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# Effective Methods to Get Volatile Compounds Out of Reflow Process

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**Abstract**
Although reflow ovens may not have been dramatically changed during the last decade the reflow process changes step by step. With the introduction of lead-free soldering not only operation temperatures increased, but also the chemistry of the solder paste was modified to meet the higher thermal requirements. Miniaturization is a second factor that impacts the reflow process. The density on the assembly is increasing where solder paste deposit volumes decreases due to smaller pad and component dimensions. Pick and place machines can handle more components and to meet this high through put some SMD lines are equipped with dual lane conveyors, doubling solder paste consumption. With the introduction of pin in paste to solder through hole components contamination of the oven increased due to dripping of the paste.
The iNemi Roadmap identified seven key metrics for the reflow process:

1. Temperature delta performance
2. Inerting capability
3. Cooling rates
4. Flux management
5. Cost of operation
6. Traceability
7. Changeover time

The current flux collection systems need to focus on improvements to minimize maintenance downtimes. Flux management and cost of operation will benefit from an efficient oven cleaning method. The filter and condensation systems that were successful running in SnPb processes have to be reviewed and new technology is introduced to have a more efficient removal of solder paste, board and component gasses.

**Introduction**
This paper studies available and potential methods to keep a reflow oven clean from flux contamination. In order to have a good understanding first the solder paste and its composition is investigated in the lab. The maintenance of the ovens at customer applications is evaluated. The different methods of flux collection systems were subjected to efficiency and potential new technologies of removing organic vapors were investigated on lab scale.

Keywords: maintenance, flux, pyrolysis, thermal oxidation, adsorbers.

**Maintenance**
Maintenance is a big contributor to the cost of ownership of a reflow oven. When the oven has to be shut down for cleaning this also includes production loss. For this reason it is preferred to have a flux collection system that allows replacing filters or fluxing collection jars during production. Accessibility of the flux management and ease of access to the internal parts of the device for cleaning is paramount.
Maintenance and interval are very much depending on the volume of products that runs through the oven and the kind of solder paste that is used. Solder paste may contain a tacky rosin where others have modified resins that returns a very easy to clean white residue.

There are many systems in the market to get the flux residues out of the oven. The more traditional way is by condensation. The gasses are collected from multiple extraction points in the oven and guided through one or multiple heat exchangers. After the heat exchangers an additional filter will remove all remaining particles.

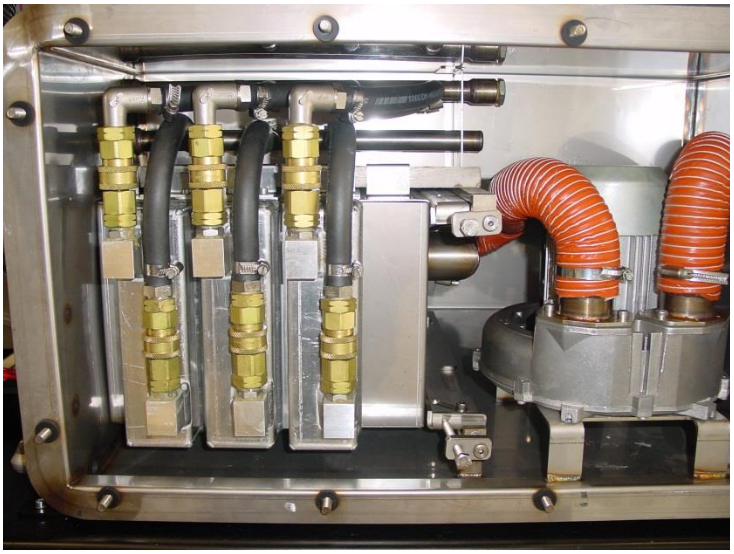

**Figure 1 – Gas recirculation system (GRS) with 3 heat exchangers and a filter in one unit**

This method has been very successful during the days of SnPb soldering. After the introduction of lead-free the chemistry changed and different filters were needed to get a better efficiency of cleaning. The principle of the concept is to let the exhausted gas condense.

This configuration is running in a high volume production line on a production oven using nitrogen atmosphere. The assembly's weight is 122 gram. The amount of solder paste per board is 4 grams. This unit requires cleaning after soldering 50.000 – 90.000 boards in a high volume production line. The remaining residues after condensation are tacky and dark colored oil. The machine downtime due to maintenance for this unit was 2 hours (2 persons doing maintenance). The time interval in between two maintenance turns was 4 weeks. Although the maintenance time and frequency for this line is minimal it still affects the cost of ownership and has a negative impact on the output. This forces engineers to look into alternative flux collection methods.

**Table 1 – Maintenance time versus number of boards soldered**

| | **Maintenance time** | **Number of boards** | **Solder paste** | **Flux [kg]** |
|---|---|---|---|---|
| Week 33 | [h] | [#] | [kg] | |
| Week 38 | 3.0 | 52.000 | 208 | 22.88 |
| Week 42 | 3.5 | 54.000 | 216 | 23.76 |
| Week 46 | 4.0 | 74.000 | 296 | 32.56 |
| Week 49 | 4.0 | 83.000 | 332 | 36.52 |

The composition of this oily residue (SnPb paste) is listed in the table (measured by gas chromatography).

**Table 2 – Composition of remaining residues in the gas recirculation system after condensation**

| | | | | | |
|---|---|---|---|---|---|
| Density | 0.988 | g/cm3 | Silver | <0.5 | mg/kg |
| Arsenic | 3.1 | mg/kg | Cadmium | <0.5 | mg/kg |
| Antimony | <0.5 | mg/kg | Lead | 2.6 | mg/kg |
| Selenium | 0.89 | mg/kg | Chrome | 0.54 | mg/kg |
| Mercury | <0.5 | mg/kg | Copper | 390 | mg/kg |
| Tin | 9.4 | mg/kg | Nickel | 2.9 | mg/kg |
| Gold | <0.5 | mg/kg | Zinc | 41 | mg/kg |

In order to have a better understanding of the contamination the project starts with in the laboratory investigating solder paste flux chemistry. Before cleaning an oven it is better to know the composition of the materials and its behavior at elevated temperatures like there are in a lead-free reflow process.

**Flux characterization introduction**

The solder pastes in reflow soldering can be divided into two groups of different chemistries. The majority of today's solder pastes are "no clean" fluxes. These fluxes do not require cleaning after reflow and contain rosin or resin system that encapsulates activators after soldering. The residues are relatively safe.

The second group is water soluble fluxes. Typically these fluxes are more aggressive and solder therefore better. However the residues aren't inert and need a washing process after soldering.

**Analytical test plan**

The objective is to investigate available methods to get volatile compounds out of the reflow oven by an efficient flux collection system. A step by step approach should result in a new design that improves the GRS system and reduces maintenance intervals. The analytical test plan contained the following milestones:

a. Obtain flux and individual ingredients
b. Identify volatile components (GC/MS) and measure decomposition rate (TGA)
c. Find catalysts that will facilitate pyrolysis of the volatile compounds
d. Build lab scale catalytic converter
e. Measure efficiency of catalysts (TGA/FT-IR)

The lab received the flux material of four different solder pastes. Since only the chemistry is examined the samples did not contain solder spheres.

Sample 1 was a no-clean SnPb solder paste. A rosin based flux for lead solder with classification ROL0.

Sample 2 was a water soluble Lead-Free solder paste. A rosin based flux with classification ROH1.

Sample 3 was water soluble SnPb solder paste. There is a minor amount of rosin in this paste and the classification is ORM0.

Sample 4 was a no-clean Lead-Free solder paste. A modified resin based flux with classification REL0.

A specific Gas Chromatography/Mass Spectrometry was used to identify volatile organic compounds present in the solder paste fluxes. Flux paste was held at 185°C for 30 minutes in sealed vial, and then the sample was taken from vial headspace and injected into GC/MS. The temperature of 185°C was selected because of the reflow profile; this corresponds to soak temperatures and places where the gasses are exhausted out of the oven. For the four samples the following compounds were found:

**Table 3: Identification of volatile compounds**

| | **Sample 1:** | **Sample 2:** | **Sample 3:** | **Sample 4:** |
|---|---|---|---|---|
| | SnPb-ROL0 | Lead-Free- ROH1 | SnPb- ORM0 | Lead-Free-REL0 |
| 1 | 1-methyl-2-pyrrolidinone | Hexylene glycol | Terpineol | 1-methyl piperidine |
| 2 | Propylene glycol | 2-methyl-1,3-pentandiene | Derivatives of terpineol | 1-butyl-2-pyrrolidone |
| 3 | 2-ethyl-4-methyl-1,3-dioxolane | Cyclohexanone | Hexaoxaoctadecane | α-Terpineol and derivatives |
| 4 | Fused ring compounds from rosin | Fused ring compounds from rosin | Glycol type compounds | Acetaldehyde |

The next step was to find catalysts that facilitate pyrolysis of the volatile compounds. Pyrolysis is the thermochemical decomposition of the organic material in the flux residues that are exhausted out of the oven. There were two concepts found that might be of interest for a reflow oven concept:

1. Thermal oxidizer

    This method converts organic vapors to carbon dioxide and water in the presents of oxygen; it is an exothermic reaction.

    i) Regenerative thermal oxidation (RTO)

        This process takes place at elevated temperatures (800-850ºC). A ceramic media that can handle up to 10 g/m³ of solvent vapor

    ii) Regenerative catalytic oxidation (RCO)

        This process uses a catalyst to reduce the temperature (250-500ºC)

2. Pyrolysis

    Decomposition of organic material at elevated temperatures (>500ºC) in the absence of oxygen; it is an endothermic reaction. The process cracks larger molecules into smaller ones. Char is generated.

The next step was to develop a laboratory method, build a catalytic converter; to characterize the efficiency of catalytic granulates for pyrolysis of solder paste flux residues. In order to do so the TGA (Thermo gravimetric analyzer) was modified. A catalytic converter was built in between the TGA and the FT-IR (Fourier Transform Infrared spectroscopy). The solder paste flux was heated in the TGA. The generated vapors are transported through a heated converter. This converter contained the different granulates and catalysts. After interaction of the vapors and the adsorber (granulate/catalyst materials) the gas flows into the FT-IR. With the FT-IR the chemical composition of the vapor can be analyzed. This method allows defining the efficiency of the catalyst/adsorbers under various conditions. The parameters that could be changed during the experiments are the gas (nitrogen or air flow) and converter temperature.

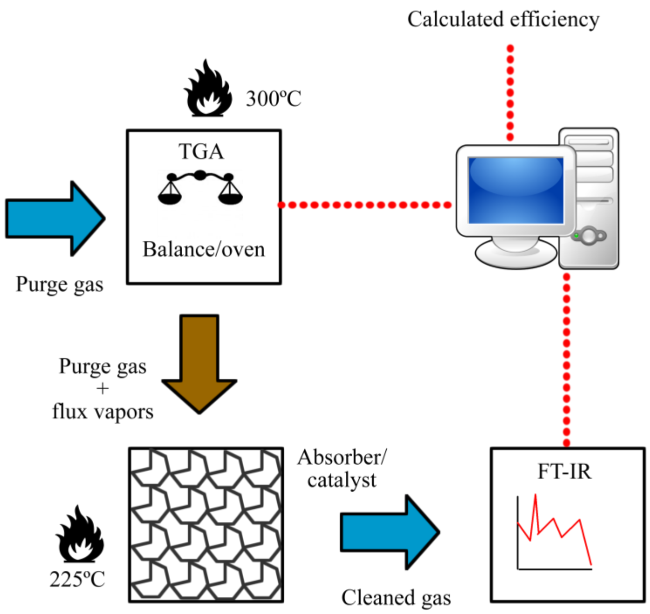


**Figure 2 – Schematic of the test**

Prior to each run the complete system, including the adsorber, was heated to 300ºC. This was done to make sure all the water or any other contaminations were removed. The FT-IR now only detects vapors generated by the flux of the paste and not by contamination in the system. The gas flow, either air or nitrogen was fixed during the experiment on 50 ml/min.

For the benchmark test between different adsorbers sample 1 (SnPb no-clean solder paste flux) was selected. This flux is infamous for its contamination and fumes in the ovens. When heated it generates a large amount of vapors. As a baseline this paste was heated in the TGA under nitrogen with a rate of 10ºC/min to a temperature of 300ºC. The flux generates 66-68% vapor during this process.

Tripropylene glycol monomethyl ether is the solvent used in this flux paste and makes up the bulk of the vapor generated when it is heated. Other chemicals are also present including isologipholene which is a fused ring hydrocarbon generated during the decomposition of rosin and acetaldehyde which was present as a decomposition product for all of the fluxes investigated.

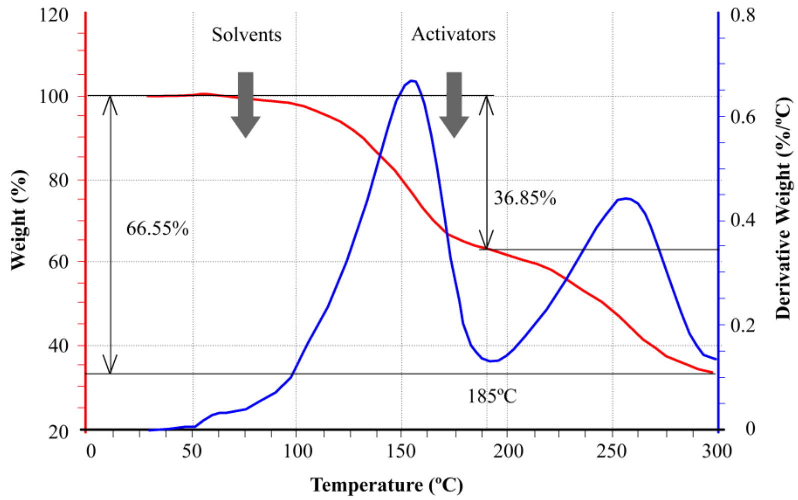


**Figure 3 – Sample 1 heated in TGA. Weight loss as function of temperature.**

The TGA of this flux shows that most of the vapors come out at 150ºC. The higher the derivative weight curve (blue line) the more chemistry is evaporating. In a leaded reflow profile this is the soak part of the reflow process. Then activation decreases but the moment the paste reaches the liquidous temperature of SnPb (183ºC) the activators starts to work eliminating oxidation during reflow part and improving the wettability.

**Adsorbers:**

It is well known that various inorganic minerals will adsorb organic vapors. These minerals are usually porous with high surfaces areas. Clay, zeolites and volcanic rocks are examples of these materials. The first part of this study is to see if these materials will adsorb some of the flux vapors at lower temperatures of 225ºC. In the second part the efficiency of the pyrolysis at 500ºC is studied for different adsorbers.

**Table 4 – sample 1 flux, converter at 225ºC and nitrogen gas**

| **Adsorber** | **Weight of adsorber (g)** | **Amount of vapor evolved (mg)** | **Intensity of signal** | **Intensity per mg of vapor evolved** | **% Reduction** |
|---|---|---|---|---|---|
| Blank (baseline) | NA | 6.35 | 0.027 | 0.0042 | ---- |
| Granulate 1 | 0.65 | 4.40 | 0.006 | 0.0013 | 69% |
| Zeolite 1 | 2.05 | 4.50 | 0.004 | 0.0009 | 79% |
| Granulate 2 | 2.40 | 6.27 | 0.009 | 0.0013 | 69% |
| Zeolite 2 | 2.66 | 4.86 | 0.018 | 0.0037 | 12% |
| Perlite | 0.39 | 4.56 | 0.006 | 0.0013 | 69% |

At 225ºC the adsorbers are able to reduce vapors by approximately 70%. If the gas is recirculated into the oven there will be 30% pollution added to the process, which is might not only contaminate the oven, but might influence the yield.

If the adsorber acts as a pyrolysis catalyst it is expected to see lower molecular weight hydrocarbons and char being formed when heated and in contact with the adsorber. To test the converter was heated to 500ºC using the same solder paste. Because the system wasn't completely oxygen free also carbon dioxide and water were formed. After being heated to 500ºC and interacting with the flux vapor, all the adsorbers darkened in color indicating the formation of char. With FT-IR the compounds detected in the cleaned gas can be found in the table.

**Table 5 – Sample 1 paste, effect of temperature (pyrolysis process)**

| **Adsorber** | **Volume of adsorber ($cm^3$)** | **Compounds detected in gas stream by FT-IR** |
|---|---|---|
| Granulate 1 | 2.57 | Carbon dioxide, water |
| Zeolite 1 | 2.57 | Carbon dioxide, water, trace amount of hydrocarbon |
| Zeolite 2 | 2.57 | Carbon dioxide, water, carbon monoxide, trace amount of hydrocarbon |

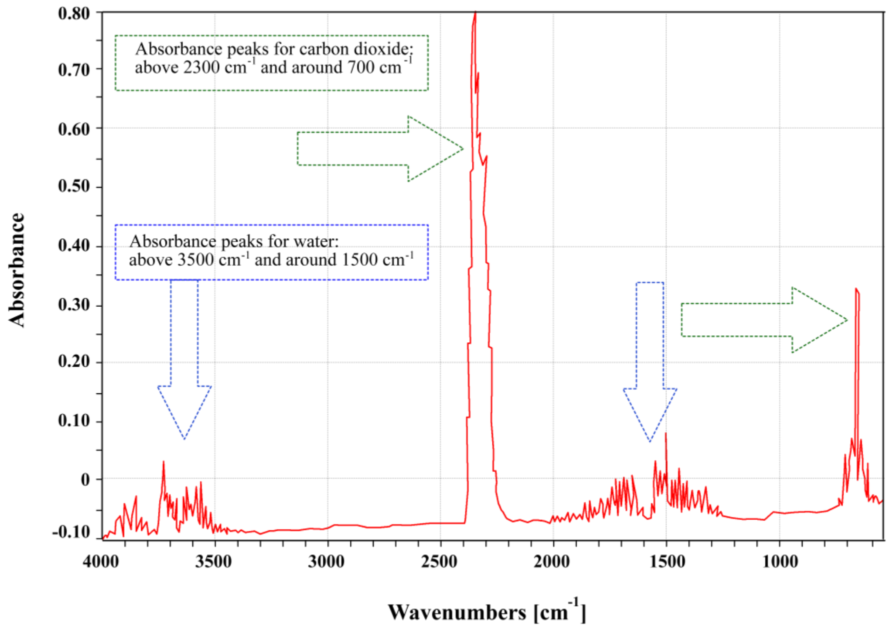


**Figure 4 – FT-IR plot of granulate 1 with sample 1 paste at 150ºC**

Conclusion adsorbers:

1. When adsorbers are heated at 225ºC no pyrolysis takes place. The vapors are either adsorbed by the material or pass through. The FT-IR signals associate with glycol ethers.
2. When adsorbers are heated to 500ºC no glycol ethers can be found using FT-IR. Peaks found are associated with carbon dioxide, water, carbon monoxide and short chain hydrocarbons indicating that pyrolysis is taking place. This is confirmed by the black char of the absorbers.

**Thermal oxidation catalysts:**

On a honeycomb structure a precious metal is coated onto a metal or ceramic support. These catalysts are used in emission control systems to remove volatile organic compounds from air emissions in other industrial applications. In thermal oxidation organic vapors are converted to carbon dioxide and water. Little or no char is produced.

To test the catalysts, three different fluxes were selected.

**Table 6 – Amount of weight loss of fluxes at 250ºC**

| Flux paste | Classification | Weight loss 250ºC $N_2$ | Weight loss 250ºC air |
|---|---|---|---|
| Sample 1 | SnPb-ROL0 | 61.5 | 65 |
| Sample 2 | Lead-Free-ORH1 | 47 | 50.5 |
| Sample 4 | Lead-Free-REL0 | 45.2 | 56 |

Sample 1 is a flux that contaminates oven a lot, where sample 4 is known for its clean residues and low maintenance. The experiment follows the steps as shown in schematic figure+:

- The sample was heated in the TGA with a heating rate of 10ºC/min from room temperature to 300ºC
- The generated vapors by the flux are carried to a heated converter by the carrier gas ($N_2$ or air at 50ml/min)
- The catalyst is in the heated converter. (Temperature 185 or 225ºC)
- The gasses flow into the gas analyzer (FT-IR) where their chemical identities are determined

**Table 7 – Results of experiments**

| Catalyst | Experiment | Flux Paste | Carrier gas | Converter Temperature (°C) | Organics present by FT/IR? |
|---|---|---|---|---|---|
| Catalyst 1 | 1 | Sample 1 | $N_2$ | 225 | No |
| | 2 | Sample 1 | $N_2$ | 185 | No |
| | 3 | Sample 2 | $N_2$ | 225 | No |
| | 4 | Sample 4 | $N_2$ | 225 | No |
| Catalyst 2 | 5 | Sample 1 | $N_2$ | 225 | No |
| | 6 | Sample 1 | $N_2$ | 185 | Yes |
| | 7 | Sample 1 | Air | 225 | No |
| | 8 | Sample 1 | Air | 185 | No |
| | 9 | Sample 2 | $N_2$ | 225 | No |
| | 10 | Sample 2 | $N_2$ | 225 | Yes |
| | 11 | Sample 2 | $N_2$ | 225 | Yes |
| | 12 | Sample 4 | $N_2$ | 225 | Yes |

Different fluxes:
In this experiment different solder paste fluxes were used and this also include different outcome. For catalyst 1 the composition of the solder paste did not have an impact on the efficiency of the catalyst. It was able to convert all vapors to carbon dioxide and water.
For catalyst 2 it was not as clear. With same amount of vapors sample 2 did show organics where sample 1 did not.

Different temperatures:
Experiment 1 and 2 show there was no impact of temperature when using catalyst 1. When the temperature of the converter was lowered to 185ºC organics were detected by the FT-IR for catalyst 2. This was not the case when nitrogen was the carrier.

Although some of the experiments did show organics at the FT-IR measurement the level of detected organics is very small. The level of organic detected is quite small compared to carbon dioxide and water.

**Transfer knowledge into flux collection system**
The laboratory tests gave very promising results. The next step in the project is to implement pyrolysis and/or thermal oxidation concepts into a flux collection system of a reflow oven. Pyrolysis has the advantage that granulate is very inexpensive; however the operation temperature is approximately 500ºC. The thermal oxidation catalyst is a more expensive material, but does not require that much heat.

A prototype was built to test the different concepts in production environments.


**Figure 5 – The prototype, an universal collection unit with place for granulate as well as catalyst.**

**Future work**

The first phase of implementation is to install the prototype flux collection unit to a test oven. Temperatures and gas flows will be measured to have the ideal exhaust conditions for the process gas. Different flux chemistries will be run through the oven in order to quantify the efficiency of the different catalyst and granulate materials before the unit will be installed on a production line to investigate the impact on maintenance.

Different granulates will be benchmarked to identify performance of a pyrolysis process. Two catalysts will be evaluated to see if a catalyst oxidation process is a more efficient way to clean ovens.

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