# Development of Lead Free Paste for Small Reflow Ovens

Bob Gilbert
FCT Assembly, Inc.
Greeley, Colorado

**Abstract**
Today, there exists a major push towards lead free soldering in the international electronics industry. It has presented a number of challenges in both the surface mount and wave soldering processes. The conversion of assembly processes to lead free from conventional tin/lead has put a strain on the smaller contract manufacturers in North America due to the perceived need for improved production equipment. This includes recommendations for wave solder upgrades, reflow ovens with seven or more heating zones, and repair equipment with improved preheating capabilities. These improvements require capital investment that many smaller contract manufacturers cannot afford in the current electronic economic climate. This paper details the development of a no clean lead free solder paste designed to be used with small reflow ovens with four to six reflow zones. The paper will review flux chemistry, and recommended oven settings and modifications. The conclusion is that there are viable lead free reflow soldering options that can be implemented with existing equipment and the process will continue to improve as companies gain more experience in the subtle differences between soldering with tin lead and lead free alloys.

Key words: Lead Free, SAC alloy, reflow oven

**Background**
The electronics assembly industry is now firmly entrenched in converting from tin/lead (63/37) to lead free soldering and this has affected all aspects of assembly soldering, from the component level all the way up to the process equipment. Combine the change to lead free with the timing (July 2006) and the pressures from Asian manufacturing; the American electronics assembly industry has a huge hurdle to clear to be competitive in the near future. The good news is there has been more than five years of high volume lead free manufacturing occurring in Asia by companies supporting the Japanese conversion and North American assembly companies can use this experience to speed up the "learning curve". The bad news is the conversion to lead free processes may require a huge expenditure in new capital equipment due to the higher temperatures and tighter tolerances in using lead free solder. This is particularly critical with reflow soldering because the complete assembly needs to reach the reflow temperature to obtain adequate soldering. For reflow soldering, the SAC alloys are the predominant ones due to their lower melting point and the perceived ability to reflow below the maximum temperatures allowed for boards and components. The new recommendations for maximum temperature exposure are now 250°C for large components and 260°C for small components. The industry recommendations for the peak reflow temperatures for the SAC alloys are to achieve a minimum peak reflow temperature of 235°C to 245°C[1]. At this peak reflow temperature, there is much less

**Reflow Lead Free Alloy Choices**
The history of high volume production use of lead free alloys in Asia has targeted the use of two major alloys: SAC305 (tin/3%silver/0.5%copper) used predominantly in Asia and SAC405 (tin/4%silver/0.5%copper) and its homologs. These two alloys make up over 90% of the lead free solder alloys in reflow production use today. They have been chosen based on a number of favorable characteristics of their composition and performance. Both are covered by patents in the major countries for assembly production.

The SAC305 alloy with 3% silver is not at the eutectic and has a pasty range of approximately 4°C but has been chosen due to the slightly lower cost than the eutectic 4% silver SAC alloy and the strong marketing push by the patent holder. Both alloys have a higher melting point than 63/37 but production history has indicated that both can be used at reflow solder temperatures in the 235°C to 250°C (455°F to 480°F) range depending on the complexity of the board. Although the melting point difference between the two alloys is 4°C, they can be used at very similar temperatures in production.

Table 1 below illustrates the major characteristics that have been considered in choosing them as the predominant lead free alloys. The key to their use as a replacement for 63/37 is the flux system, the capability of the process equipment, and the types of products being manufactured. Both alloys are being used with existing equipment and on existing electronics products. The difference between their melting points and the process temperature is called the superheat temperature. The superheat for the SAC alloys in reflow soldering is typically 10°C lower than the superheat used for SN63 tin/lead soldering.

This difference may induce difficulties with using current reflow ovens as the temperature approaches the maximum allowable for the components used.

**Table 1 - Lead Free Alloy Characteristics**

| CHARACTERISTIC | Sn/3Ag/.5Cu | Sn/4Ag/.5Cu |
|---|---|---|
| Melting Point (°C) | 217-221 | 217 |
| Density (g/cc) | 7.5 | 7.4 |
| Tensile Strength (M•Pa) | 52 | 52 |
| Elongation (%) | 27 | 27 |
| Spread Factor (250°C) | 77% | 77% |
| Wettability | | |
| 250°C Wet Time (s) | 1.5 | 1.5 |
| 250°C Max Force (g) | .21 | .21 |
| Copper Erosion | Fast | Fast |
| Joint Appearance | Grainy | Slightly grainy |
| Microcracking | Extensive | Minor |
| Creep Strength (180°C, 1KG Load) | >300 Hrs | >300 Hrs |
| Thermal Shock (-40/+80°C) | >1000 Cycles | >1000 Cycles |

**Flux Chemistry for Lead Free**

High temperature reflow soldering has been performed for many years in specialized applications such as component manufacturing, automotive underhood, and downhole well equipment. These solder pastes required a different flux chemistry to address the higher reflow temperatures the process required. A number of issues occur when the peak reflow temperature is increased including:

1. More protection needed to reduce powder oxidation.
2. Flux dries more completely.
3. Resin can darken due to increased oxidation.
4. Activators can decompose.
5. Resins can further polymerize.
6. Pin probability is reduced.
7. For water wash fluxes, decomposition and side reactions can reduce solubility of residues in water.

In addition to a higher peak temperature, if a small oven (less than 5 zones) is being considered, the speed of the reflow process may need to be reduced. For some assemblies, a higher soak temperature may need to be used to ensure less temperature difference ($\Delta T$) across the board and components. Optimizing the flux chemistry for lead free requires a compromise between the many characteristics required for solder paste. No Clean and Water Wash systems will be addresses separately.

**No Clean Flux Chemistry**

The no clean flux chemistry is considered a mature product as it has been utilized as a major option since the elimination of CFC's in the early 1990's. In fact, even before this change, RMA fluxes were not cleaned in many applications. The no clean fluxes used today have evolved into products that leave lower residue levels which can be pin probeable, clear and colorless, high activity, and have excellent printing rheology. Unfortunately, these formulations do not perform as well in the higher peak reflow environment required with the new lead free alloys being considered. This is evidenced by the many "new" formulas being offered by all of the solder paste manufacturers today. Very few of the tin/lead paste fluxes are recommended for lead free alloys. The new formulas are being developed to perform as close as possible to the tin/lead fluxes but the higher reflow temperatures are causing some compromises with many characteristics.

One of the key issues with a higher temperature profile is keeping the powder from oxidizing in the process so that an acceptable joint is formed. In order to accomplish this, a number of changes in the flux chemistry are possible:

1. Increase the resin content to give more coating on the powder.
2. Change resin type to increase softening point.
3. Increase activity to reduce the oxides as they form.
4. Change the activator system to be more heat stable.
5. Change the rheology of the flux to allow less hot slump so the flux "stays" with the powder and does not flow away from the printed area.
6. Use lower boiling point solvents, which evaporate quicker and more completely also allowing the flux solids to stay with the powder.

Since flux formulas can typically have over 10 ingredients, modifying only one can impact the formula. To complicate matters further, fluxes will sometimes react with the powder in storage and this can affect characteristics over time. Since most solder pastes have 6 month shelf lives, any modified formula needs at least 6 months storage testing to confirm storage stability.

Increasing the resin content affects system solubility as the resin content is typically close to the solubility limit and any increase may push it over the limit. This causes crystallization and the flux would then behave more like a solid than a liquid and this would dramatically affect printing. In the printing process, the flux allows the solder paste to behave like a liquid so it flows under pressure. Increasing the resin content or changing the resin type can affect which solvent is used as the common solvents used in flux formulation have different solubility strengths. Increasing the resin content will also leave more visible residues on the board. If clear, colorless resins are used; the appearance will be less noticeable. Higher softening point resins are also harder and this can reduce the pin probe ability of the residue. The viscosity of the flux at elevated (130°C to reflow) temperature can be increased using high softening point resins so that the flux does not flow away from the printed area during the reflow process.

Activator changes can also improve the performance of the paste at high reflow temperatures. The activators are chosen based on their inherent stability (inertness) at room temperature up to product use temperatures and their ability to become active at reflow temperatures. Activators can be organic acids, amines, halogenated amine salts, and organohalogens. Each activator has a decomposition temperature and this must be considered when choosing ingredients. There are a finite number of activators for no clean flux chemistry and any "new" activator used must be thoroughly tested for reliability before release in a no clean paste product. Simply increasing the level of existing activators may be all that is needed.

The key to protecting the powder from oxidizing is keeping a good coverage of flux on the surface of the powder to slow the diffusion of oxygen to the powder surface. Changing the rheology of the flux can improve hot slump so more flux stays with the powder on the printed pad. The rheology of the flux is determined by the complex interactions of the resins, solvents, and the rheology modifiers added to the formula. The rheology modifiers are added to give the solder paste a thixotropic characteristic. The desire is for the paste to have a high viscosity when no force is applied (after printing and through reflow) but have a low viscosity when a force is applied to the paste (during printing). The modifiers used have different strengths at elevated temperatures and it is possible to choose ones that do not break down at elevated temperatures. This aids in keeping the flux in contact with the powder during the reflow process.

Solvent changes can also improve hot slump, and reduce the flux spread. The current tin/lead formulas have evolved into utilizing very high boiling point solvents (greater than 250°C) which vastly improves tack time and open time in the printing process. These solvents can also keep tin/lead residues softer to aid pin probing as they do not completely evaporate in the reflow process. Lower boiling point (200°C to 250°C) solvents can be used to increase the evaporation rate during reflow so the flux stays with the powder. Unfortunately, these solvents will also dry out quicker on the stencil and this may affect open time and tack time. As the flux dries more completely after reflow, this may also affect the probing characteristics of the residue.

No Clean flux chemistry is a complex system with considerable interaction between the ingredients and it is critical that the formula addresses all of the current requirements in the tin/lead process.

**Water Washable Flux Chemistry**

Water washable flux chemistry has many of the same requirements as no clean. The main difference is the flux residues after soldering are removed in plain hot water. As with no clean flux ingredients, the ingredients used in water washable fluxes may decompose or react causing changes in their solubility in hot water. These changes will increase as the temperature is increased for lead free processing. The flux needs to be soluble in hot water after reflow but not too hygroscopic during printing and component placement to cause slumping and solderballing.

**Oven Settings and Modifications**

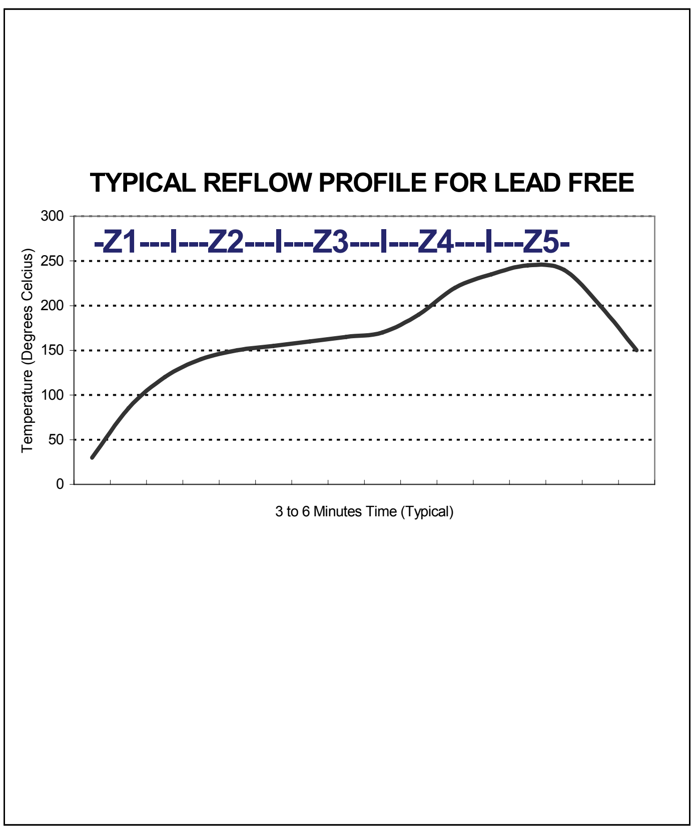
The concern with attempting to use a lead free alloy for reflow soldering has been the higher melting point and the effect this would have on the reflow requirements and components. The evidence now is that even the SAC alloys need to be soldered at temperatures exceeding 235°C due to the limitations in ovens and the complexity of boards today. Table 2 illustrates the typical parameters required to successfully utilize the tin/silver/copper alloy as a reflow solder (1).

**Table 2- Reflow Solder Machine Parameters**

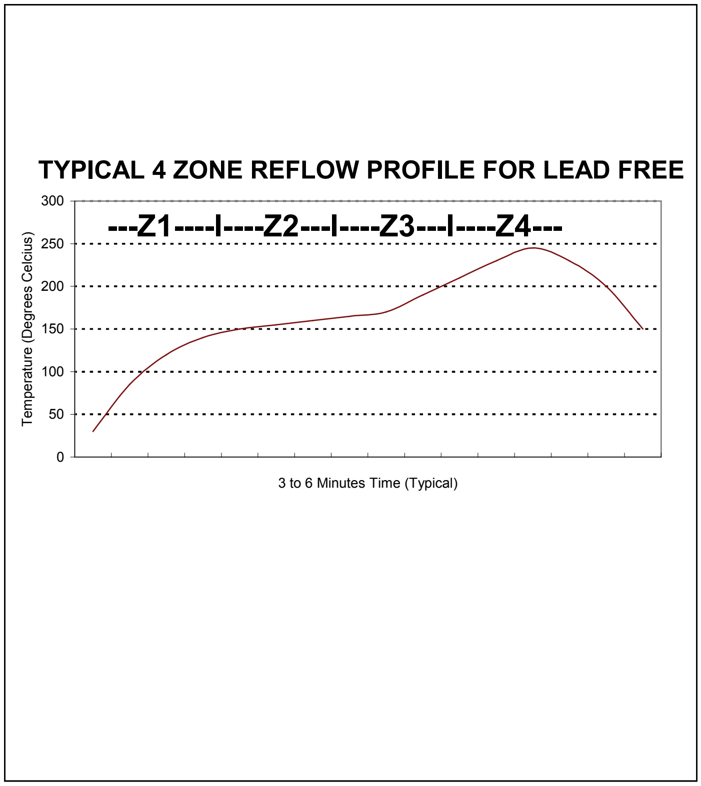
| MACHINE PARAMETERS | 63/37 | Sn/3Ag/. 5Cu | Sn/4Ag/. 5Cu |
|---|---|---|---|
| Soak Range (°C) | 120-160 | 150-180 | 150-180 |
| Peak Reflow Temp. (°C) | 200-230 | 235-250 | 235-250 |
| Time above Liq. (sec) | 30-60 | 30-90 | 30-90 |

As the temperature of the process increases the temperature difference between components becomes greater unless the process is slowed down or a longer soak time is used. For simple assemblies with thin boards and similar sized components, this is not an issue. Unfortunately, much of the assembly business left in North America today is more "high mix/low volume" contract manufacturing and they do not have control of the types of assemblies built. Production today may be a thin, simple board and tomorrow may be a thick, complex double-sided board with large components and ground planes. This is the driving reason the industry is recommending new ovens if the current oven is not capable of the higher temperatures and does not have adequate zones to fine-tune the process. Generally, the electronics industry recommends a minimum of 5 zone ovens due to the requirement of using 2 heating zones for the reflow process on the profile. This allows a flatter peak, (see Graph 1) which reduces the chance of overheating some of the smaller parts in order to get the larger components to the recommended minimum temperature. If the oven has less than 5 zones, it will be difficult to use 2 zones for the reflow portion of the process and the profile will have a more typical tin/lead rounded appearance at peak (see Graph 2).

**Graph 1- 5-Zone Lead Free Reflow Profile**

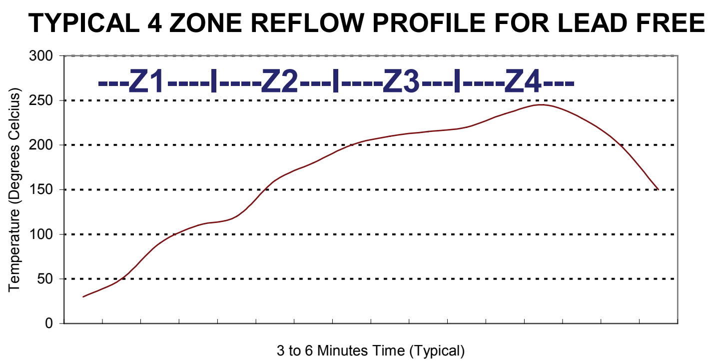


**Graph 2- 4-Zone Lead Free Reflow Profile**




One alternative that would allow a 4-zone oven to be used in lead free reflow is if the paste is stable at a higher soak temperature. This would require the assembly to be heated a quick as possible in the first 2 zones. The limiting factor on ramp rate is the maximum recommendations of the components being soldered. Typically, a ramp rate of less than 3°C per second is recommended. At a ramp rate of 2°C per second, the assembly can reach 200°C in 88 seconds. This allows 2 zones to be used in the 200-250°C region, which allow a flattening of the profile. This allows the components to reach similar temperatures with reduced temperature differences. This type of profile (see Graph 3) will require a more heat stable flux system. For ovens with top and bottom heating, the settings can be optimized to assist the components to reaching similar temperatures while maintaining a tighter tolerance on the peak reflow temperature.

**Graph 3- High Soak 4-Zone Lead Free Reflow Profile**




The more heat stable flux chemistries developed have higher resin contents but the residue appearance is very similar to current tin/lead formulations. Table 3 illustrates the results of recent developments of improved fluxes for lead free reflow soldering. Changes to improve the heat stability of the flux systems were made to the resins, solvents and activators. In addition, it was determined that a higher concentration of resin gave the optimum result. A new solvent was included that allows the post solder residue to be pin probe able, even at the higher resin content (see Figure 1).

**Table 3- Reflow Result with Modified Flux Chemistry Rating- 1-Best to 4-Worse**

| FLUX TYPE | LF PROCESS RATING |
|---|---|
| STANDARD FLUX | 4 |
| PLUS HT RESIN | 3 |
| PLUS LOW CONTENT SOLVENT | 2 |
| PLUS ACTIVATOR MODIFICATION | 3 |
| PLUS HT RESIN, LOW CONTENT SOLVENT, AND ACTIVATOR MODIFICATION | 1 |

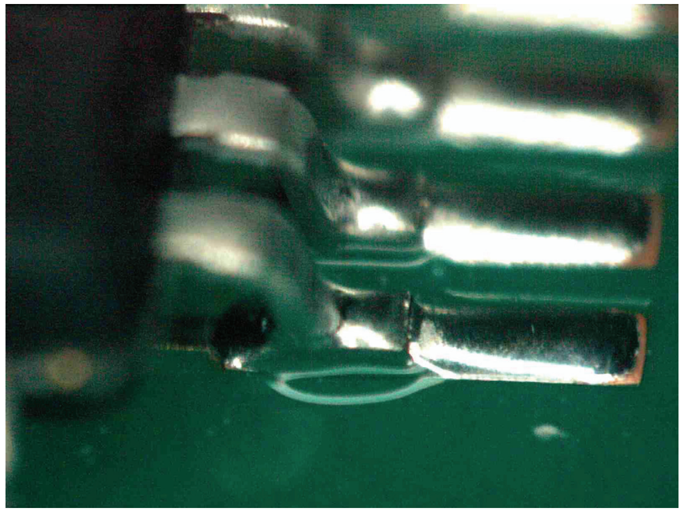


**Figure 1- Lead Free Joint with Modified No Clean Flux run with Graph 3 Profile Showing Smooth, Shiny Appearance**

## Conclusion

Converting to a lead free soldering process will require the proper equipment and knowledge to be successful. Because lead free soldering has been in full production in Asia for over five years, much of the trial and error has already been accomplished. Unfortunately, there is less than one year left for assembly companies to be fully converted to a lead free process if they will be offering product for sale into the European community. The choice of alloys will have an affect on the conversion process and many companies will change after experiences with some of the alloys being considered. In addition, the choice of flux chemistry may allow the smaller ovens currently in use with the tin/lead process to be used with lead free alloys

## References

[1] Solder Product Value Council (SPVC), "A Research Program on SAC Lead Free Alloys", http://leadfree.ipc.org/files/spvc_presentation.pdf, 2004.