do not place on a hot plate, furnace, reflow oven or any other artificial means to warm it. This will adversely affect its performance.

### **Evaporation of the solvent**

Once the solder paste jar is open, there is a risk that elements of the flux chemistry of the solder paste will begin to evaporate once they come in contact with air and ambient temperature. The first part of this study is intended to achieve an understanding of how much of the paste is evaporating under predefined conditions.

Achieving a stencil life and tack time of 8 hours and longer requires the selection of a solvent system with extremely low volatility at ambient temperatures. Even without this prerequisite, the solder paste formulator has to tackle many problems to select the right solvent system. That is, because - as with most other functionalities in chemistry - there is no such thing as the ideal universal solvent when it comes to solubility power for the considerable number of different types of organic materials that may form the flux vehicle.

The paste may become dry on the stencil for several reasons:

- Evaporation of volatile solvents
- Too high operating conditions, e.g., temperature, humidity or air draft
- High flux activity at room temperature (too strong activation system of the paste)

The viscosity of the solder paste is difficult to keep under control in an environment with fluctuating ambient temperature and humidity.

In order to gain an understanding of how much flux is evaporating on the stencil, two different experiments were designed. The first includes a study that defines the impact of the amount of solder paste on the stencil and how much of the amount is exposed to the air. In the second experiment, the impact of air draft and temperature were examined during a "Box Behnken" type of experiment using a TGA instrument.

### **Experiment 1:**

For the experiments, five different pastes were selected. Four different paste depositions were printed and weighed on a balance every day. Weight losses are compared with another and discussed.

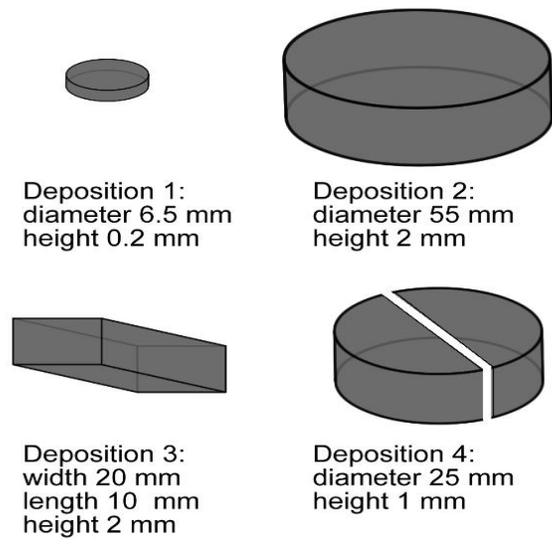


Figure 1: Four different solder paste depositions. Dimensions are listed in Appendix 1.

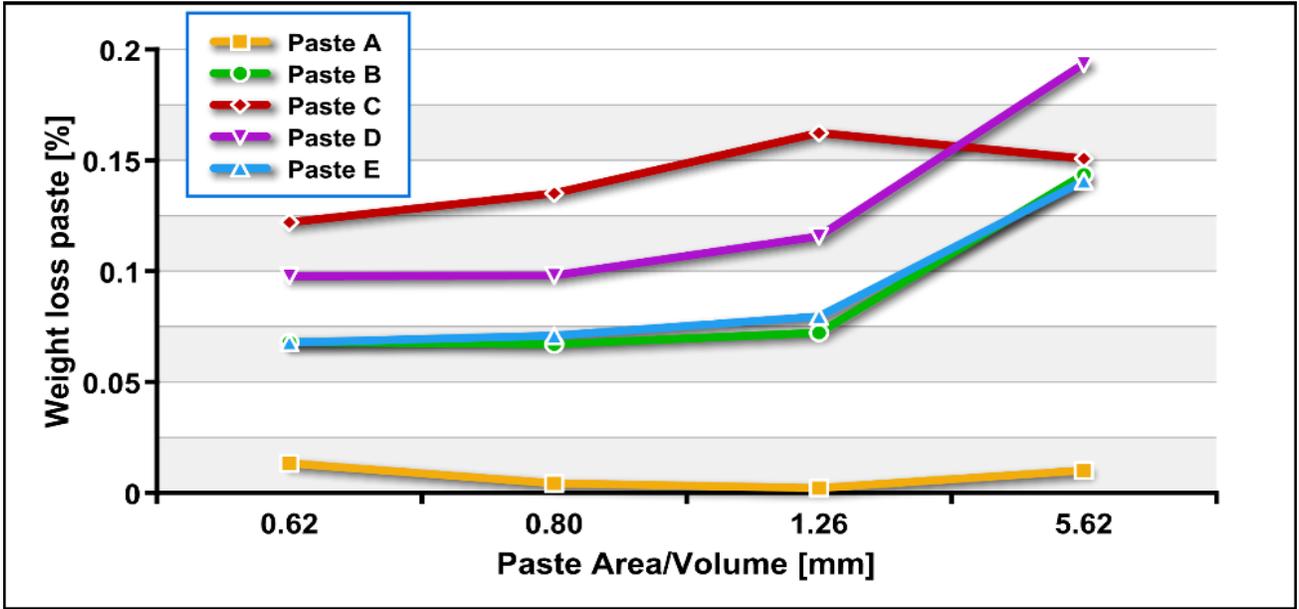


Figure 2: Solder pastes B, D and E are more sensitive to large surfaces exposed to air after 48 hours for the different deposits.

The more flux there is in contact with air, the more potential evaporation there may be. For all depositions, the area at the surface, in contact with air, is calculated. In Figure 2, the amount of paste flux evaporated is monitored versus the Paste Area/Volume.

The raw data is listed in Appendix 1. Solder paste A has a very long stencil life. The major reason for this is that the flux used for this paste is a very low activated one. Solder paste B, D and E have the same flux formulation but different powders. It is possible that powder D is less oxidized, resulting in a slightly shorter stencil life than the other two.

**Experiment 2: Box-Behnken**

The next experiment was run for solder paste A and D. Solder paste A was chosen due to its excellent stencil life characteristics. For solder paste D, which exhibits excellent soldering properties, it was desirable to find the optimal conditions to limit evaporation of the solvent on the stencil. For this experiment, a “Thermo-gravimetric Analysis” instrument was used. Box Behnken is an experimental design for quadratic relations. This technique is used because some of the parameters may not show a linear relation. This type of experiment will provide a formula that can be used to predict evaporation under different conditions.

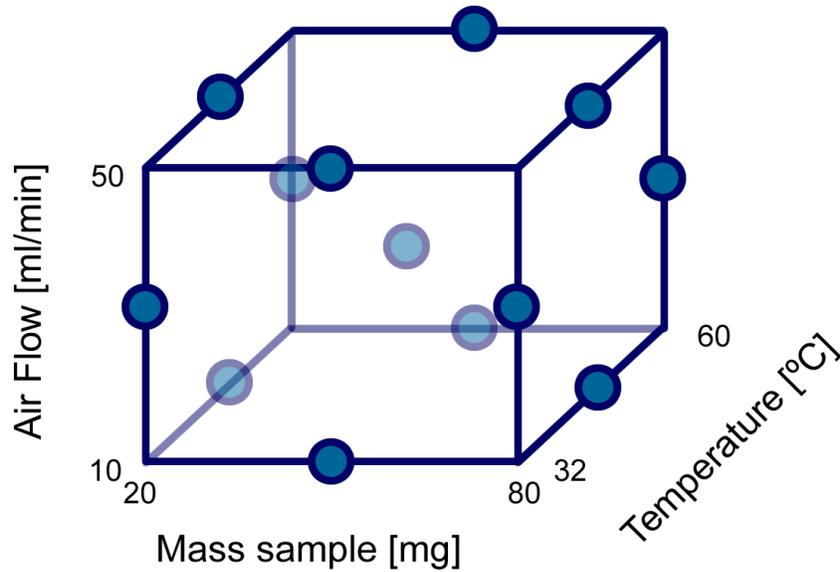


Figure 3: This shows the experimental setup of the Box Behnken trials. The data from the runs is shown in Appendix 2.

There are three different parameters at three levels in the factorial design:

- Mass of the solder paste sample
- Temperature
- Air flow

The analysis shows that for solder paste A all of the factors have a significant impact on the evaporation rate ( $P < 0.05$ ). For solder paste D, the mass of the sample is most affecting the evaporation rate and temperature and airflow have a minor impact.

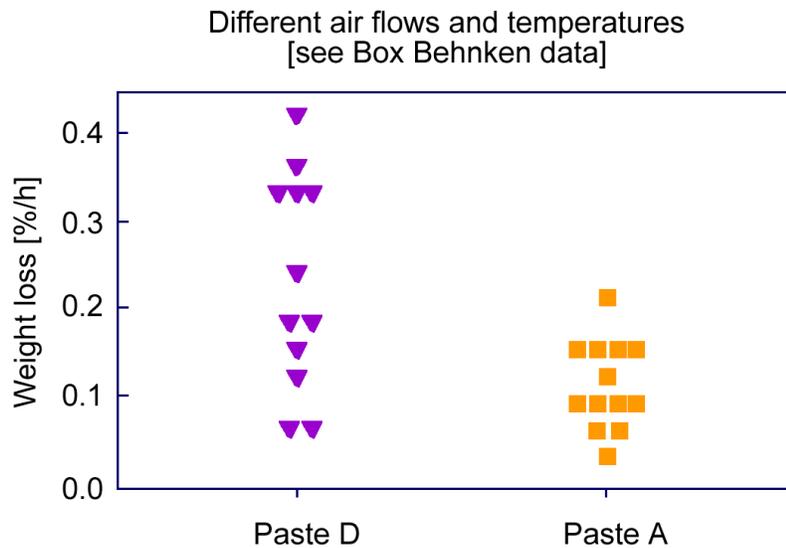


Figure 4: Individual value plot for both pastes (A and D). Solder paste A is less sensitive to higher temperature and airflow.

When comparing the two different pastes in an individual value plot of all the runs in the experiment, it is obvious that paste A is more stable under all conditions. However, when the temperature is not extreme (up to 32 °C) and we have a minimal air flow, solder paste D is equal to A.

The model explains (R-Sq =) 99 % and 95% of observed variation and is, therefore, powerful as a predictor.

$$\text{Evaporation of solder paste A} = 0.035151 - 0.004148 * M + 0.004554 * T - 0.001462 * A + 0.000046 * M^2 + 0.000049 * A^2 - 0.000027 * M * T \text{ [%/h]}$$

$$\text{Evaporation of solder paste D} = 0.318151 - 0.014469 * M + 0.000128 * M^2 \text{ [%/h]}$$

M = Mass of solder paste in mg

T = Temperature in °C

A = Air flow in ml/min

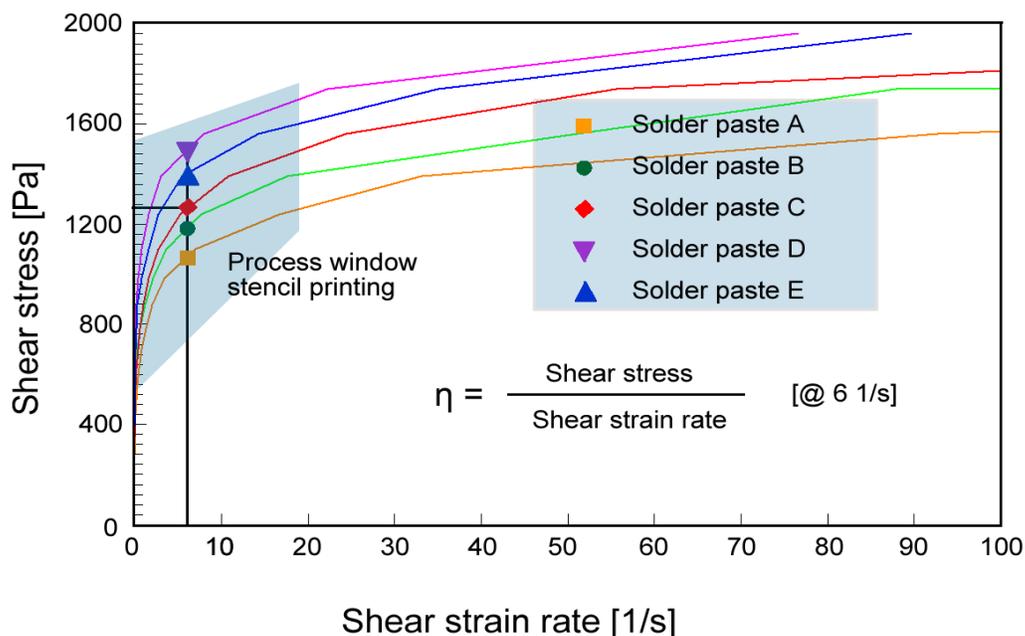
Since the volume and solder paste surface exposed to air are playing a significant role, as we learned in the first experiment, these formulae only apply to small amounts of paste.

### Impact on paste rheology

First, it is important to understand the printing process before evaluating the effects of evaporation of the flux chemistry. During printing, the paste is rolling under pressure from the squeegee at a speed up to 100 mm/sec or even more. For good filling of the apertures, the paste should roll and not shear over the stencil. Once all apertures are filled, during the stencil separation, the adhesive force between deposit and stencil walls must be smaller than the adhesion force between print deposit and substrate and the cohesive force within the deposit.

The rheology of a solder paste is a complex science and cannot be simplified to a single viscosity number for the paste. Viscosity reflects only on static properties of the solder paste. For the dynamic properties (printing is a collection of different dynamic stress levels) oscillation tests need to be performed. The oscillation test is a non-destructive test that determines the visco-elastic properties of the paste.

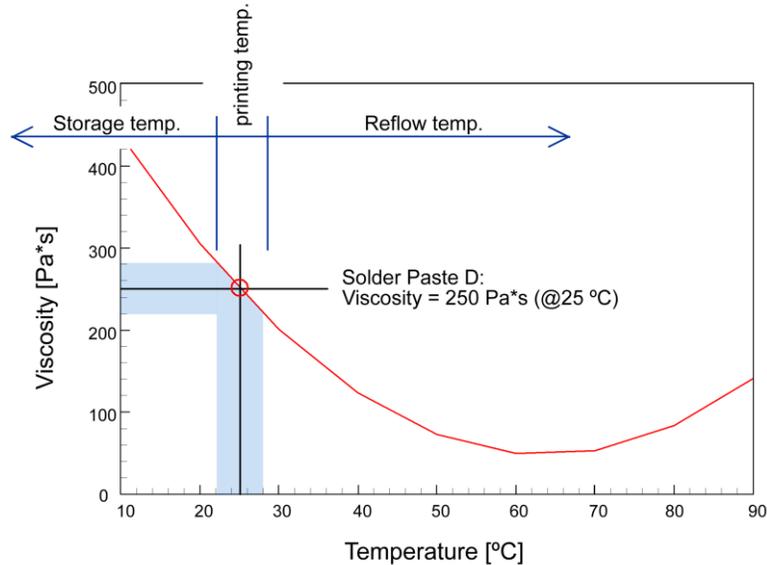
With the first measurement, the static properties of the pastes are defined. The viscosity is defined with a parallel plate rheometer. Temperature is 25°C and controlled during the measurements. The flow curve describes the relationship between the shear strain rate and shear stress applied to the different solder pastes.



**Figure 5: The flow curves for the different solder pastes. Pastes B, D and E have the same chemistry, but different powders. (Plate diameter 30 mm and measurement gap 1 mm)**

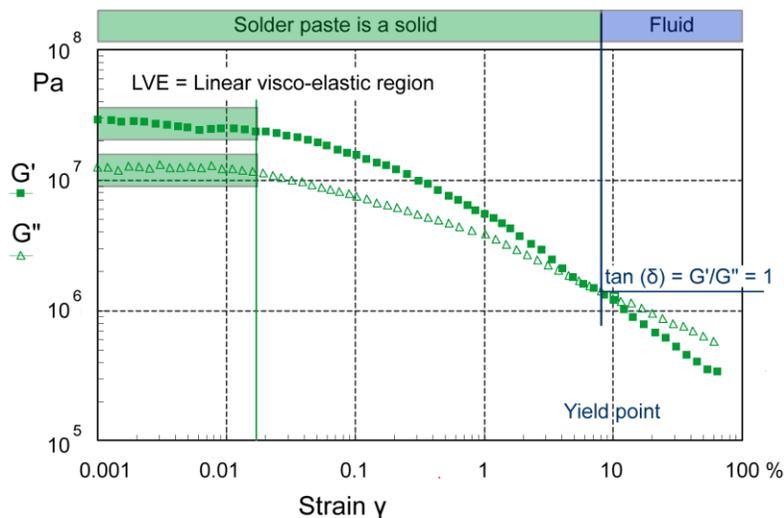
The powder topography and alloy have impact on the rheology of the paste. For statistical analysis, the viscosity at a shear rate of 6 [1/s] is measured. The viscosity for the different pastes is plotted in Table 1.

The viscosity depends on the temperature. The effect of the temperature on the viscosity is shown in Figure 6. Increasing the temperature reduces the viscosity until the moment that the temperature becomes so high that the solvent begins to evaporate during measurement. From that point on, the metal content increases, resulting in a higher viscosity.



**Figure 6: Increasing temperature affects the viscosity of the paste. The light blue area indicates the printing window from 22 to 28 °C for this paste. In this window the viscosity varies from 220 to 280 Pa\*s.**

The dynamic properties of the solder pastes are measured with an amplitude sweep. During this measurement, a parallel plate of 50 mm (spindle) was used. The frequency was fixed at 1 Hz, temperature at 25 °C and the gap between the plates 2 mm. Increasing oscillations of shear stress generate a graph. The visco-elastic region, as well as the storage modulus, loss modulus and yield point of the solder paste can all be defined from this graph.



**Figure 7: This graph shows the Linear Visco-elastic Region of paste D. The Yield Point at 8.03**

Within the Linear Visco-elastic Region, the paste response is independent of the magnitude of the deformation and the solder paste structure is maintained intact. The solder paste has both viscous and elastic properties.

The viscous properties are identified as the Loss Modulus ( $G''$ ) and the elastic properties as the Storage Modulus ( $G'$ ). The ratio between both properties is very important. It is expressed as the quotient of  $G''$  and  $G'$  and it is identified as the Damping Factor ( $\tan \delta$ ).

During storage, transport and after printing, the elastic properties in the solder paste (Storage Modulus) should dominate. Therefore  $\tan \delta$  should be  $< 1$ . A high  $G'$ -value generally is an indication of a high resistance to separation and slumping. The downside of a high  $G'$ , however, may be paste hang-up on squeegees, limited print-speeds, ski-sloping and dog-ears.

The yield value or yield point is the highest shear stress value in a flow curve at which the solder paste still does not flow. It is the point where the external forces (gravity, squeegee) applied are greater than the internal forces of the rheological network in the solder paste. Below the yield value, the behavior of the solder paste is elastic. It behaves more like a solid substance. It does not deform: It neither separates nor slumps. The higher the yield point, the stronger the rheological network and the lower the tendency for separation of solder particles.

Of all five (5) solder pastes, the oscillation swap was made. After three days stored on a stencil at ambient temperatures, this measurement was repeated. The result is listed in Table 2.

**Table 1: Rheological properties of the solder paste.**

		Paste A	Paste B	Paste C	Paste D	Paste E
Storage Modulus	$G'$	1.65E+07	5.49E+07	2.81E+07	2.62E+07	2.55E+07
Loss Modulus	$G''$	5.86E+06	2.08E+07	1.07E+07	1.09E+07	9.99E+06
Linear Viscoelastic Region	%	0.01	0.005	0.01	0.01	0.005
Tau	Pa	1.75	2.86	2.90	0.20	1.28
Yield point	%	6.67	8.02	3.20	8.03	4.62
Viscosity	Pa*s	180	199	210	251	234

**Table 2: Rheological properties after 3 days on the stencil.**

		Paste A	Paste B	Paste C	Paste D	Paste E
Storage Modulus	$G'$	2.04E+07	3.01E+07	1.77E+07	1.96E+07	1.60E+07
Loss Modulus	$G''$	1.05E+07	1.14E+07	6.03E+06	7.64E+06	6.56E+06
Linear Viscoelastic Region	%	0.01	0.001	0.01	0.01	0.005
Tau	Pa	2.10	0.32	2.10	1.98	0.821
Yield point	%	1.84	4.62	1.84	3.20	2.67
Weight loss paste	%	0.013	0.090	0.151	0.098	0.089

For all pastes (except Paste A) the Storage Modulus decreases after drying. This results in a higher risk for defects such as slump. The yield point decreases for all pastes which may increase the number of defects during printing. Lower elastic properties (Yield Point) may result in stencil clogging, since the paste does not pull together enough during stencil release.

### Effect on tackiness

The drying of the solvent also has an impact on the tackiness of the solder paste. A minimum tack force is needed to hold components to the paste during the pick and place stage as well as on the transport system through the reflow process. To keep the components where they are placed, many parameters have an effect:

- Insufficient solder paste
- Handling of the board (acceleration)
- Board support (preventing warpage)
- Tack force of the solder paste

Tack time is of interest because this defines how much time between printing and component placement is allowed, which is important for those who have small or medium batch sizes.

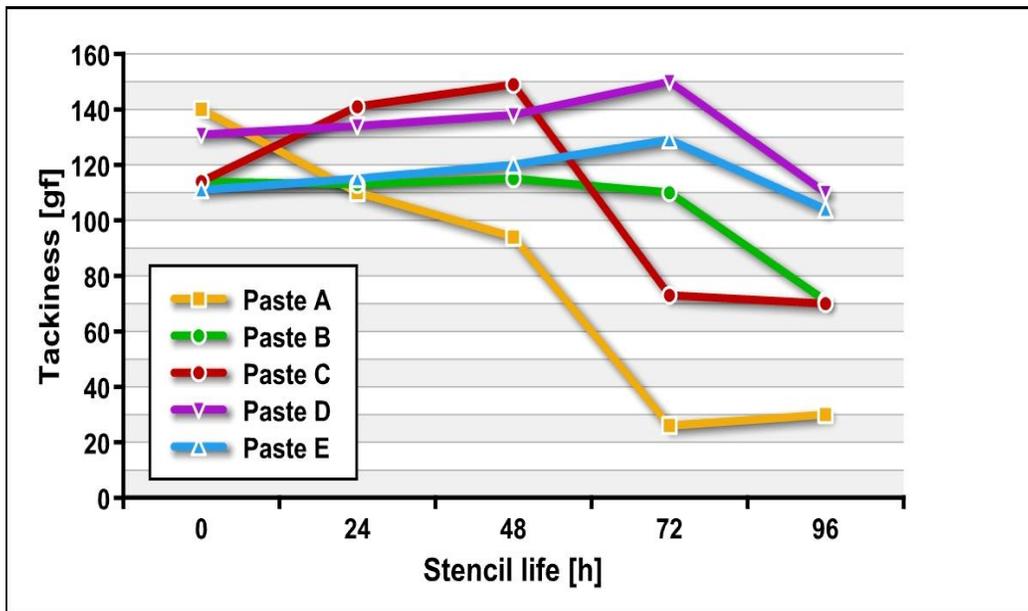


Figure 8: Tack force of the samples after 4 days (deposition 4 of Figure 1)

From the data we learn that paste A and C lose tack force after more than 2 days. The chemistry in paste B, D and E is stable for at least 72 hours. There is no correlation between the amount of evaporate solvent and the tack force or time.

Table 3: Tack force and time

Drying time [h]	Paste A		Paste B		Paste C		Paste D		Paste E	
	Weight loss [%]	Tack force [gf]								
0	0.000	140	0.000	114	0.000	114	0.000	131	0.000	111
24	0.001	110	0.050	113	0.122	141	0.053	134	0.054	115
48	0.002	94	0.072	115	0.162	149	0.076	138	0.079	120
72	0.008	26	0.104	110	0.197	73	0.116	150	0.122	129
96	0.016	30	0.137	71	0.247	70	0.156	110	0.164	104

### Reflow soldering impact

The reflow soldering process can be run with an inert (nitrogen) atmosphere or just in air. The nitrogen prevents oxidation and is therefore preferred. However, the additional cost of nitrogen and typical related defects such as tomb-stoning usually means that most processes are run in ambient atmosphere.

Advanced TGA instruments have the ability to simulate a reflow process under different atmospheres. A solder paste can be heated in nitrogen or air with different gas flow speeds over the sample. The next experiments were run to illustrate the difference between air and nitrogen reflow effects on a solder paste. All samples were reflow soldered according a standard 5-minute ramp-soak-spike lead-free reflow profile in the TGA. The TGA precisely measures the weight of the sample during the experiment.

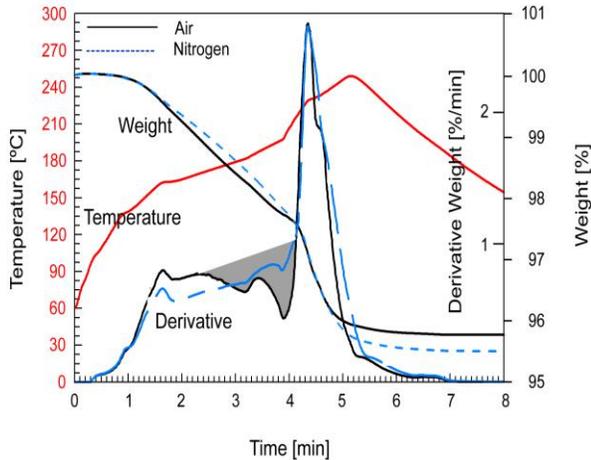
Table 4: Weight loss in different process areas in %. During the measurement the air/nitrogen flow over the sample was 15 ml/min.

Reflow zones	Paste A		Paste B		Paste C		Paste D		Paste E	
	Air %	Nitrogen %								
Preheat	0.76	0.65	1.05	1.13	0.76	0.69	1.05	0.59	1.13	1.11
Soak	1.56	1.63	1.47	1.52	1.07	1.42	0.99	1.11	1.02	1.39
Peak	1.87	2.15	1.41	2.75	2.39	2.41	1.85	2.90	1.83	2.44
Cooling	0.04	0.06	0.09	0.22	0.06	0.09	0.07	0.55	0.06	0.15
Weight at end	95.76	95.48	95.96	94.35	95.68	95.35	96.02	94.79	95.94	94.88

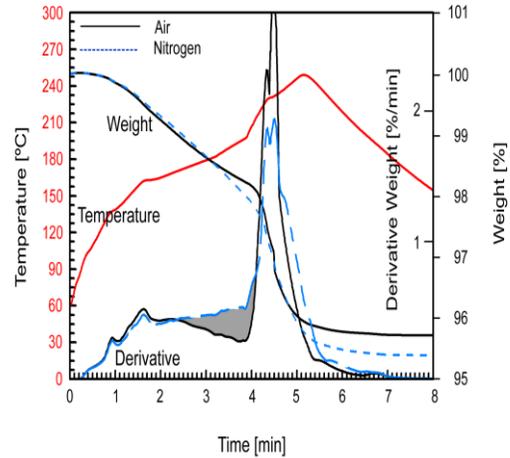
Two trends can be recognized in the data:

- In the first part (preheating) the solder paste evaporates faster in air atmosphere.
- In the peak zone there is more evaporation in an inert atmosphere.

It is obvious that oxidation has an impact on the recognized trends. Due to oxidation, the sample gains weight, this reduces the weight loss rate.



**Figure 9:** Paste A shows that in air atmosphere there is oxidation from 170 °C to its melting point.



**Figure 10:** For solder paste C, the identical oxidation situation begins at 170 °C.

Paste A does not show significant difference between the air and nitrogen reflow profile. In the peak zone, there is a slight difference such that at the end of the process, there are only 0.27% more residues for the air process.

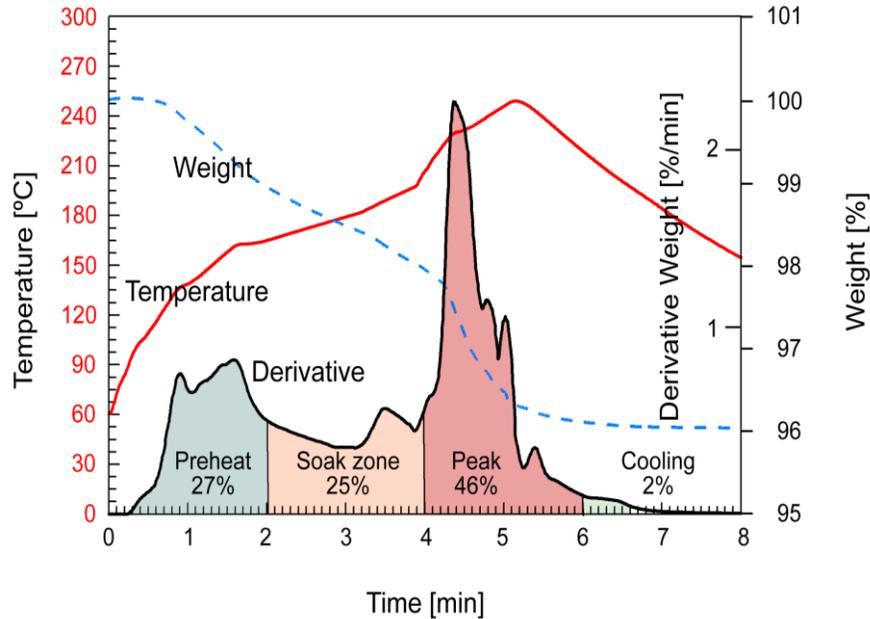
Paste C, however, shows that oxidation already begins at 170 °C (gray marked area in the figures). From this point up to the melting of the powder, the gap or difference between air and nitrogen increases and results at the end in 0.33% more residues with air.

### Design of Experiment

To study the effect of the solvent evaporation on the reflow, a Design of Experiment was performed with the following parameters:

- Weight loss (0, 0.1%, 0.2%)
- Air flow (0, 15, 30 ml/min)
- Atmosphere (air – nitrogen)

To achieve 0.1% evaporation of the paste before the reflow heating profile starts, the sample was preheated at 60 °C for 15 minutes with an air flow of 25 m/min. Heating time for 0.2% was 30 minutes.



**Figure 11: This illustrates the weight loss (measured with TGA) of solder paste D in an air reflow process. The process can be divided into 4 sub-processes in which the activity of the solder paste can be defined and expressed in % of overall activity in the reflow process.**

Observations in the preheat part of the profile:

The preheat zone is of interest since the solder paste lost a percentage of its solvents (due to stencil life) before soldering. The area underneath the derivative of the weight loss (%/min) is an indicator for the activity in that part of the soldering. Figure 11 shows the calculation of activity at different process steps.

**Table 5: Activity defined with TGA for paste D (gas flow 25 ml/min):**

Reflow zones	Zero weight loss		Weight loss 0.1%		Weight loss 0.2%	
	Air %	Nitrogen %	Air %	Nitrogen %	Air %	Nitrogen %
Preheat	26.65	22.10	22.86	21.08	24.17	17.39
Soak	25.02	23.58	20.97	27.12	26.06	23.87
Peak	46.53	50.31	52.03	47.98	47.86	54.61
Cooling	1.80	4.00	4.14	3.82	1.90	4.13
Weight end	96.02	94.80	96.07	94.87	95.98	94.71

The analysis shows that, in air, there is significant impact from the flow in the preheat zone, whereas there is less in nitrogen. As expected, activity decreases when more solvent evaporates prior to the soldering process. All parameters have significant impact on the activity. Also, the interaction between atmosphere (air vs. nitrogen) and the flow is influenced. The average % activity in the preheat is 25% for fresh solder paste. This decreases to 20% when the solder paste has lost 0.2% of its weight. Plots of main parameters are shown in Figure 12.

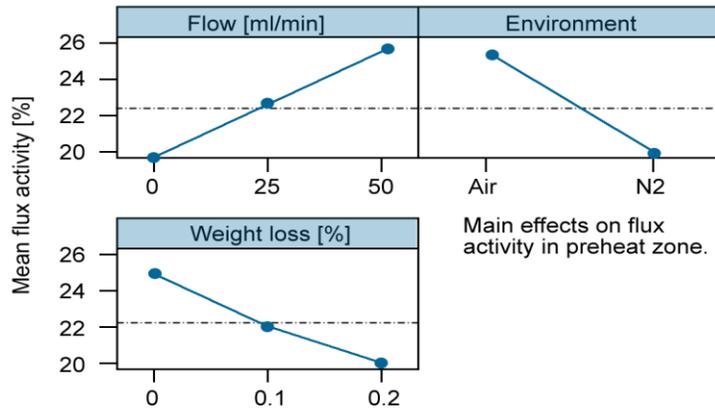


Figure 12: Plot of parameters and impact on flux activity in preheat zone.

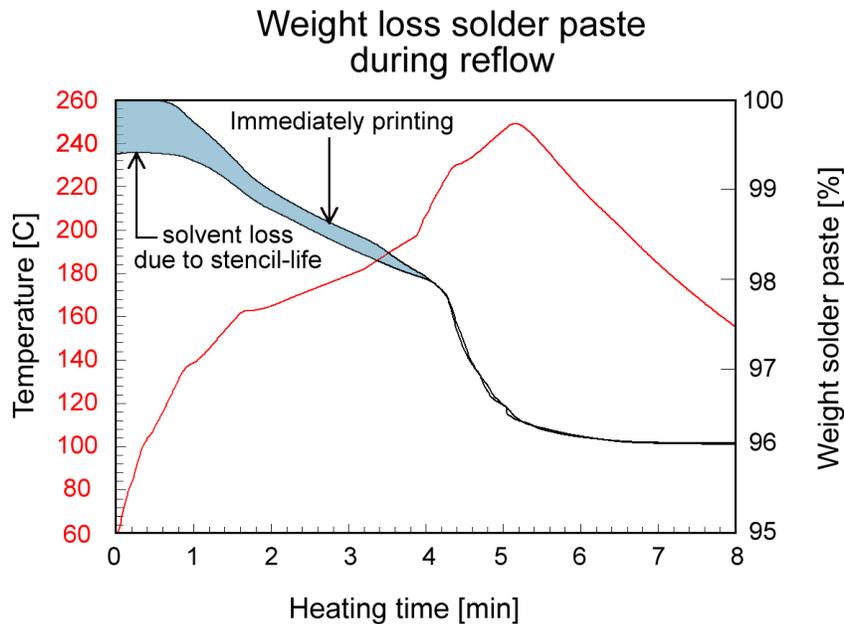


Figure 13: This shows that the impact of evaporated solvent is gone after the soak zone. This is an overlay of two graphs; one with 0.2% and one without evaporated solvent.

In the peak zone, the activation is higher when nitrogen is used. A higher airflow rate results in more oxidation. In nitrogen, the flow rate is not significant. The activity level of the 0.2% evaporated flux is higher because this calculation is a percentage change and therefore caused by the less activated preheat part. The 0.2% weight loss only impacts the first part of the reflow process. It doesn't affect the peak area, where solidification takes place and oxidation is most critical.

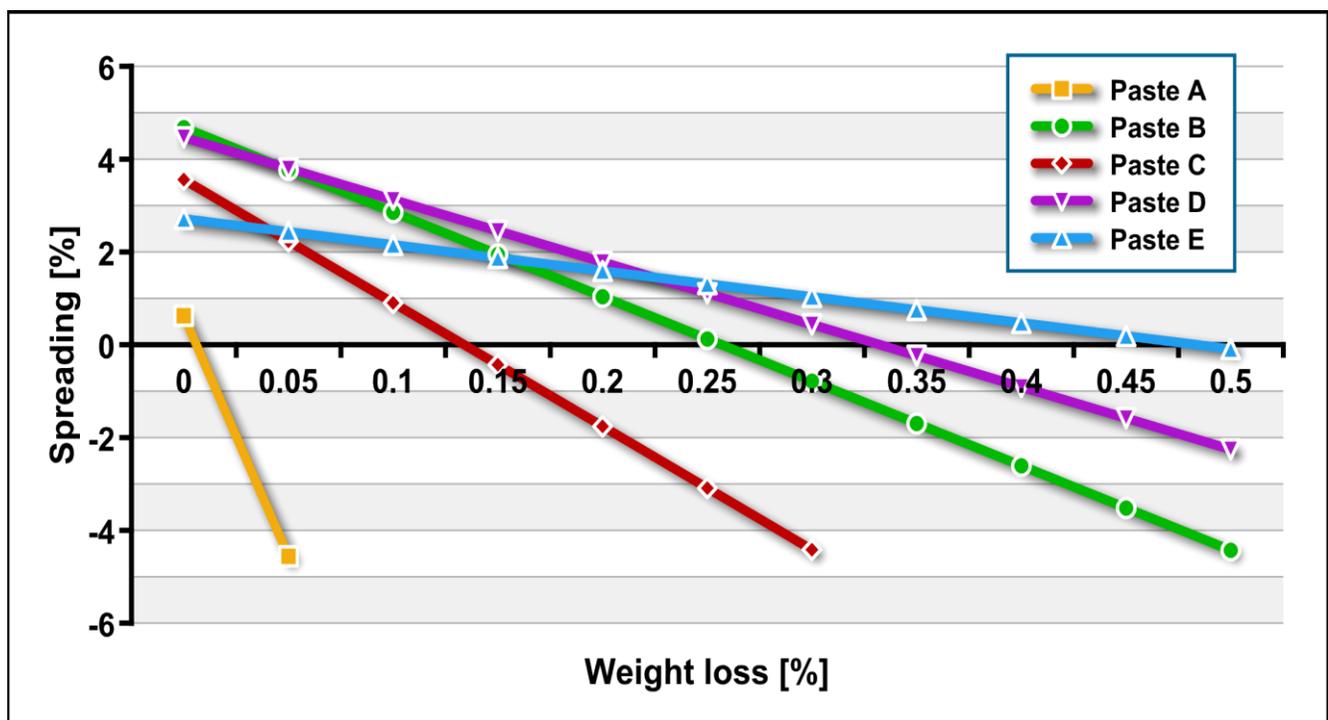
### Spreading experiment

The last experiment is designed to show how much effect all the evaporation has on the solderability of the solder paste. Solder paste is therefore printed on a copper coupon that is free of oxides (protected by plastic shielding). The solder paste is printed and the diameter of the solder deposition is measured with a microscope. After reflow soldering (air atmosphere) this diameter is measured again. The experiment is also described in the IPC-TM-650 method 2.4.45.

**Table 6: Showing how much the solder paste spread. After longer stencil life, the spread decreases and for some samples it even showed a negative spread (= dewetting).**

Stencil-life [h]	Paste A		Paste B		Paste C		Paste D		Paste E	
	Weight loss [%]	Increase spread [%]								
0	0	1.23	0	4.75	0	3.54	0	4.39	0.000	2.80
6	0.001	1.11	0.037	4.19	0.038	1.78	0.047	4.30	0.029	2.80
24	0.003	-0.48	0.099	2.89	0.107	0.59	0.126	3.15	0.097	1.92
48	0.015	-0.84	0.126	1.81	0.151	0.12	0.163	1.80	0.146	2.02
72	0.020	-1.41	0.144	2.56	0.171	-1.41	0.173	2.32	0.211	1.55

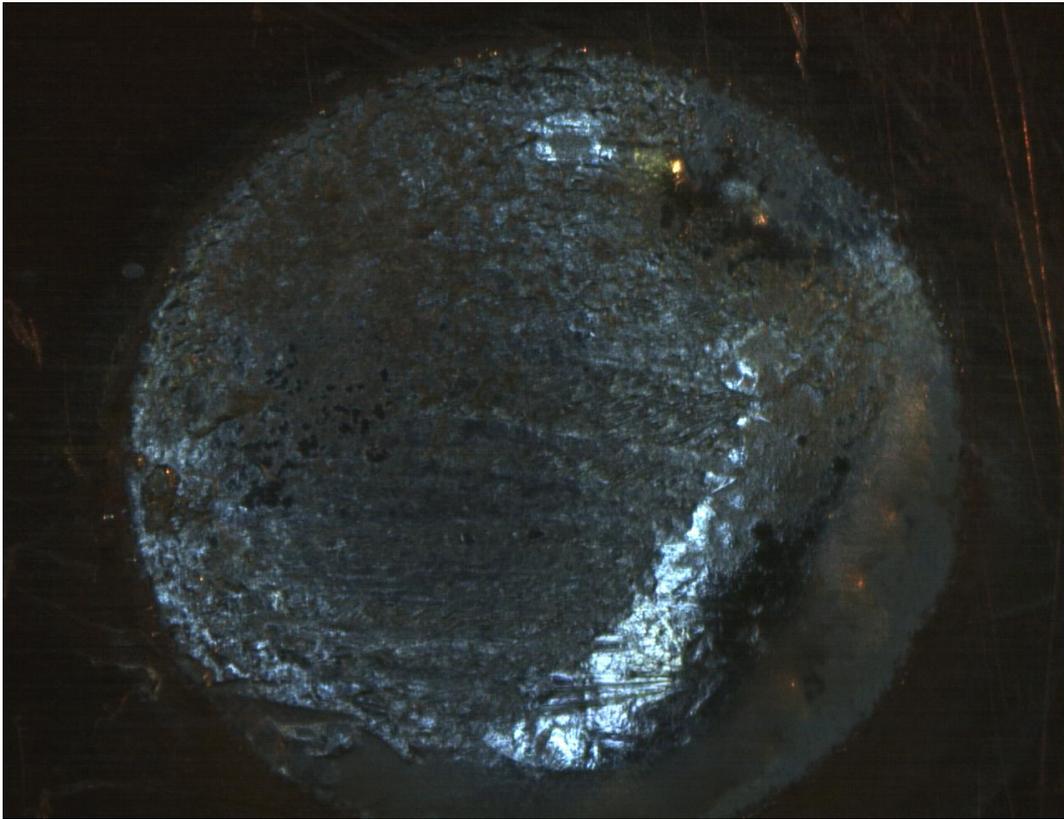
Paste A has a very small weight loss, but the soldering performance is poor. Higher activation in general results in more weight loss. Pastes B, D and E have a strong flux chemistry which results in excellent wetting, but their weight loss is relatively high. The spread also depends on the solderability of the different powders.



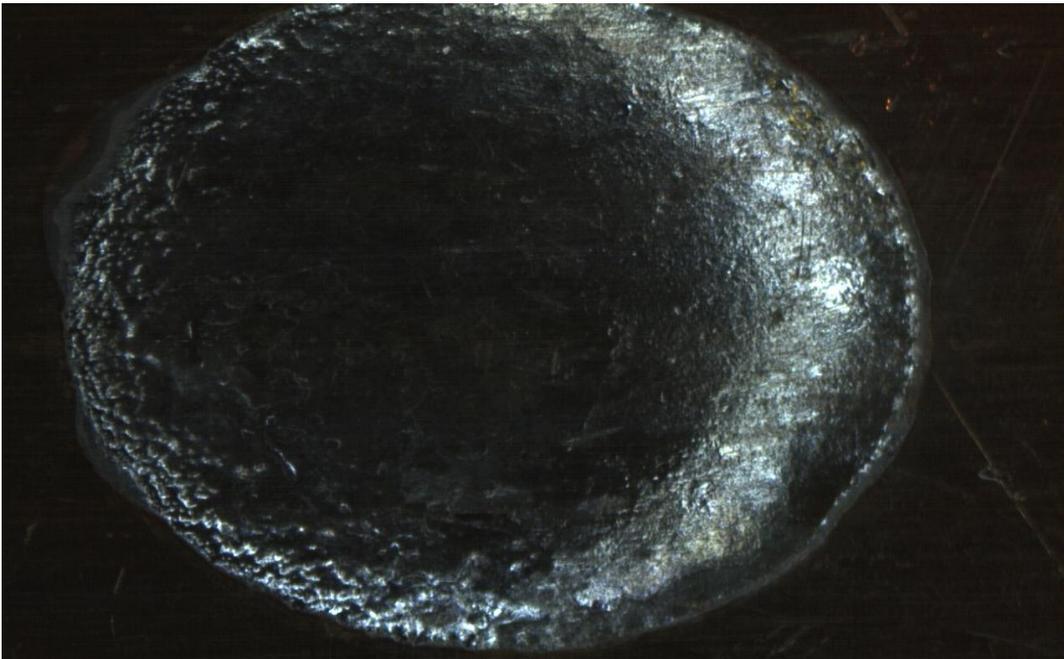
**Figure 14: Spreading as a function of weight loss.**

Paste A	Paste B	Paste C	Paste D	Paste E

**Figure 15: Spreading test for the different samples after 72 hours.**



**Figure 16 A**



**Figure 15 B**

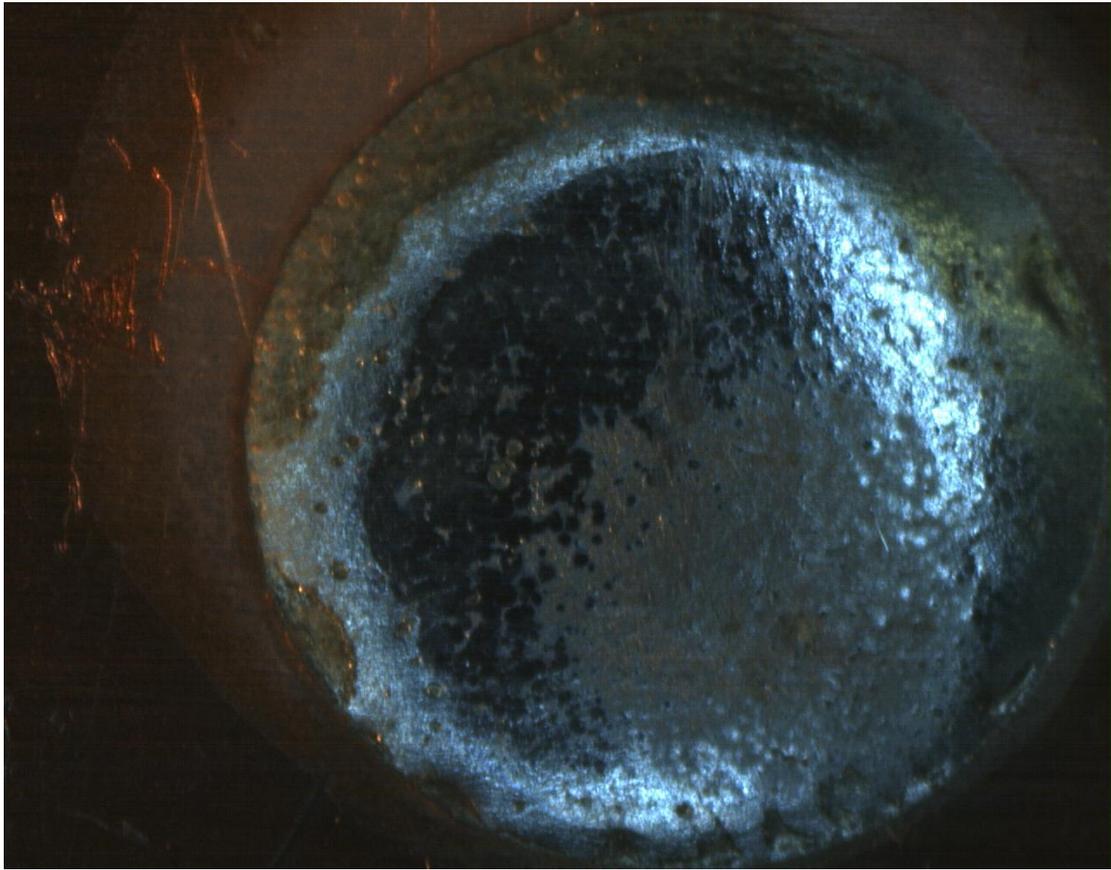


Figure 15 C

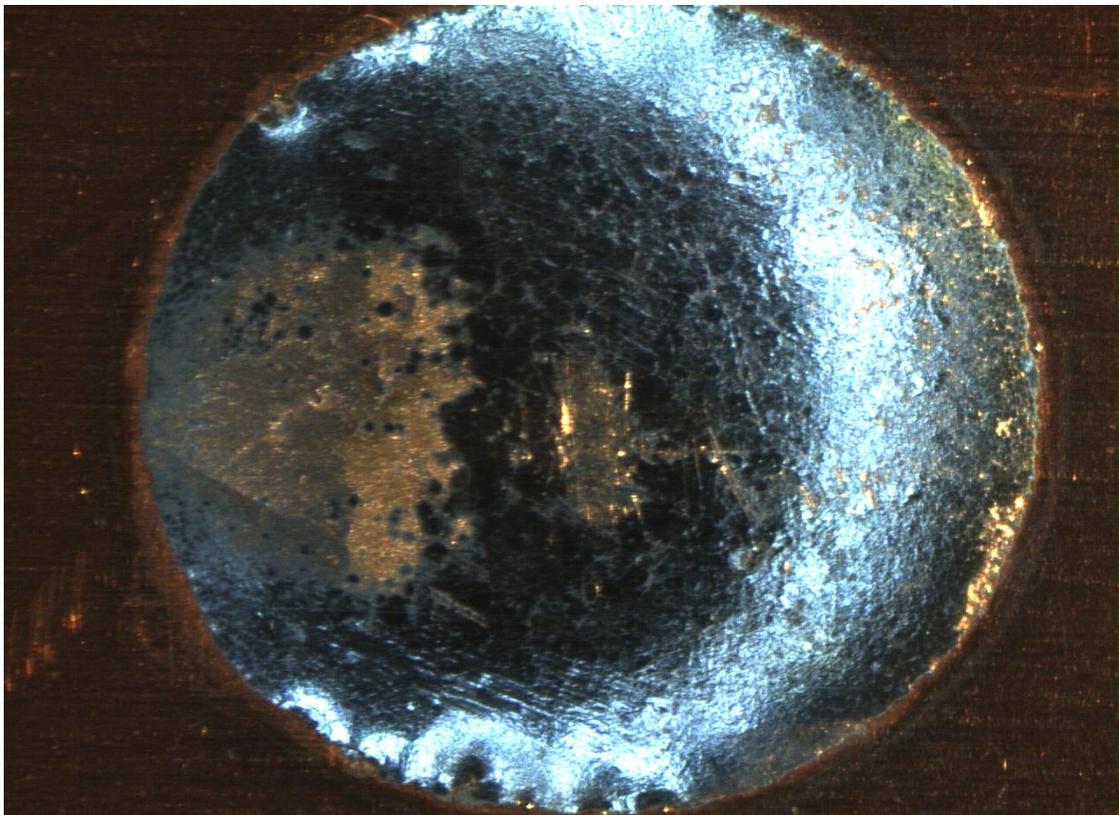


Figure 15 D

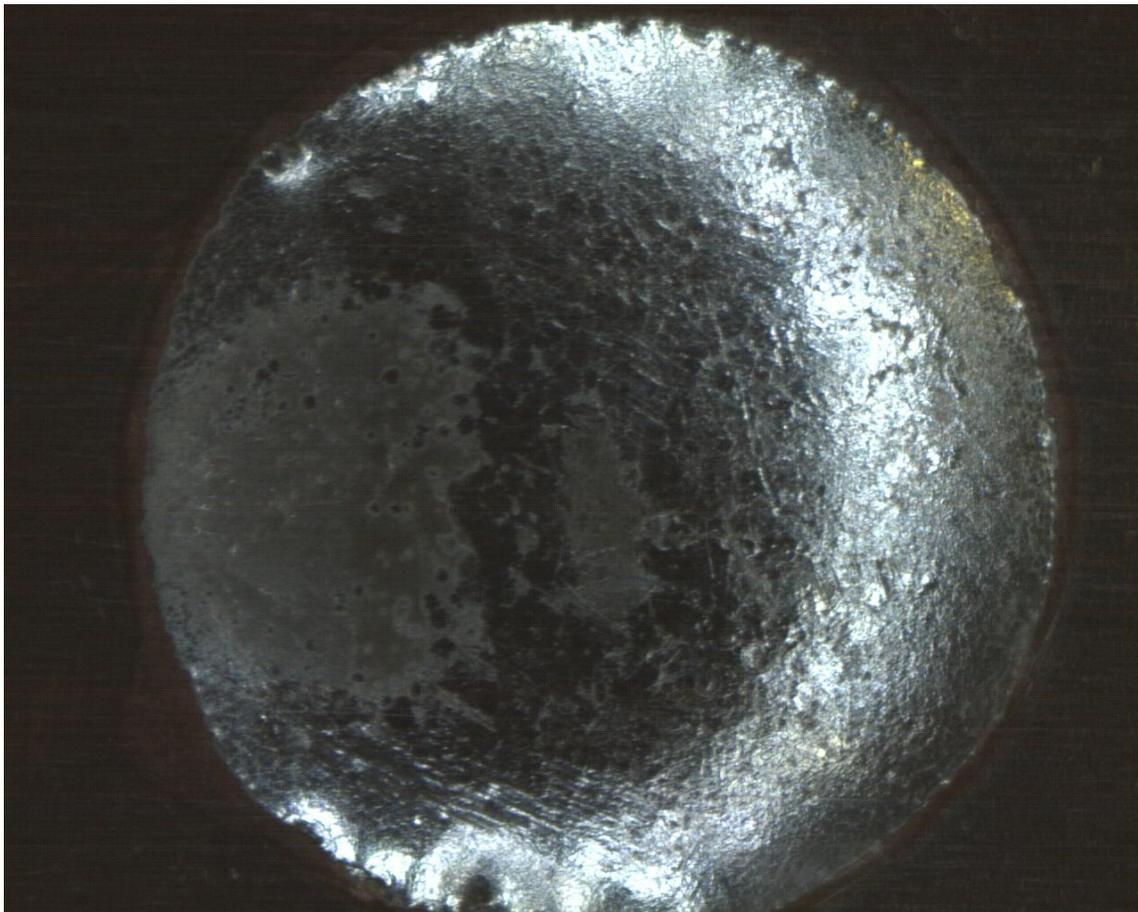


Figure 15 E

**Summary**

It has already been mentioned that a solder paste flux has to fulfill a large number requirements, many of which are not necessarily completely compatible or optimally suitable for a single formulation. Compromises must be made, and this somewhat explains the great variety of lead-free solder pastes.

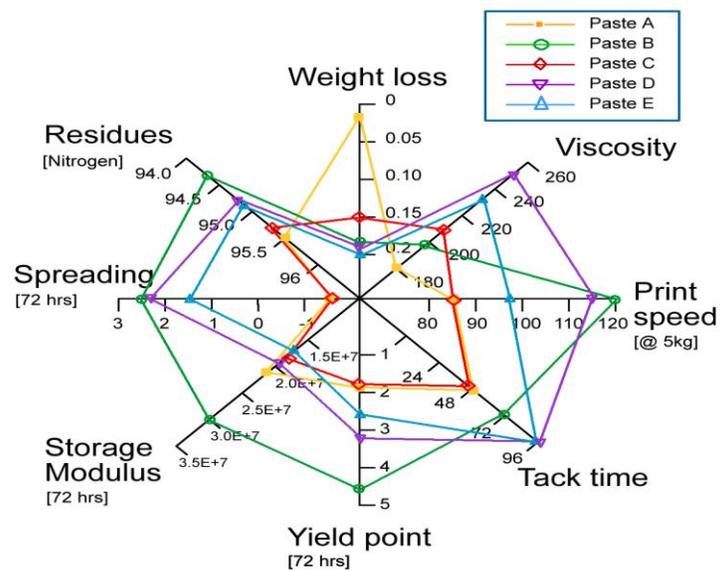


Figure 17: Solder pastes and impact on characteristics after stencil life.

From this study a number of conclusions with respect to stencil-life can be made:

- Weight loss is different for pastes with different flux chemistry.
- Even with the same flux chemistry, the evaporation rate can be different due to the oxidation level of the powder.
- Some fluxes are more sensitive for the area exposed to air than others. Evaporation depends on the mass of the solder paste.

With respect to soldering, the experiments did show that spreading (wetting) decreases when the paste is dry (see Table 6). It also shows that there are significant differences in spread, which make some pastes only suitable for nitrogen atmospheres.

Thermo-gravimetric Analysis is a nice instrument that can be used to study performance of a solder paste in a reflow process. When used in combination with a Rheometer, printing and soldering characteristics of solder pastes can be monitored and used for statistic process control of solder paste manufacturing.

## References

1. Thixotropy of Solder Paste Impacts Repeatability and Reproducibility of Rheometric Results, Inneke van Tiggelen-Aarden, Eli Westerlaken, APEX 2007.
2. Thixotropy of Solder Paste Impacts Rheometric Results, Circuit Assembly July 2007, Inneke van Tiggelen-Aarden and Eli Westerlaken.
3. Rheology Testing of Solder Pastes and Conductive Adhesives – A Guide, Miloš Dušek and Christopher Hunt, NPL.
4. Reflow Soldering Processes and Troubleshooting, Ning-Cheng Lee.

## Appendix I

### Evaporation test – Experiment 1

	<b>Deposition 1:</b>	<b>Deposition 2:</b>	<b>Deposition 3:</b>	<b>Deposition 4:</b>
Area [mm <sup>2</sup> ]	186	2691	320	619
Volume [mm <sup>3</sup> ]	33	4329	400	491
Area/Volume [1/mm]	5.62	0.62	0.80	1.26
<b>Paste A:</b>	Weight loss [%]	Weight loss [%]	Weight loss [%]	Weight loss [%]
Time zero	0.000	0.000	0.000	0.000
24 hours	0.010	0.009	0.001	0.001
48 hours	0.010	0.013	0.004	0.002
72 hours	0.020	0.013	0.007	0.008
96 hours	0.040		0.020	0.016
<b>Paste B:</b>	Weight loss [%]	Weight loss [%]	Weight loss [%]	Weight loss [%]
Time zero	0.000	0.000	0.000	0.000
24 hours	0.126	0.041	0.015	0.050
48 hours	0.144	0.068	0.067	0.072
72 hours	0.179	0.090	0.085	0.104
96 hours	0.188		0.135	0.137
<b>Paste C:</b>	Weight loss [%]	Weight loss [%]	Weight loss [%]	Weight loss [%]
Time zero	0.000	0.000	0.000	0.000
24 hours	0.121	0.083	0.041	0.122
48 hours	0.151	0.122	0.135	0.162
72 hours	0.151	0.151	0.156	0.197
96 hours	0.151		0.190	0.247
<b>Paste D:</b>	Weight loss [%]	Weight loss [%]	Weight loss [%]	Weight loss [%]
Time zero	0.000	0.000	0.000	0.000
24 hours	0.132	0.040	0.027	0.053
48 hours	0.173	0.073	0.072	0.076
72 hours	0.193	0.098	0.098	0.116
96 hours	0.255		0.160	0.156

<b>Paste E:</b>	Weight loss [%]	Weight loss [%]	Weight loss [%]	Weight loss [%]
Time zero	0.000	0.000	0.000	0.000
24 hours	0.090	0.038	0.019	0.054
48 hours	0.141	0.068	0.071	0.079
72 hours	0.131	0.089	0.094	0.122
96 hours	0.201		0.138	0.164

## Appendix 2

### Box Behnken experiment

Run order	Mass solder paste [mg]	Temperature [°C]	Air flow [ml/min]	Solder Paste A Evaporation rate [% weight loss/hour]	Solder Paste D Evaporation rate [% weight loss/hour]
1	40	32	0	0.06	0.06
2	60	60	15	0.12	0.36
3	40	60	0	0.15	0.33
4	20	46	0	0.15	0.33
5	40	46	15	0.06	0.18
6	20	60	15	0.21	0.81
7	60	46	0	0.09	0.12
8	40	32	30	0.06	0.06
9	60	46	30	0.09	0.18
10	40	60	30	0.15	0.42
11	60	32	15	0.03	0.09
12	20	46	30	0.15	0.33
13	40	46	15	0.09	0.24
14	20	32	15	0.09	0.18
15	40	46	15	0.12	0.15

#### Solder paste A:

Term	Coef	SE Coef	T	P
Constant	0.035151	0.023676	1.485	0.176
Solder paste mass	-0.004148	0.000786	-5.280	0.001
Temperature	0.004554	0.000446	10.216	0.000
Airflow	-0.001462	0.000430	-3.399	0.009
Solder paste mass*Solder paste mass	0.000046	0.000008	6.047	0.000
Airflow*Airflow	0.000049	0.000014	3.591	0.007
Solder paste mass*Temperature	-0.000027	0.000011	-2.550	0.034

S = 0.00588348

**R-Sq = 99.08%**

PRESS = 0.00178061

R-Sq(pred) = 94.11%

R-Sq(adj) = 98.40%

#### Solder paste D:

Term	Coef	SE Coef	T	P
Constant	0.318151	0.247930	1.283	0.247
Solder paste mass	-0.014469	0.004221	-3.428	0.014
Temperature	-0.001843	0.009799	-0.188	0.857
Airflow	0.001417	0.002892	0.490	0.642
Solder paste mass*Solder paste mass	0.000128	0.000052	2.471	0.048
Airflow*Airflow	0.000147	0.000106	1.386	0.215
Solder paste mass*Temperature	-0.000006	0.000092	-0.060	0.954

S = 0.0359253

**R-Sq = 95.35%**

PRESS = 0.0306918

R-Sq(pred) = 81.59%

R-Sq(adj) = 90.71%

### Appendix 3

#### Design of Experiment

General Linear Model: Preheat versus Flow, Atmosphere, Weight loss

<b>Factor</b>	<b>Type</b>	<b>Levels</b>	<b>Values</b>
Flow	fixed	3	0, 25, 50
Atmosphere	fixed	2	Air, Nitrogen
Weight loss	fixed	3	0.0, 0.1, 0.2

#### Analysis of Variance for Preheat, using Adjusted SS for Tests

<b>Source</b>	<b>DF</b>	<b>Seq SS</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F</b>	<b>P</b>
Flow	2	119.741	100.703	50.351	57.97	0.000
Atmosphere	1	93.733	86.135	86.135	99.17	0.000
Weight loss	2	69.100	53.260	26.630	30.66	0.000
Flow*Atmosphere	2	31.080	30.522	15.261	17.57	0.002
Atmosphere*Weight loss	2	4.691	4.691	2.346	2.70	0.135
Error	7	6.080	6.080	0.869		
Total	16	324.426				

S = 0.931955

R-Sq = 98.13%

R-Sq(adj) = 95.72%

# **Estimate Stencil Life and Ideal Heating Profile of solder Paste**

**(using advanced thermo-gravimetric analyze techniques)**

Gerjan Diepstraten

**COBAR®**

# Content

- **Stencil life**
  - Definition
  - Flux system
  - Visual check on printer
  - Print performance
- **Weight loss**
  - Box Behnken experiment
  - Thermal gravimetric Analysis
  - Rheology
- **Reflow impact**
  - Atmosphere
  - Design of Experiment
  - Residues
  - Spreading
- **Conclusions**



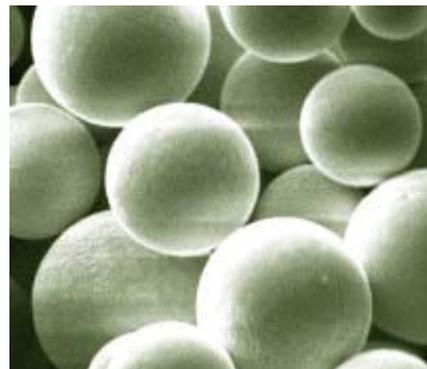
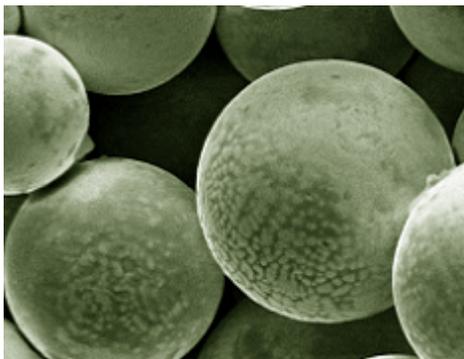
# Definition stencil life

## Stencil Life definition:

The time that a paste can be hold on the stencil without loosing its rheological properties or solderability.

## Reasons for dry paste:

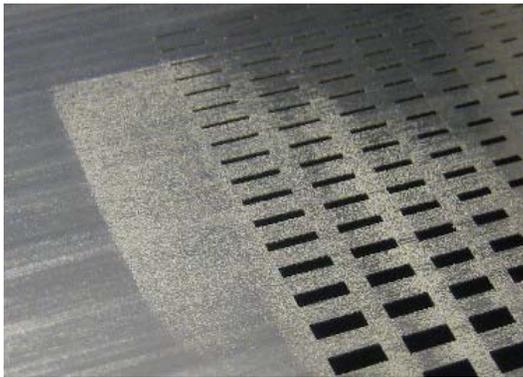
- Evaporation of volatile solvents
- Do high operation conditions, e.g. temperature, humidity or air draft
- High flux activity at room temperature



# Flux system functions

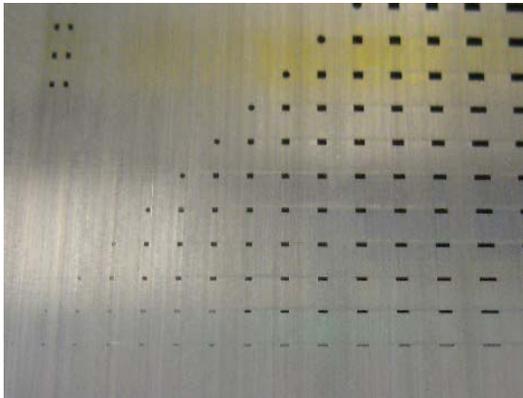
- Provide a homogeneous suspension of the powder
- Prevent oxidation of the powder and surfaces
- Provide flow properties in printing
- Hold powder in place after printing
- Provide tack to hold components in position
- Remove metal oxides, grease, metal carbonate during soldering
- Provide self-alignment of components during reflow
- Inhibit reoxidation of powder surfaces to be joined during reflow
- Provide controlled cooling of the joint

# Visual on stencil

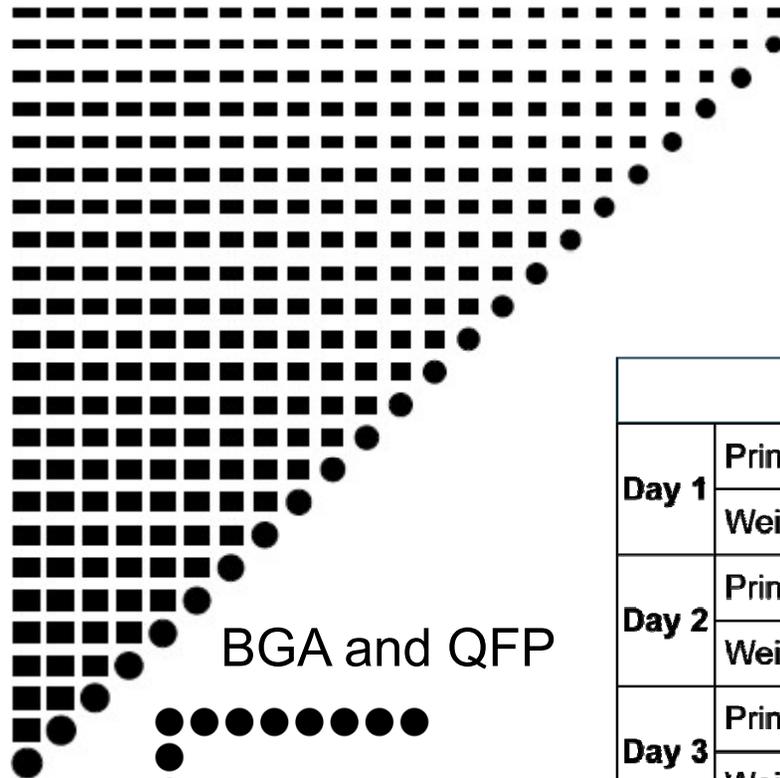


## **Dry solder paste on stencil:**

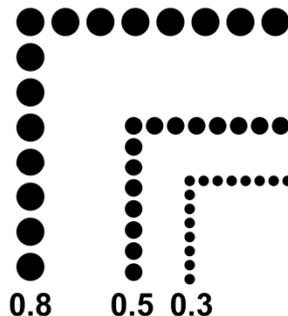
- Smearing of paste on the screen.
- Clogging of apertures.
- Solder paste moves instead of roles.
- Solder paste sticks to squeegee.



# Print yield



BGA and QFP



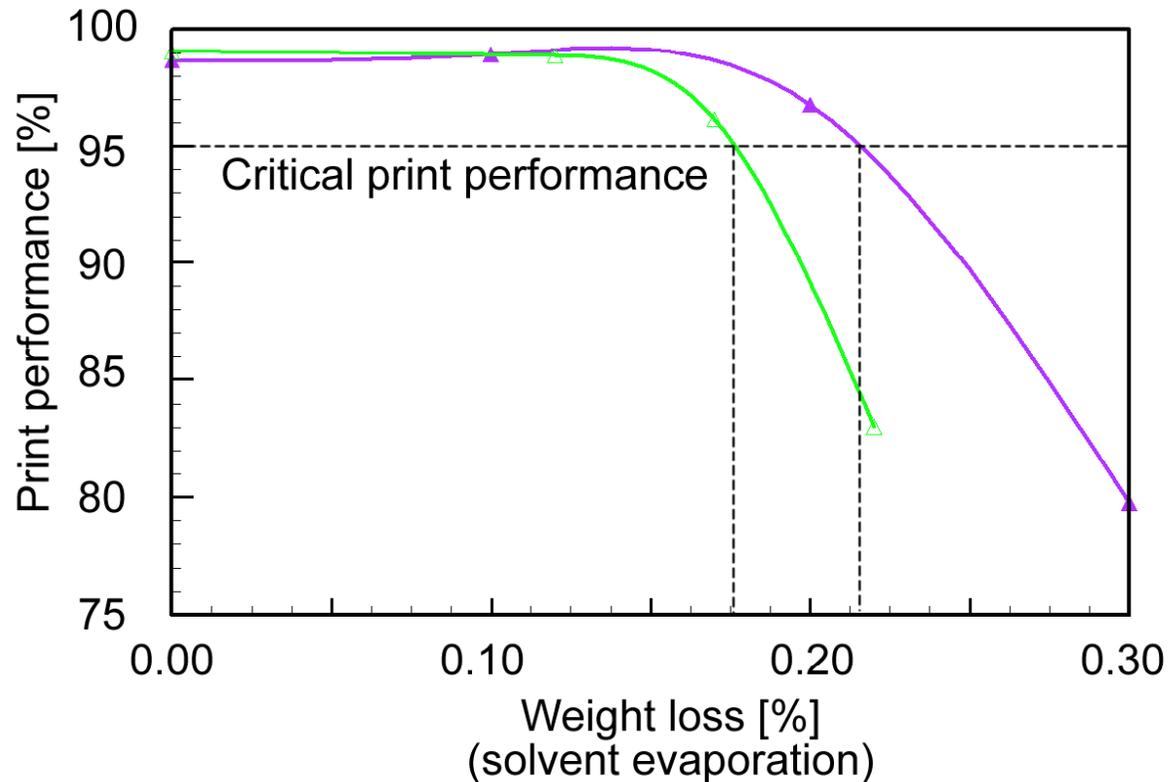
## Print sequence:

20 boards – analyze board  
no: 1 - 10 - 11 - 20

Print interval 24 hours

		Paste A	Paste B	Paste C	Paste D	Paste E
Day 1	Print performance	95.52%	99.40%	98.80%	98.67%	99.10%
	Weight loss	-	-	-	-	-
Day 2	Print performance	88.43%	89.54%	84.80%	98.94%	98.88%
	Weight loss [%]	0.26	0.37	0.54	0.10	0.12
Day 3	Print performance				96.76%	96.15%
	Weight loss [%]				0.20	0.17
Day 4	Print performance				79.76	83.04%
	Weight loss [%]				0.30	0.22

# Weight loss - printing



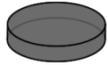
**Print conditions:**  
DEK 260 printer  
Speed: 80 mm/sec  
Pressure: 5 kg  
Squeegee: SS-60°

## Critical values solvents loss:

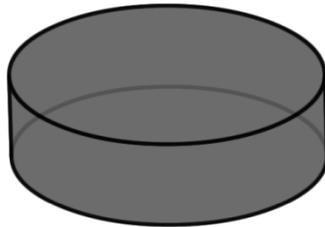
Approximately 0.20% weight loss.

This means that 5% of the solvent has been evaporated.

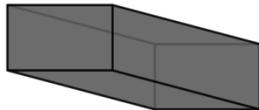
# Paste depositions



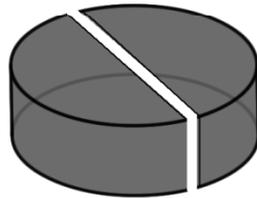
Deposition 1:  
diameter 6.5 mm  
height 0.2 mm



Deposition 2:  
diameter 55 mm  
height 2 mm



Deposition 3:  
width 20 mm  
length 10 mm  
height 2 mm

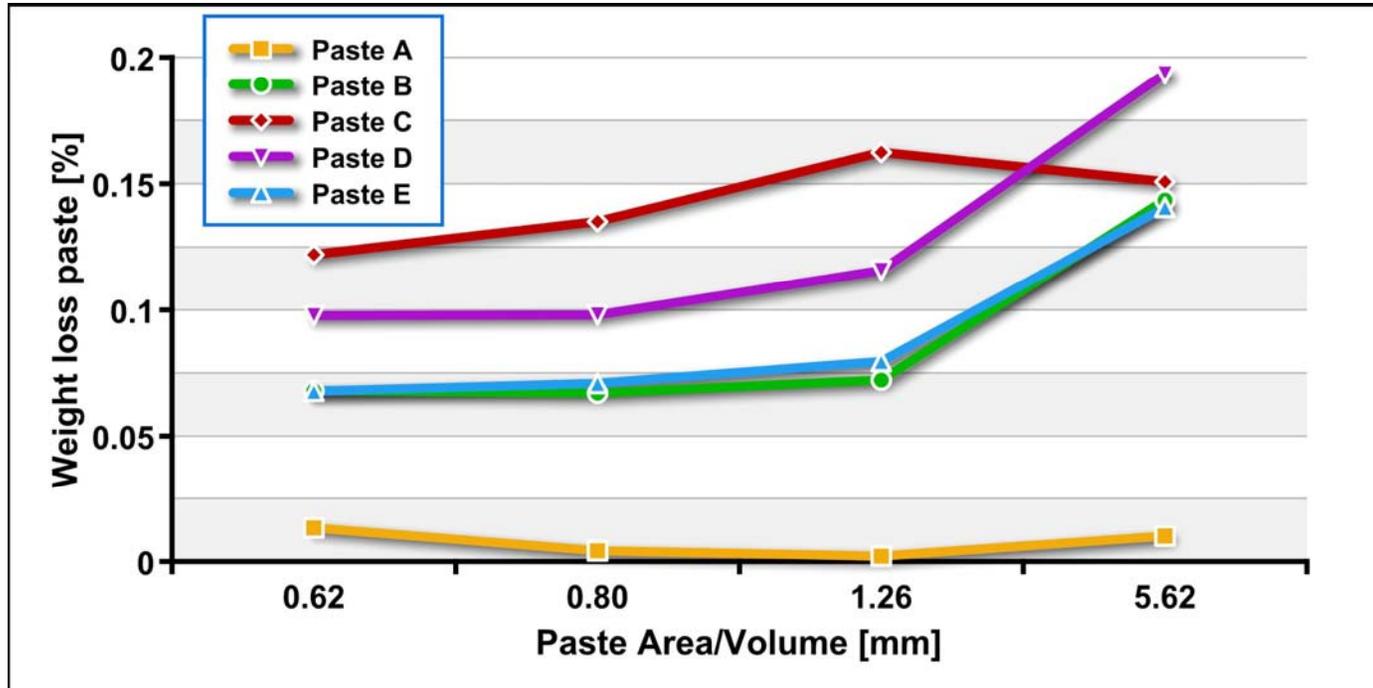


Deposition 4:  
diameter 25 mm  
height 1 mm

Solder paste deposits on stencil		
	Shape	Ratio Area/Volume
1	Small cilinder	5.62
2	Large circle	0.62
3	Square box	0.80
4	2 half cylinders	1.26

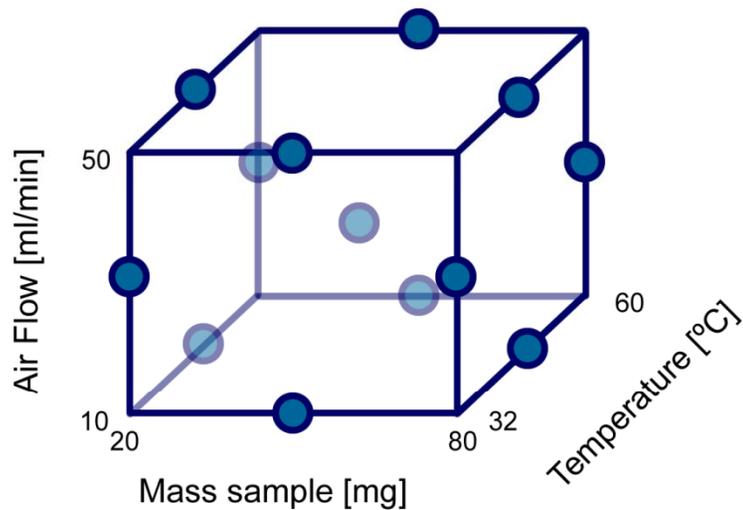
After 48 hours the weight loss was measured

# Weight loss



After 48 hours on stencil for different depositions of solder paste.

# Box Behnken experiment



Weight loss influenced by:

1. Air flow
2. Mass sample
3. Temperature

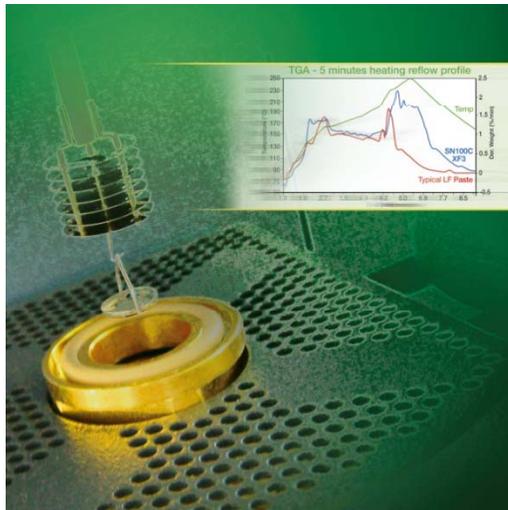
## Box Behnken:

This technique is used because some of the parameters may not show a linear relation.

# Thermo-gravimetric Analysis

## Thermogravimetry:

In a thermo gravimetric analysis the mass of a sample in a controlled atmosphere is recorded continuously as a function of the temperature or time.



Output characteristics:  
Define the weight loss per time.

# Analysis Box Behnken

Different air flows and temperatures  
[see Box Behnken data]



Solder paste D is sensitive for volume/area

Solder paste A all factors have significant impact on weight loss gradient

Weight loss per hour:

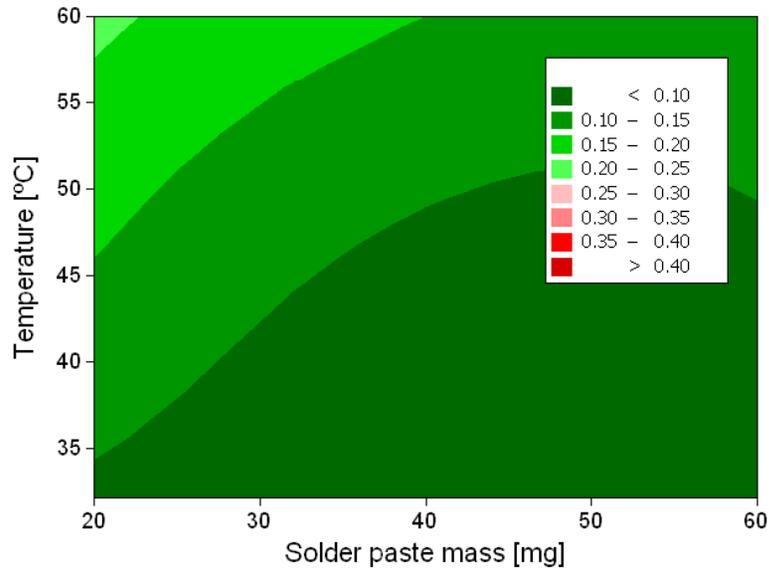
$$\text{Solder paste D} = 0.318151 - 0.014469 \cdot M + 0.000128 \cdot M^2$$

M = mass sample in mg

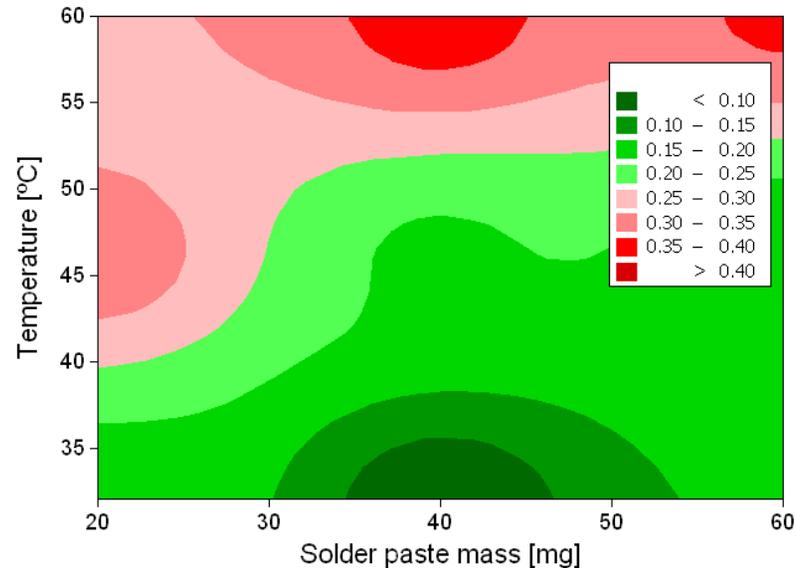
# Contour plot

Weight loss [%/h] as a function of

- Solder paste mass
- Temperature



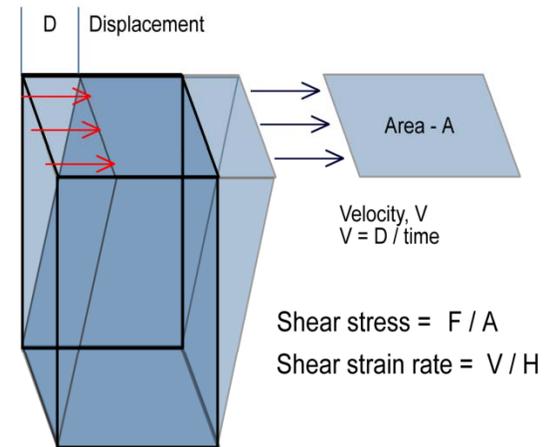
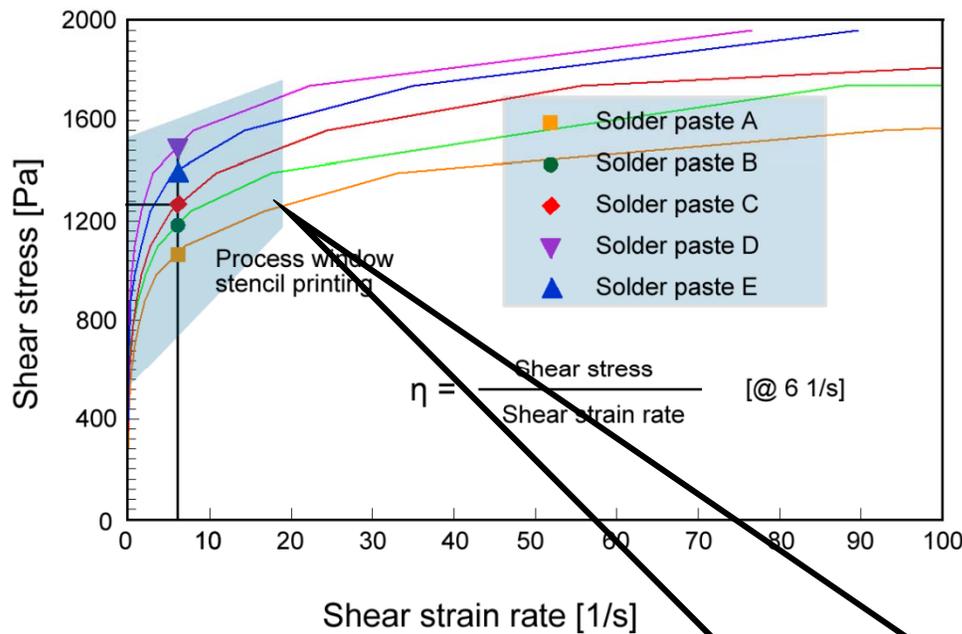
Paste A



Paste D

# Solder paste rheology

$\eta$  = viscosity

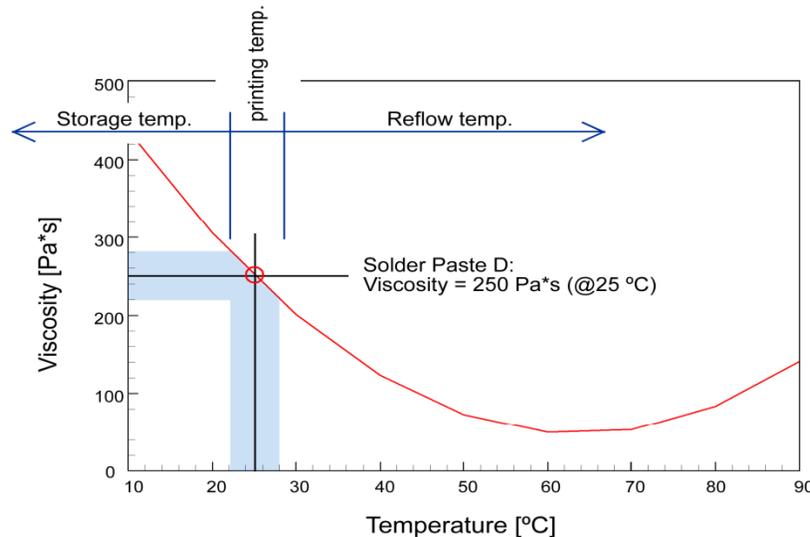


For stencil printing:  
shear strain rate is  
1 – 20 per second

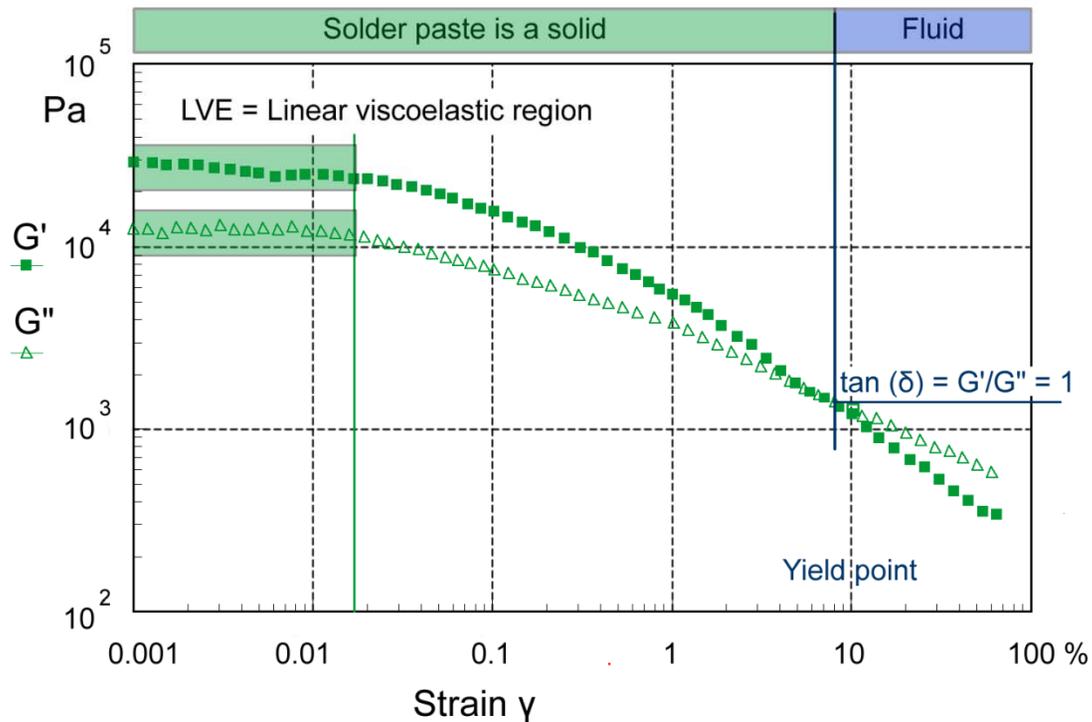
# Viscosity - temperature

Viscosity is measure of resistance of the paste which is being deformed.

- Viscosity is temperature and humidity sensitive
- Printing temperature 22 - 28 ° C
- 30-70 % Relative Humidity
- Time depended behavior (thixotropic)



# Thixotropic



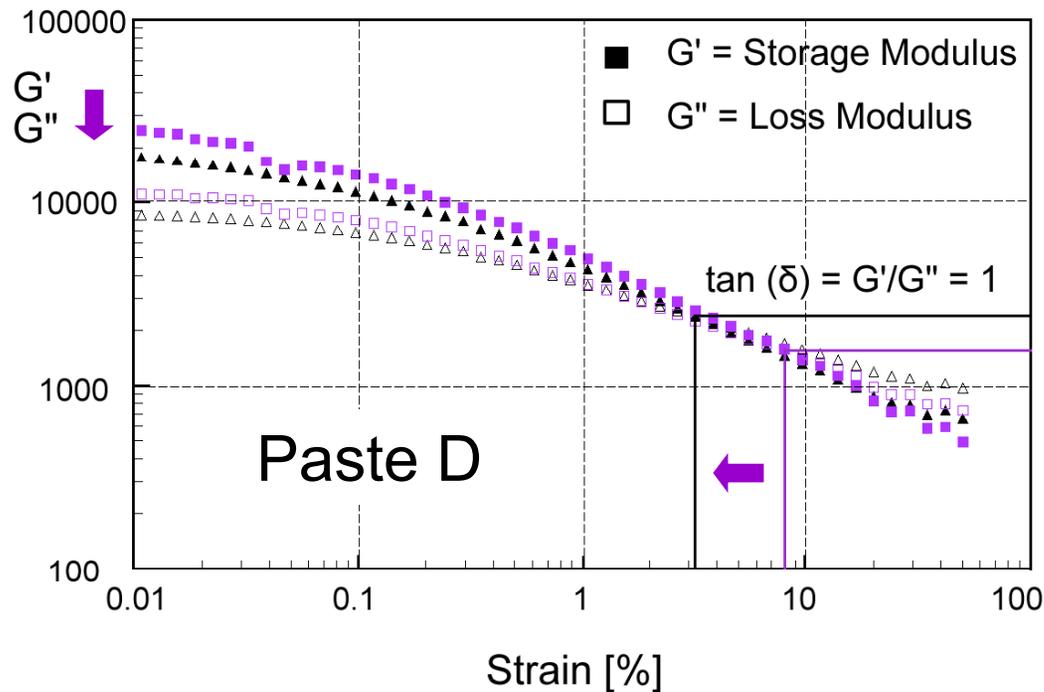
Viscoelastic behavior

Viscous properties – Storage Modulus  $G'$   
Elastic properties – Loss Modulus  $G''$

# Rheology after weight loss

Changes in viscoelastic behavior after 3 days on stencil:

- Yield point decreases
- Storage Modulus decreases



Solder pastes with higher elastic properties ( $G''$ ,  $G'$ ) and yield stress are desired in order to minimize print defects

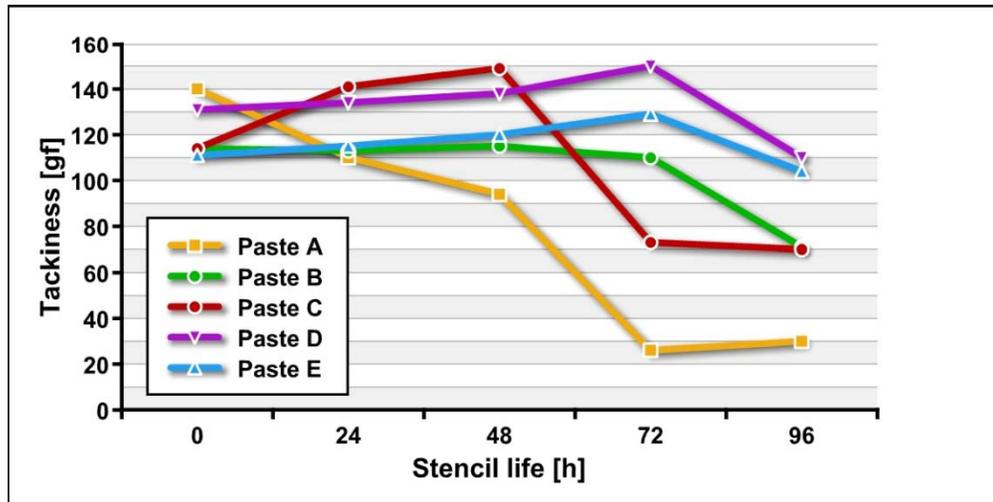
# Tackiness



High tack force  
sticky paste

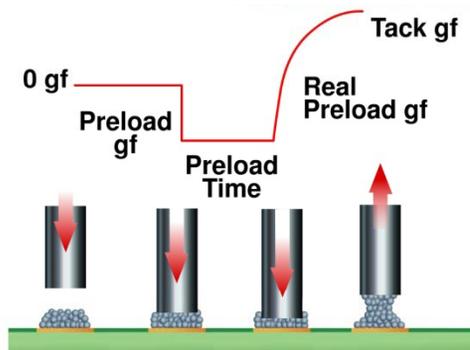
Low tack force

# Tack force and time



## Tack time:

Time allowed between printing and component placement

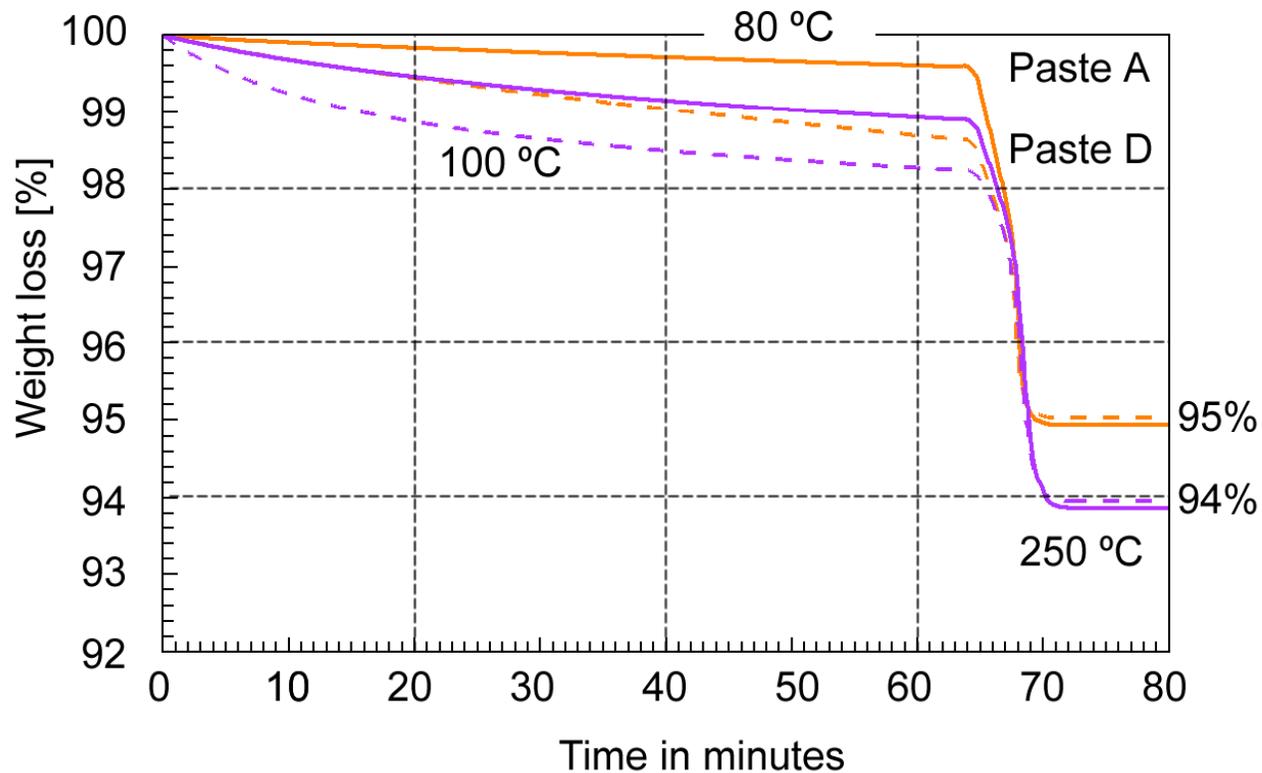


## Tackiness:

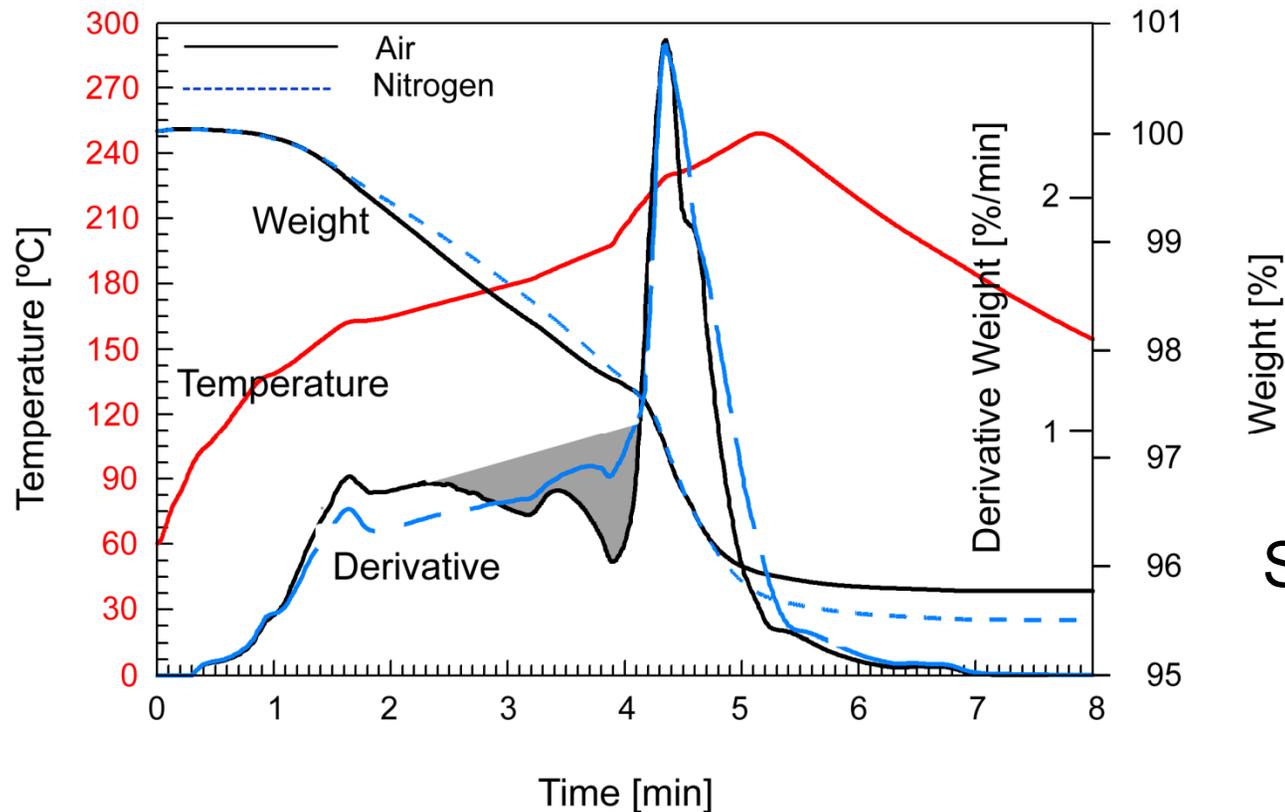
- Non-tacky to release from stencil aperture
- Tacky to hold on the substrate
- Tacky enough to hold components

# Predrying effects

Predrying of the paste (after placing components) may have positive effects on the soldering.



# Reflow atmosphere

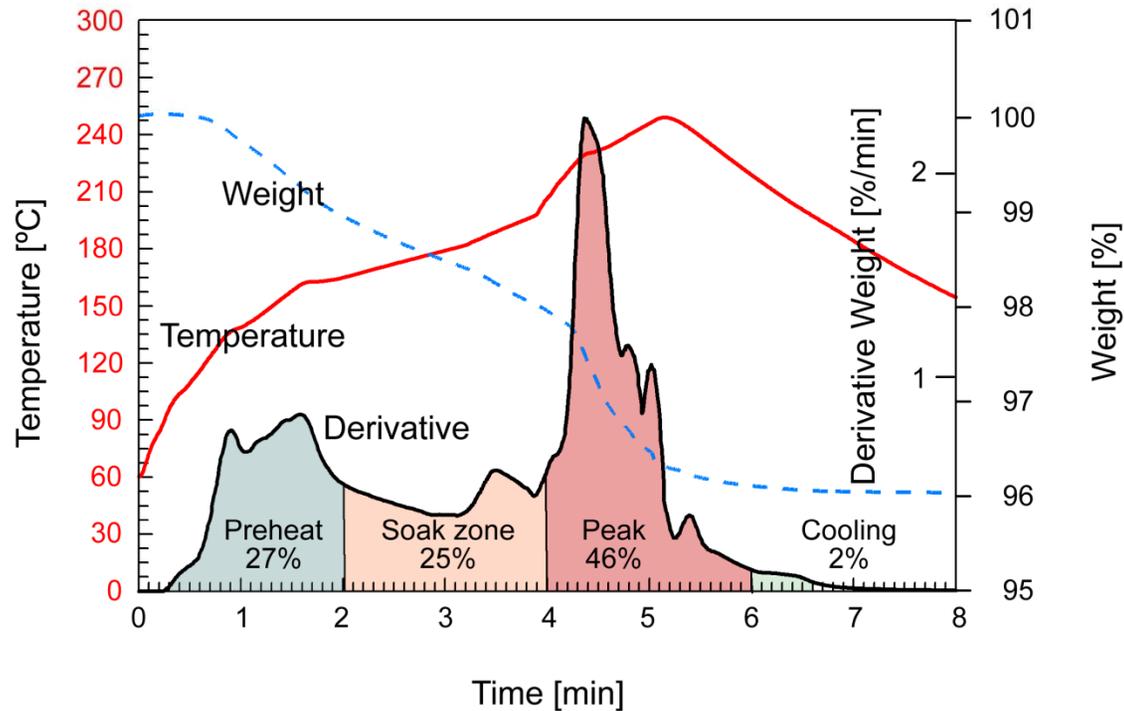


Solder paste A

Inert atmosphere versus air:

Oxidation from 170 ° C to melting point of the paste

# TGA – Reflow [air]



Divide the reflow process into 4 steps.

	Preheat [%]	Soak zone [%]	Peak zone [%]	Cool zone [%]
Paste A	18	37	44	1
Paste B	26	37	35	2
Paste C	18	25	56	1
Paste D	27	25	47	2
Paste E	28	25	45	1

# Design of Experiment

Effect of the solvent evaporation on the reflow process and flux residues.

Design of Experiment				
Parameter	Units	Level 1	Level 2	Level 3
Gas flow	ml/min	0	25	50
Environment		Air	Nitrogen	
Evaporated solvent [wl]	%	0	0.1	0.2

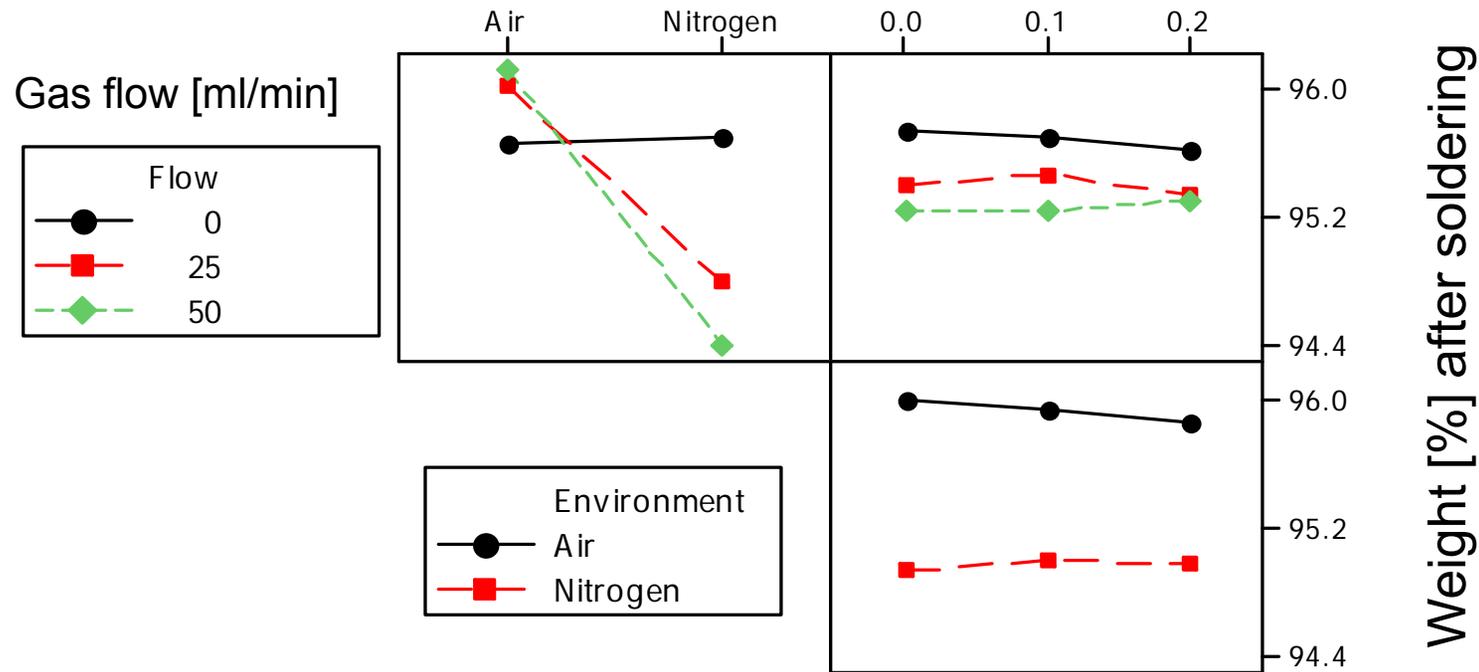
Ramp soak spike heating profile

Total heating time = 5 minutes

Time above liquidus = 90 seconds

Peak temperature = 248 °C

# Residues (Paste D)

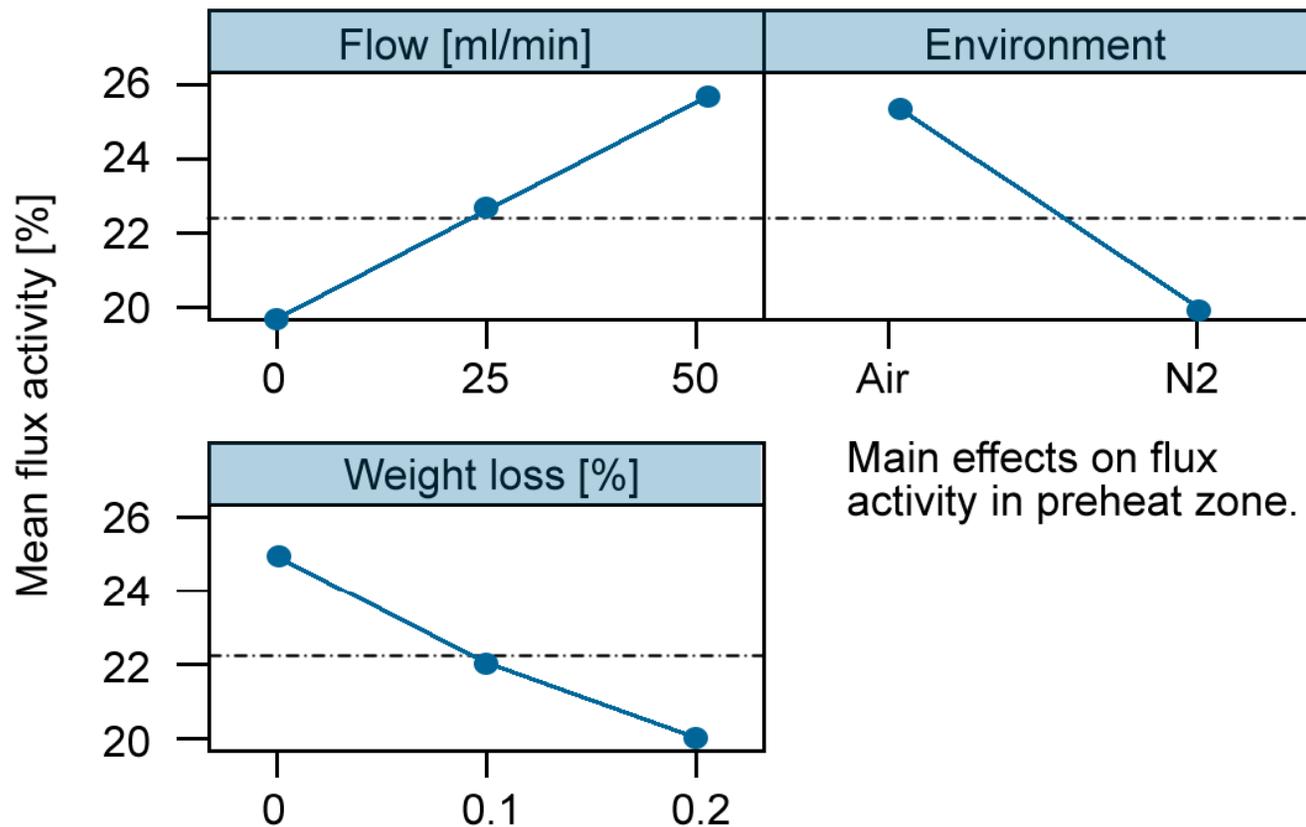


## Analysis:

Amount of flux residues depends on the environment and gas flow in the oven. Solvents have no impact.

# Analysis DoE - Preheat

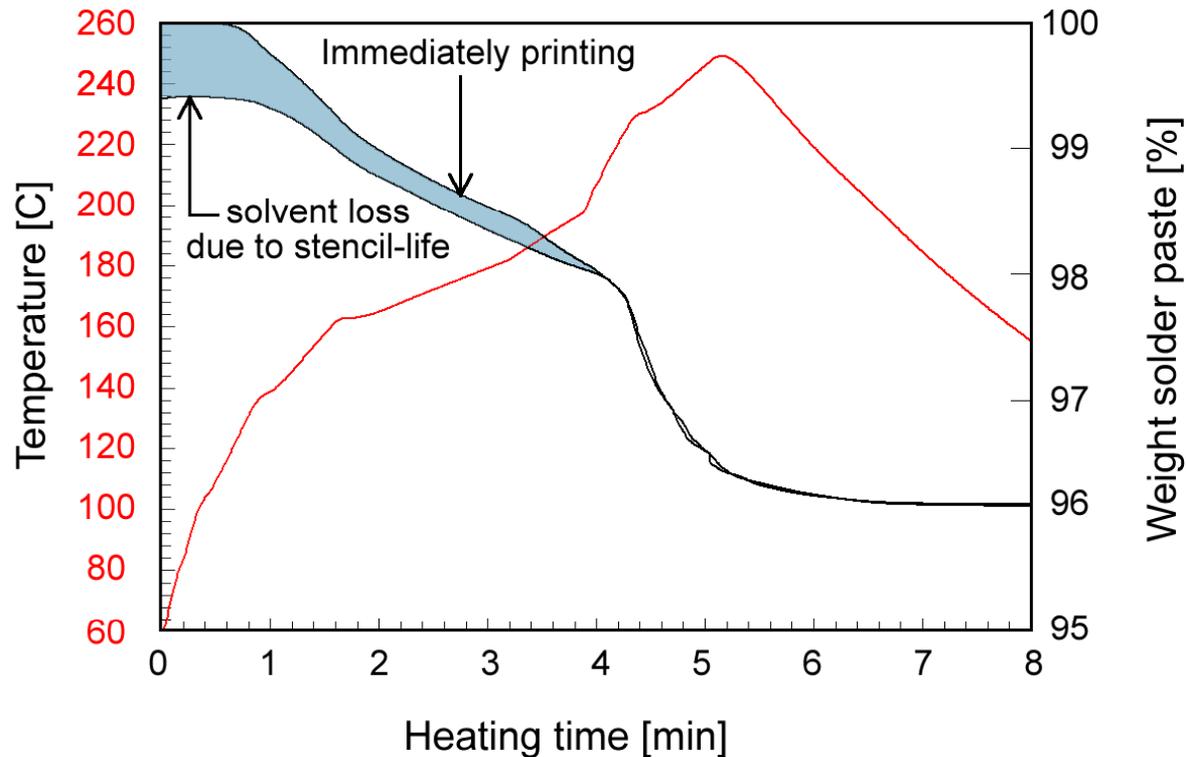
Flux activity in preheat zone of reflow process



A high air flow in a reflow oven will affect the performance.

# Weight loss and reflow

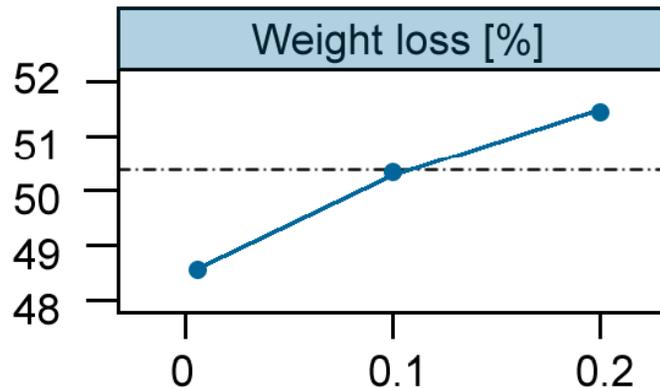
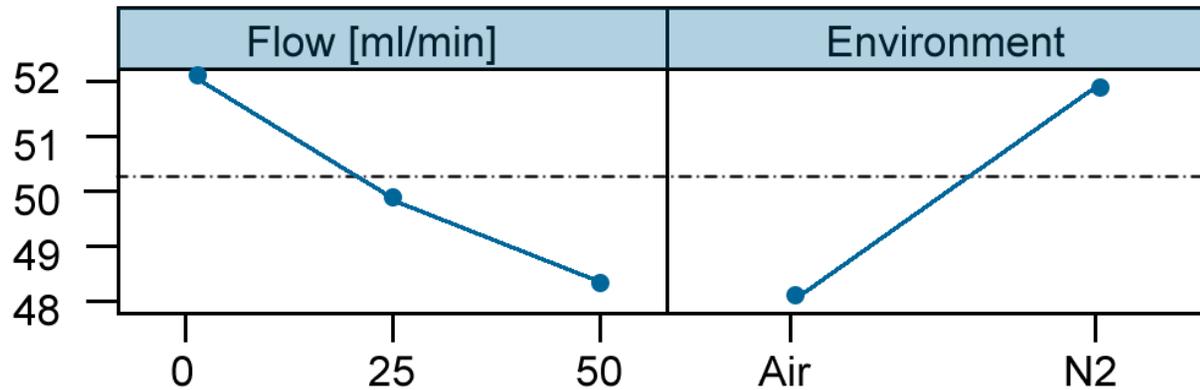
Weight loss solder paste during reflow



Evaporation of solvents only affect the preheat and soak part of the reflow process.

# Analysis DoE – Peak zone

Flux activity in peak zone.



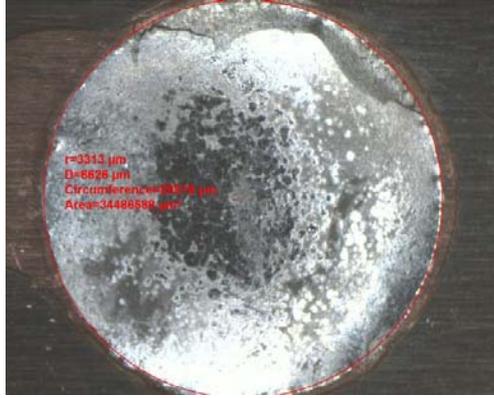
Main effects on flux activity in peak zone.

In air minimum flux activity (oxidation)

Weight loss: when solvents are evaporate ->

% wise more activators left.

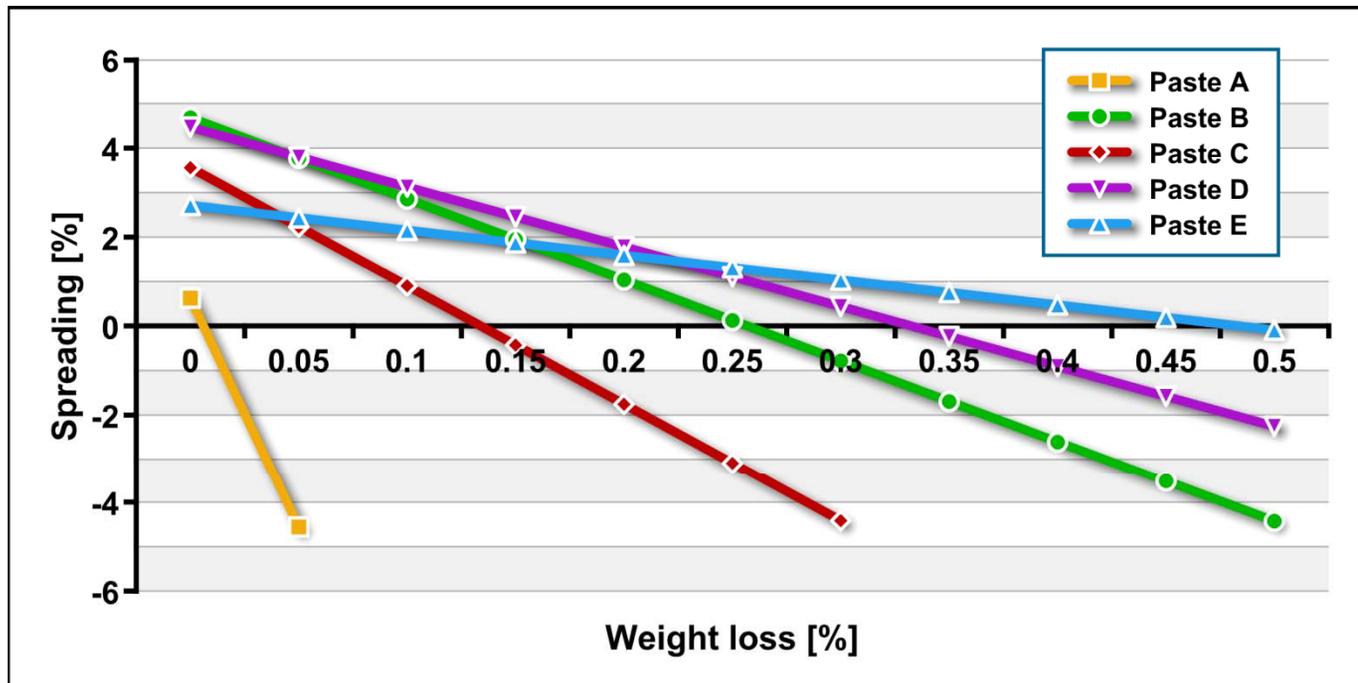
# Spreading



Wetting on Copper.  
4 Points diameter measurement  
microscope.  
After 2 days on stencil.  
Paste A and C show dewetting

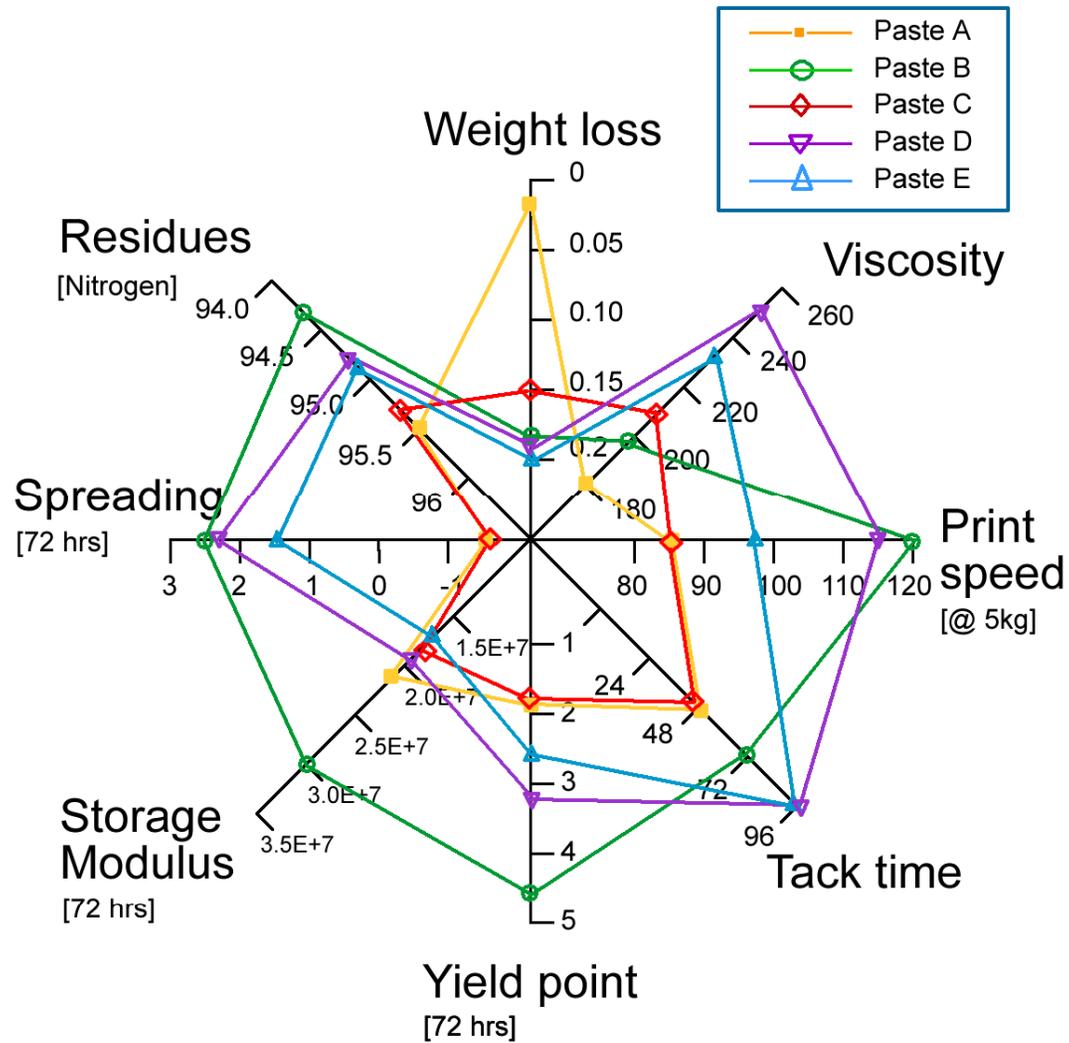
Solder paste	Spreading		Remarks
	0 hours	48 hours	
Paste A	6.580	6.445	Dewetting
Paste B	6.809	6.618	
Paste C	6.730	6.508	Minor
Paste D	6.786	6.617	
Paste E	6.682	6.632	

# Impact weight loss on spread



- Spreading depends on flux system of paste
- Spreading reduces after evaporation of solvent
- Dewetting if too much solvent is evaporated

# Summary



# Conclusions

- Solder paste flux has to fulfill a large number requirements, many of which are not necessarily completely compatible or optimally suitable for a single formulation.
- Stencil life:
  - Weight loss is different for pastes with different flux chemistry
  - Even with the same flux chemistry, the evaporation rate can be different (powder)
  - Some fluxes are more sensitive for the area exposed to air than others
- Spreading is also affected by dry solder paste and may result in dewetting.