A Comparison of Lead Free Solder Assembly Defluxing Processes

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Abstract
The enactment of the Restriction of Hazardous Substances (RoHS) Directive is prompting significant changes in solder paste formulations and their process conditions as manufacturers move to Lead Free electronics assemblies. The residues remaining after reflow of these new Lead Free materials are proving much more difficult to remove. This study evaluates the cleaning capability of aqueous, semi-aqueous, solvent, and vapor degreasing including co-solvent products and processes. Lead Free eutectic solder pastes from three leading suppliers were selected and cleaning results were evaluated and results are compared to leaded eutectic materials.

Key Words: Lead Free, cleaning, aqueous, semi-aqueous, solvent, vapor degreasing, cosolvent

Introduction
As solder paste manufactures strive to offer new Lead Free formulations, as mandated by the impending RoHS Directive, electronics assembly manufacturers are forced to reexamine their entire manufacturing process, including cleaning. Both no-clean and water-washable lead–free paste formulations often incorporate new flux systems. These systems are designed to be compatible with higher reflow temperatures, reduced wetting, and increased surface tension of the tin-rich alloys. Both the changes to the composition of the flux systems and the changes to the processing parameters are leading to an increase in post solder residues that are also harder to clean. While many Lead Free pastes are being developed for the consumer electronics market which may not be cleaned, manufacturers of electronics for aircraft, military, space, medical, and other high-reliability or high-frequency devices will need to clean these residues to maintain reliability and performance. In fact, the need for post reflow cleaning is expected to increase with Lead Free processing due to the higher activity level of the soldering fluxes, the cosmetic effects due to higher reflow temperatures, and the potential for increased rework requirements of Lead Free assemblies.

Prior to the Montreal Protocol and the elimination of ozone-depleting substances, the vast majority of circuit boards were cleaned in vapor degreasers using CFCs. Other aqueous cleaning technologies were employed for only a small percentage of the circuit boards being manufactured. After the Montreal Protocol took effect, multiple soldering and cleaning technologies were developed, including no-clean and water washable flux technologies, improved aqueous cleaning products, new solvent and semi-aqueous defluxers, and non-CFC azeotropic and co-solvent vapor degreasing products. While there have been huge advancements in electronics manufacturing since these developments, this was the last time the industry as a whole had to reconsider their approach to cleaning.

Environmental concerns will continue to drive enactment of more stringent regulations regarding volatile organic compound (VOC) emissions and rinse water effluent limits in the future. Therefore, when evaluating cleaning options for Lead Free pastes, the environmental characteristics of any cleaning technology must be considered.

Background
Aqueous Defluxing Process
In typical aqueous cleaners the cleaning solution contains high pH saponification agents and additives to prevent solder joint dulling and improve performance. The saponification agents could either be organic or inorganic. The concentrate is diluted with deionized water, usually 10% or 25% for hard to clean pastes, and used as the wash solution in a batch style spray-in-air or inline spray-in-air machine. The first wash step is followed by a deionized water rinse with either multiple spray-in-air or cascading immersion tank stages. Due to the nature of this type of cleaning system the rinse water which contacts the assembly immediately after the wash step is directed to the drain as it contains higher amounts of wash solution drag out than subsequent rinses. Drying stages can be either forced air, forced heated air, or radiant heat.

Semi-Aqueous Defluxing Process
For semi-aqueous cleaning a batch style spray machine is typically used with an undiluted water rinse able cleaning solvent in the wash step. The initial wash step is usually followed with a recirculating emulsion rinse made up of a mixture of cleaning solution and water which can be easily separated allowing for a cleaning process that may eliminate the requirement for a rinse waste stream. The emulsion rinse stage is followed by rinsing and drying stages similar to those described above in *Aqueous Defluxing Process*.

Solvent Defluxing Process

In solvent defluxing the cleaning process can employ the same blend of solvents for use in the wash and rinse solutions, or two different solvents. Because of flammability concerns of misting of combustible solvents, solvent cleaning is generally accomplished under immersion with spray or ultrasonic agitation. It generally involves multiple cleaning tanks. After the boards go through the wash tanks whose temperatures are set below the solvents flashpoints, they move through the multiple rinse tanks of progressively cleaner solution and are finally dried.

Vapor Degreasing Process

Commonly vapor degreasers employ a one- or two-step process wherein the cleaning solvent is a single non-flammable solvent or azeotrope. In one-sump degreasers, boards are lowered into a vapor-only region where condensing vapor cleans and flushes residues from their surfaces. With two-sump degreasers, boards may be immersed into the solvent in the clean (non-boiling) sump to remove tenacious residues, and then held in the vapor area for a final rinse of condensing vapor.

Co-Solvent Cleaning Process

Co-solvent cleaning is similar in method to traditional two-sump vapor degreasing. However, with this method two solvents are used in the boiling (wash) sump. One solvent (solvating agent) is a high-vapor-pressure solvent chosen for its high level of solvency for the soils of interest. The second solvent (rinsing agent) has a low vapor pressure and is non-flammable. The currently available choices for these solvents are poor cleaners and not effective alone. The two solvents are combined in the boiling sump where the lower boiling, low vapor pressure solvent will readily boil and produce vapor for the vapor area. The second, non-boiling sump is referred to as the rinse sump (or sometimes as the clean sump). In this method it is essential that the boards are lowered into the boiling sump where the cleaning solvent is maintained. Rinsing is accomplished by then transferring the boards to the rinse sump with a final rinse in the vapor area.

Experimental Method

Test Board Preparation

Solder paste was hand printed onto the test boards using a stencil with a matching pattern. The printed test boards were processed in a combination air convection and radiation reflow oven. Reflow profiles with a standard linear ramp-up and rapid cool down were used. The peak temperatures were 236°C for the Lead Free solder pastes and 207°C for the leaded solder pastes. Dwell time above liquidus was approximately sixty seconds with time to liquidus being approximately two hundred seconds. The reflow atmosphere was air. The reflow profiles are shown in Figure 1.

Solder Pastes

The list of solder pastes used in this study is listed in Table 1. These solder pastes were selected from a larger more comprehensive study. The Lead Free pastes were 96.5Sn3.0Ag0.5Cu (SAC305) alloy and the leaded pastes were eutectic 63Sn37Pb or near eutectic 62Sn36Pb02Ag alloys.

Defluxing Processes

All reflowed no-clean flux residues were cleaned separately in aqueous, semi-aqueous, solvent, standard vapor degreasing and co-solvent cleaning chemistries. The process parameters are listed in Table 2. After each defluxing process, the boards were visually evaluated under magnification and scored for visual cleanliness on a scale of 1 to 10, with 8 or higher being acceptable and 10 being perfectly clean. Figure 2 shows a picture of a solder joint before cleaning and Figure 3 shows a picture of a solder joint with a clean rating of 10.

Cleaning Test Results

Aqueous Cleaning

In both types of equipment the boards with leaded pastes appeared clean at 10% concentration but boards prepared with Lead Free pastes did not. It was noted that on some of the test boards a higher concentration (25%) was needed to significantly improve the cleaning results. However the process was not optimized and concentrations between 10% and 25% were not evaluated. Of the aqueous cleaners tested at 25% concentration in batch type equipment, as listed in table 3, both the organic and inorganic saponifiers cleaned equally well for the Lead Free pastes as they did for the leaded ones. Aqueous cleaning using the in-line type equipment (Table 4) showed very good cleaning for the leaded type pastes with both the organic and inorganic saponifiers. However in the Lead Free pastes at 25% concentration, the organic saponifier out performed the inorganic with very good cleaning for the former and only moderate cleaning for the latter.

Semi-Aqueous Cleaning

The overall cleaning ability of the semi-aqueous defluxers for the Lead Free pastes was good for one of the two ester-based solvents and moderate for the other as listed in Table 5. The leaded pastes performed very well with both solvents. These results are consistent with the prevailing thinking that Lead Free pastes are more difficult to remove than those from the leaded residues.

Solvent Cleaning

The terpene-based solvent cleaning process for Lead Free pastes did not perform well using spray under immersion as listed in Table 6. In addition, the solvent performed only moderately well at removing leaded solder paste residues. The use of ultrasonic's with the glycol-ether-based solvent showed only moderate removal of residue for Lead Free but was very effective with leaded pastes as listed in Table 7. Other solvent blends which are not detailed in this paper yielded better cleaning results for Lead Free pastes. The results indicate that to be effective in solvent type cleaners using Lead Free pastes the solvent has to be matched with the paste type for maximum cleaning.

Vapor Degreasing

The vapor degreasing solutions used in this paper were either azeotropic or co-solvent in nature. The nPB-based azeotropic solutions listed in Table 8 did not perform well at removing either Lead Free or leaded solder pastes residues. The co-solvent based solutions listed in Table 9, on the other hand, performed very well for two out of three Lead Free pastes giving results equal to, or better than, their leaded counterparts.

Conclusions

This study was undertaken to evaluate the performance of various defluxing processes in cleaning post-reflow Lead Free solder residues from printed circuit boards and to compare the effectiveness of each process in cleaning Lead Free pastes versus traditional eutectic solder pastes. Cleaning studies were conducted on three leaded and three Lead Free solder pastes using aqueous, semi-aqueous, solvent, and vapor degreasing processes. The results indicate that various options are available for cleaning the new Lead Free pastes. Though the new Lead Free solder pastes are difficult to clean, currently available cleaning technologies can be easily optimized to accommodate the high temperature residues left behind. Choosing the right chemistry and the cleaning process will be a key factor in the successful transformation to Lead Free manufacturing.

Aqueous cleaning processes using either batch or inline equipment can easily be adapted to clean the Lead Free pastes, though a higher concentration of the cleaner may need to be used. Semi-aqueous cleaning processes can be used without any modification and show promise in cleaning tough-to-clean, Lead Free solder paste residues. Solvent cleaning can be adapted to clean some Lead Free pastes, but finding a universal solvent to clean various Lead Free pastes may be difficult. The traditional vapor degreasing process based on nPB/ nPB azeotropes was found to be ineffective in cleaning many Lead Free pastes, but co-solvent processes using newly developed co-solvent systems show promise in cleaning most of the Lead Free pastes.

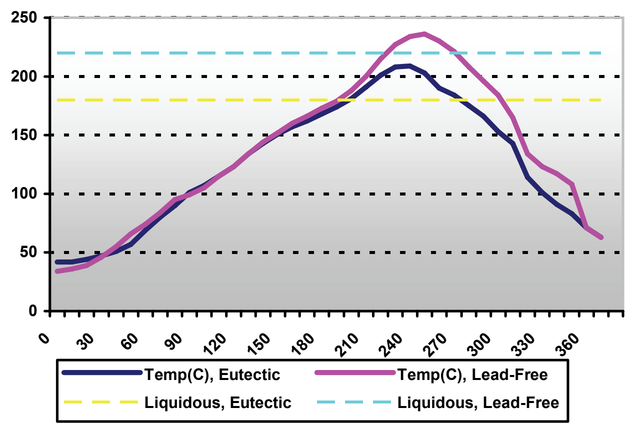

Figure 1 - Eutectic and Lead Free Reflow Profiles

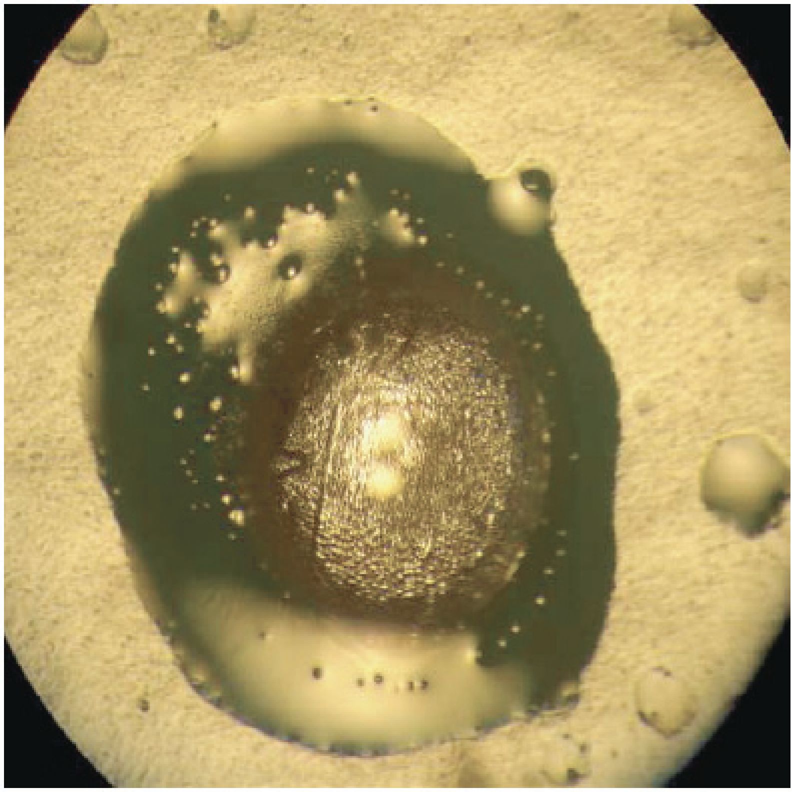

Figure 2 – Flux residue on Solder Before Cleaning

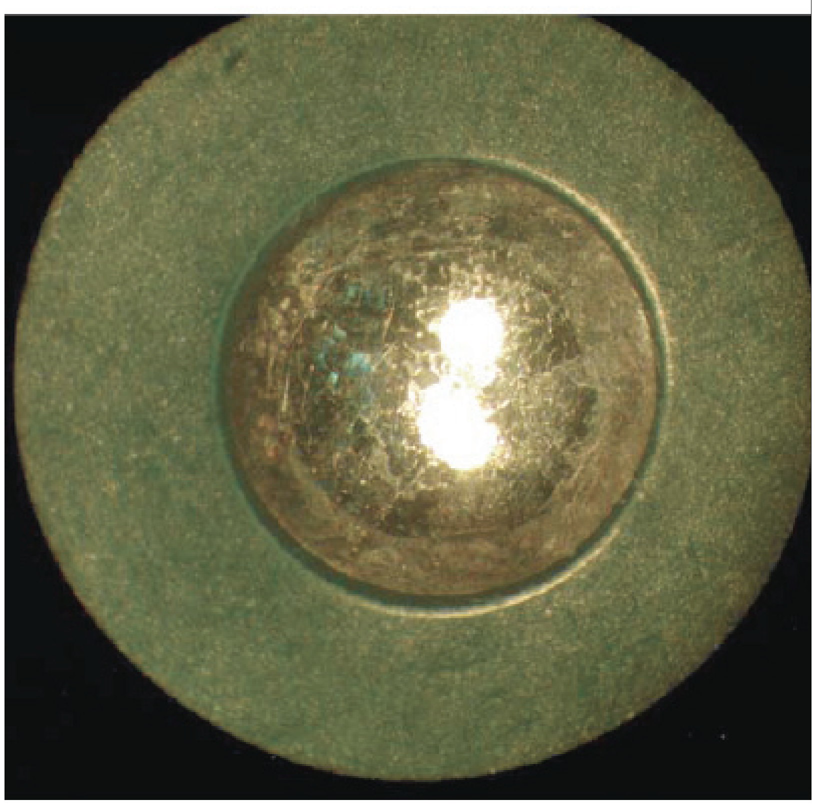

Figure 3 – Solder with a Clean Rating of 10

Table 1 – List of Solder Pastes Tested

Paste Type	Paste	Paste Reference	Paste Description
Leaded	Alpha UP-78	Paste 1	Sn63/Pb37, No-Clean
	Kester Easy Profile EP256	Paste 2	Sn62/Pb36/Ag02, No-Clean
	Indium NC-SMQ92J	Paste 3	Sn63/Pb37, No-Clean
Lead Free	Alpha OM 338T	Paste 4	SAC 305 (Sn96.5/Ag3.0/Cu0.5), No-Clean
	Kester Enviormark EM907	Paste 5	SAC 305 (Sn96.5/Ag3.0/Cu0.5), No-Clean
	Indium 5.8LS	Paste 6	SAC 305 (Sn96.5/Ag3.0/Cu0.5), No-Clean

Table 2 - Defluxing Process Parameters

Process	Type	Key Processing Parameters
Aqueous Cleaning	In-Line	Wash: 2 minutes at 140ºF(60ºC) and 90 psi Rinse: heated DI water Dry: heated forced air
Aqueous Cleaning	Batch	Wash: 10 minutes at 140ºF(60ºC) and 60 psi Rinse: heated DI water Dry: heated forced air
Semi-Aqueous Cleaning	Ultrasonic (U/S)	Wash: 10 minutes at 150ºF (65ºC) Rinse: heated DI water Dry: heated forced air
Solvent Cleaning	Spray Under-Immersion (S.U.I)	Wash: 5 minutes at 105ºF(40ºC) and 90 psi Rinse: ambient deionized (DI) water Dry: heated forced air
Solvent Cleaning	Ultrasonic (U/S)	Wash: 10 minutes at 150ºF (65ºC) Rinse: heated DI water Dry: heated forced air
Vapor Degreasing	Azeotrope	Boil Sump: 2 minutes at 154ºF(69ºC) Rinse Sump: 2 minutes at 130ºF(54ºC) Vapor Zone: 30 seconds at 152ºF(67ºC)
Vapor Degreasing	Co-solvent	Boil Sump: 2 minutes at 154ºF(69ºC) Rinse Sump: 2 minutes at 130ºF(54ºC) Vapor Zone: 30 seconds at 152ºF(67ºC)

Table 3 – Aqueous Cleaning Results for a Batch Process

		Leaded		Lead Free	
	Cleaner Conc.	**Paste**	**Clean Rating**	**Paste**	**Clean Rating**
Organic Saponifier	10%	Paste 1	10	Paste 4	9 (10*)
		Paste 2	10	Paste 5	1 (10*)
		Paste 3	10	Paste 6	2 (9*)
Inorganic Saponifier	10%	Paste 1	10	Paste 4	10 (10*)
		Paste 2	10	Paste 5	9 (10*)
		Paste 3	10	Paste 6	8 (9*)

* at 25% concentration

Table 4 – Aqueous Cleaning Results for an In-line Process

		Leaded		Lead Free	
	Cleaner Conc.	**Paste**	**Clean Rating**	**Paste**	**Clean Rating**
Organic Saponifier	10%	Paste 1	10	Paste 4	10 (10*)
		Paste 2	10	Paste 5	2 (10*)
		Paste 3	10	Paste 6	2 (10*)
Inorganic Saponifier	10%	Paste 1	10	Paste 4	10 (10*)
		Paste 2	10	Paste 5	2 (9*)
		Paste 3	10	Paste 6	1 (5*)

* at 25% concentration

Table 5 – Semi-Aqueous Cleaning Results (Ultrasonics)

	Leaded		Lead Free	
	Paste	**Clean Rating**	**Paste**	**Clean Rating**
Ester-based solvent - 1	Paste 1	10	Paste 4	8
	Paste 2	9	Paste 5	9
	Paste 3	9	Paste 6	10
Ester-based solvent - 2	Paste 1	10	Paste 4	8
	Paste 2	9	Paste 5	8
	Paste 3	10	Paste 6	1

Table 6 – Solvent Cleaning Results (Spray-Under-Immersion)

	Leaded		Lead Free	
	Paste	**Clean Rating**	**Paste**	**Clean Rating**
Terpene-based solvent	Paste 1	8	Paste 4	1
	Paste 2	9	Paste 5	2
	Paste 3	1	Paste 6	3

Table 7 – Solvent Cleaning Results (Ultrasonics)

	Leaded		Lead Free	
	Paste	**Clean Rating**	**Paste**	**Clean Rating**
Glycol ether-based solvent	Paste 1	10	Paste 4	7
	Paste 2	9	Paste 5	9
	Paste 3	9	Paste 6	6

Table 8 – Vapor Degreasing Cleaning Results

	Leaded		Lead Free	
	Paste	**Clean Rating**	**Paste**	**Clean Rating**
nPB azeotrope	Paste 1	7	Paste 4	1
	Paste 2	3	Paste 5	8
	Paste 3	1	Paste 6	2

Table 9 – Cosolvent Vapor Degreasing Cleaning Results

	Leaded		Lead Free	
	Paste	**Clean Rating**	**Paste**	**Clean Rating**
Hydrocarbon solvent	Paste 1	10	Paste 4	2
	Paste 2	8	Paste 5	9
	Paste 3	9	Paste 6	9

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