Final Finishes for High Temperature Applications: A Comparison of OSP and Immersion Silver Final Finish Coatings

Michael Carano, Bill Bowerman & Lee Burger
OMG
Maple Plain, MN

Abstract
With the increased use of lead-free alloys there has been interest in understanding the applications and limitations of final finish coatings for lead-free assembly processes. The higher temperatures needed for lead-free assembly make it more challenging to provide good protection of the underlying copper surface while maintaining acceptable solderability. Coatings that provided good solderability when using eutectic solder may no longer be acceptable when using lead-free alloys. This is especially true when multiple lead-free reflows are incorporated into the assembly process. Coatings that stand up to eutectic solder reflow temperatures may degrade or tarnish when exposed to lead-free reflow temperatures. The purpose of this paper is to provide information on the applications and limitations of OSP and immersion silver coatings in lead-free assembly processes. Solderability testing included evaluation of hole fill and wetting balance performance using SAC 305 solder. Solderability was evaluated on panels as coated as well as after durability testing. Solderability testing after multiple reflows was conducted to simulate production requirements. Surface preparation prior to application of the final finish coating was studied and included evaluation of etch type.

Introduction
Over the last ten years, a transformation has taken place in the printed wiring board industry. This transformation has touched the entire supply chain and is being driven primarily by the move to lead-free assembly. Consequently, the rise of alternative surface finishes as replacements for hot-air-solder leveling is nothing short of remarkable. During this transformation period, two finishes in particular have carved out a significant niche in the surface finish market: Organic solderability preservatives (OSP) and Immersion Silver (ImAg).

Organic Solderability Preservatives
Organic coatings (OSP) have been utilized to maintain solderability of copper surfaces in electronic assemblies for over 20 years. Initially materials based on benzotriazoles (BTA) and imidazole chemistries provided a thin (< 200 angstroms (Å)) protective layer requiring very active flux or inert reflow processes. No-clean assembly materials, air reflow, handling issues, and shelf life considerations hindered these thin materials from becoming a true replacement for Hot Air Solder leveling (HASL). The introduction of substituted benzimidazoles (SBI) rendered significant improvements in solderability protection. Typically, the SBI were thicker coatings (2500-6000 Å) and provided added protection against heat excursions required for complex assembly. While these particular formulations performed adequately with lead-based solders, concerns with the higher peak temperatures required for lead-free assembly arose. Adding to these concerns was the fact that some assembly firms instituted pre-assembly baking procedures to drive out moisture. This issue was primarily driven by the moisture absorption tendencies of some of the newer laminate materials that have made their way into the market place. Thus increased protection from added heat was necessary. The mode of operation, then, was to employ the SBI and use the bulk thickness of the coating to aid in resisting oxygen penetration to the base copper. These formulations typically contained copper ions that served as a catalyst for organic film thickness growth.

However, as the complex circuit designs continued its evolution, clearly a newer and more robust OSP needed to be developed. With the migration to SAC alloys and peak reflow temperatures reaching and sometimes exceeding 260°C, minimization of oxygen penetration to the base copper was paramount. In addition, it wasn't surprise that SAC based alloys exhibited less solder paste spread than the lead based materials. Thus, the concerns over the preservation of the base copper that arose due to the lead-free movement further required the rethinking of the OSP process. This included looking at all aspects of the process including microetching, OSP film formation and thickness, and the stability of the OSP molecule itself. The issue with OSP film thickness was quite simple. The thicker coatings tended to resist paste spreadability. A thinner coating provides a much easier pathway for the flux vehicle to cut through the film (after all OSP is a sacrificial coating). With the trend toward lower activity fluxes, removal of thicker organic films is more difficult. Thus the degree of solder spread is reduced. However, others may be concerned that thin coatings would not suffice under multiple reflows. The research and development work has debunked this concern, since the shear bulk thickness is not in itself sufficient to protect the underlying copper. What must also be considered is the actual decomposition temperature of the organic film. The newer development is based on an aryl-phenyl imidazole (API) that is significantly more stable at higher temperatures than SBI. This is critical as one moves up the assembly temperature curve. Consequently, it was determined that the API molecule was able to achieve the desired solderability requirements with a thinner coating (1500-3000 Å, which is equivalent to 0.15-0.3 microns).

Immersion Silver (ImAg)

The development of and introduction of Immersion Silver as an alternative to hot air leveling quickly found its niche as a viable process. As opposed to OSP, ImAg can be "seen" on the surface. Some consider this an advantage with respect to inspection as one can easily see that the "silver is there." Regardless, silver has met with some resistance in part due to concerns with laminar voids above the intermetallic layer (noticed after assembly) (1), tarnishing and discoloration of the finish. Tarnish of ImAg deposits must render the finish unsolderable to be considered an issue. Others that have studied and implemented silver in production have recognized that only the most corrosive of environments cause a degree of tarnish that will render the finish unsolderable. Solderability of tarnished silver is only affected once the tarnish is highly visible. Minor discoloration has never been proven to be an issue. Tarnished silver on non-soldered areas does not increase any tendency towards electromigration (2). Perhaps most importantly, electrical contact remains quite good even on surfaces tarnished by mixed flowing gas (3).

There are two schools of thought with respect to the proper thickness of the silver deposit. One camp espouses a thickness range of 0.05 µm (2µ") minimum at -2σ from process mean as measured on a pad of 1.5 µm X 1.5µm (60 mil X 60 mil) or equivalent area 2.25^2µm (3600^2 mils). A typical value is 0.07µm (3µ") to 0.12µm (5µ"). (3) Depending on the porosity of the coating and any anti-tarnish used the thinner coatings may not be as robust with respect to preserving solderability.

The other camp prefers a thicker deposit. In this case the immersion silver thickness is 0.12µm (5µ") minimum at -4σ from process mean as measured on a pad of 1.5µm X 1.5µm (60 mil X 60 mil) or equivalent area 2.25^2µm (3600^2 mils). A typical value is 0.2µm (8µ") to 0.3µm (12µ"). (4)

If other process steps are not properly controlled, thicker coatings may result in more attack at the solder mask interface as shown in Figure 1. This attack is a galvanic reaction so thicker coatings tend to enhance the amount of attack. By properly controlling surface preparation and silver bath parameters solder mask interfacial attack can be greatly reduced. (5)

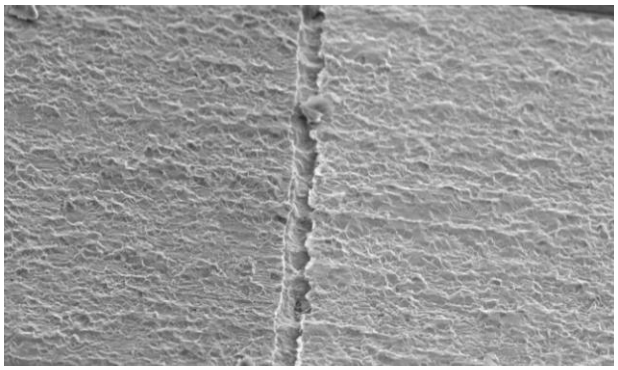
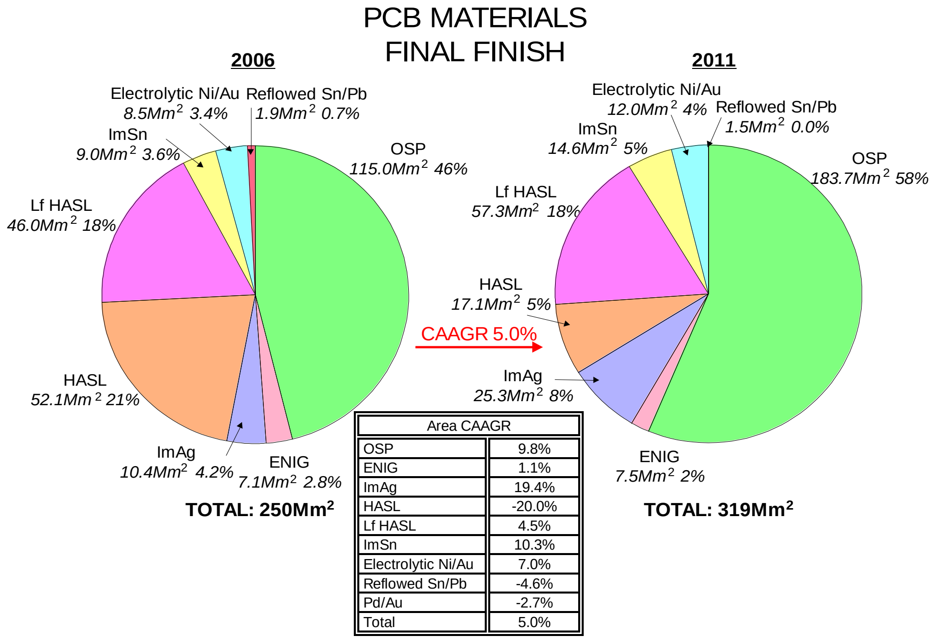


Figure 1 - Solder Mask Interfacial Attack

Higher silver thickness, in excess of 0.5µm (20µ"), combined with small feature size on a PWB and subsequent low solder paste volume may result in an excessive amount of Ag_3Sn IMC in the solder joint. This additional amount of silver may negatively impact the long-term reliability of the solder joint. More studies must be conducted on the use of silver bearing lead-free material and what effect, if any, it has on the strength of the lead-free solder joint.

Regardless of these concerns, immersion silver and OSP have gained considerable market share globally as solderable final finishes (Figure 2). Use of OSP and Immersion Silver are found across the entire electronics supply chain, including computer and office equipment, telecommunication and internet infrastructure, mobile phones, automotive and aerospace. Despite the widespread use of OSP and ImAg, the introduction of newer solderability standards and lead-free assembly protocols has placed these finishes in a higher level of scrutiny. To be specific, OSP and ImAg must be able to withstand multiple reflows (under lead-free conditions) and potentially a preassembly moisture bake-up (according to J-STD-003B) (6). And this is the subject matter of this paper.



Area CAAGR	
OSP	9.8%
ENIG	1.1%
ImAg	19.4%
HASL	-20.0%
Lf HASL	4.5%
ImSn	10.3%
Electrolytic Ni/Au	7.0%
Reflowed Sn/Pb	-4.6%
Pd/Au	-2.7%
Total	5.0%

Figure 2 - Overview of Surface Finish Market (Source: Prismark Partners)

Project Scope and Methodology

In order to investigate the performance of both the API (OSP) and ImAg processes, a standard test vehicle designed to measure wetting force was employed. (Figure 3). In addition, the ImAg underwent further testing with a different test vehicle (Figure 4).

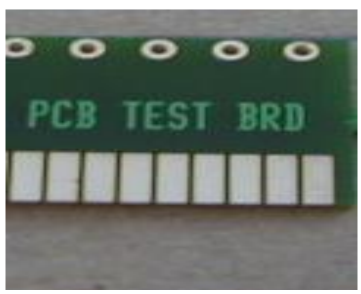


Figure 3 - Wetting Balance Test Coupon

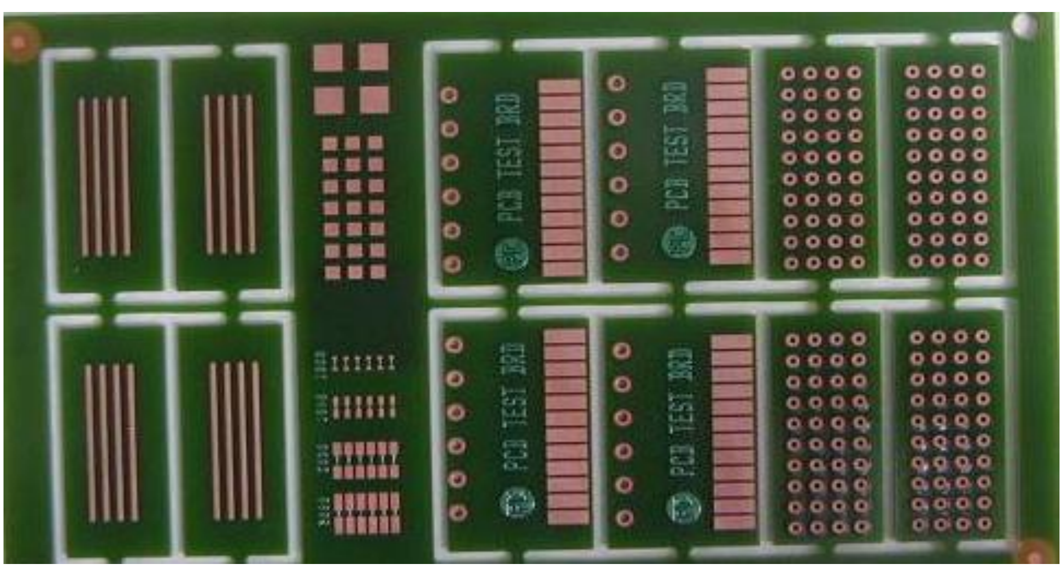


Figure 4 - Solderability Test Panel

OSP Testing and Methodology

Test vehicles were processed according to standard procedure for OSP application:

1. Acid Clean
2. Rinse
3. Micro-etch
4. Rinse
5. Dry
6. OSP
7. Rinse
8. Dry

Effect of Different Micro-etchants and fluxes on solderability of the API (OSP)

The authors wanted to understand the effect of sodium persulfate versus hydrogen peroxide/sulfuric acid type etchants on solderability. Due to the general thinness of the OSP coating, there is a concern that solderability may be affected due to the type of topography and overall surface morphology of the copper imparted by different etchants. In addition, the authors studied the effects of two different fluxes. One flux, Standard Flux #2, is called out in the J-STD 003B. A second flux, rated as ROL0, was used for comparison. To determine the effect of microetchant and flux type on solderability, wetting balance, edge dip testing, and hole fill were used to evaluate solderability. Copper coupons were treated with the API OSP (process cycle described above). The degree of copper removal with each microetchant was set for approximately 0.75μ (30 μin). The OSP thickness achieved for this study was ranged from 0.2-0.4 μ (2000-4000 Å). The coupons were tested for solderability under the following conditions:

OSP Solderability Testing

Wetting balance, edge dip and hole fill solderability tests were conducted in accordance with IPC J-STD-003B.

Wetting Balance Testing

- OSP coating thicknesses were 0.2, 0.3 and 0.4μ.
- Processed samples were run through 0, 2 and 4 lead free reflows (peak board temperature of 253°C).
- Persulfate and peroxide-sulfuric etchants were compared
- Standard Flux #2 per J-STD-003B was compared with a commercial ROL0 flux using the SAC 305 solder at 255ºC, time in solder was 10 seconds

Wetting Balance Test Results

Test results are summarized in Table 1 and are shown graphically in Figure 5. Without any reflows the wetting force was fairly consistent across the range of coating thickness. At 2 and 4 reflows the wetting force increased as the coating thickness increased.

# of Reflows	OSP Thickness (microns)	Wetting Force (μN/mm, 10 sec.)		
		Peroxide Etchant/ Standard Flux #2	Persulfate Etchant/ Standard Flux #2	Peroxide Etchant/ ROL0 Flux
0	0.2	220	187	197
2	0.2	125	67	97
4	0.2	30	0	0
0	0.3	205	200	220
2	0.3	190	167	143
4	0.3	145	107	0
0	0.4	200	193	200
2	0.4	190	220	190
4	0.4	135	160	60

Table 1 - Summary of OSP Wetting Balance Testing

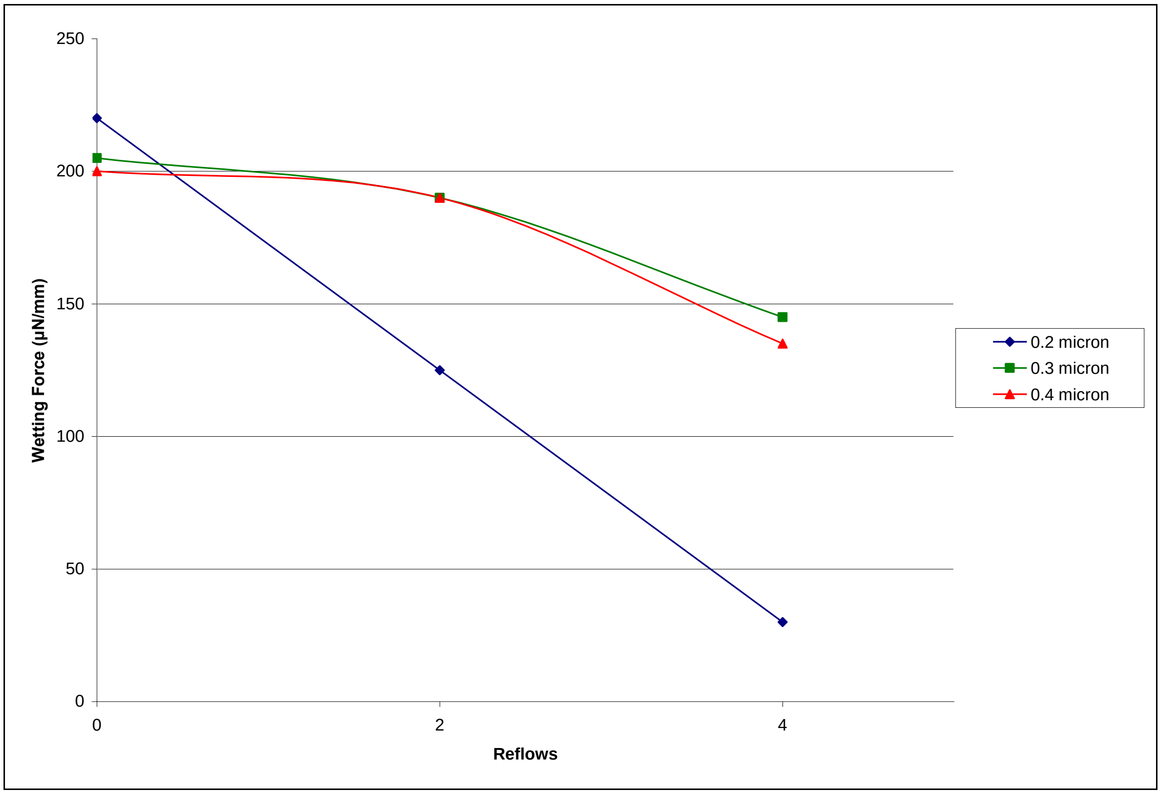


Figure 5 - Wetting Force vs. Reflow Cycles

A paired t-test was used to compare wetting force vs. etchant type and flux type. Results are shown in Tables 2 and 3 respectively. Etch type did not show a statistical difference while flux type showed that Standard Flux #2 gave a higher wetting force.

Table 2 - Paired t-Test Comparing Etchant Type

t-Test: Paired Two Sample for Means	**peroxide**	**persulfate**
Mean	160	144
Variance	3500	5256
Observations	9	9
Pearson Correlation	0.92	
Hypothesized Mean Difference	0	
df	8	
t Stat	1.60	
P(T<=t) one-tail	0.07	
t Critical one-tail	1.86	
P(T<=t) two-tail	0.15	
t Critical two-tail	2.31	

Table 3 - Paired t-Test Comparing Flux Type

t-Test: Paired Two Sample for Means	Standard Flux #2	ROL0 Flux
Mean	160	123
Variance	3500	7573
Observations	9	9
Pearson Correlation	0.85	
Hypothesized Mean Difference	0	
df	8	
t Stat	2.28	
P(T<=t) one-tail	0.03	
t Critical one-tail	1.86	
P(T<=t) two-tail	0.05	
t Critical two-tail	2.31	

Edge Dip Testing

- OSP coating thickness was 0.4µ.
- Processed samples were run through 0, 2, 4 and 6 lead free reflows (peak board temperature of 253°C).
- Persulfate and peroxide-sulfuric etchants were compared
- Standard Flux #2 and SAC 305 solder at 255ºC were used, time in solder was 3 seconds.
- Surface Evaluation Pass/Fail Criteria – A minimum of 95% of each of the surfaces being tested shall exhibit good wetting. The balance of the surface may contain only small pin holes, dewetted areas, and rough spots provided such defects are not concentrated in one area.

Edge Dip Test Results

Table 4 shows the results vs. number of reflows. The coating process that used a peroxide/sulfuric etchant passed 4 reflows while the coating process that used a persulfate failed at 4 reflows.

Table 4 - Edge Dip Results vs. Tin/Lead Reflows

Reflows	Persulfate Etch	Peroxide/Sulfuric Etch
0	Pass	Pass
2	Pass	Pass
4	Fail	Pass
6	Fail	Fail

Solder Float Testing

- One 2.6mm thick coupon with two sections of 40 holes each.
- OSP coating thickness was 0.4µ.
- Processed samples were run through 0, 2, 4 and 6 lead free reflows (peak board temperature of 253°C).
- Persulfate and peroxide-sulfuric etchants were compared
- Standard Flux #2 and SAC 305 solder at 255ºC were used with a float time of 5 seconds
- Surface Evaluation Pass/Fail Criteria - Solder shall fully wet the wall area of the plated-through holes, and plug holes less than 1.5mm diameter (complete filling is not necessary).

Solder Float Test Results

Table 5 shows the results vs. number of reflows. As seen in the edge dip testing, the coating process that used a peroxide/sulfuric etchant passed 4 reflows while the coating process that used a persulfate failed at 4 reflows.

Table 5 -Hole Fill vs. # of Tin/Lead Reflows

Reflows	Persulfate Etch	Peroxide/Sulfuric Etch
0	Pass	Pass
2	Pass	Pass
4	Fail	Pass
6	Fail	Fail

Immersion Silver Solderability Testing

Durability conditioning and testing were per IPC-4553 and J-STD-003B.

Test parameters

- Copper loading of silver bath (0 and 3 g/L copper)
- With and without durability condition (8 hrs at 72ºC ± 5ºC, 85% RH ±3%)
- Nominal thicknesses of 0.18 and 0.35 μ
- 0,1, 2 and 4 reflow cycles
- Two solder types, Tin/Lead and SAC 305

Data Evaluation

- Wetting Balance (J-STD-003B): Solderability after 0, 1, 2, and 4 reflow cycles with Tin/Lead and Lead Free profile.
- Solder Float (J-STD-003B): Solderability of Plated Through Hole after 0, 1, 2, and 4 reflow cycles with Tin/Lead and Lead Free profile for maximum 5 seconds.

Tin/Lead Profile

- Solder: 63/37 Sn/Pb
- Flux: J-STD-003B Standard Flux#1
- Solder temperature: 235ºC
- Reflow oven profile:
    - Peak temperature of 219°C
    - 73 seconds above 179°C

Lead Free Profile

- Solder: SAC 305
- Flux: J-STD-003B Standard Flux#2
- Solder temperature: 255ºC
- Reflow oven profile:
    - Peak temperature of 243°C
    - 44 seconds above 217°C

Tin/Lead Test Results

Table 6 shows a summary of results after 4 reflows. Wetting time, wetting force and % hole fill all show consistent and acceptable results. Main effects for wetting time and wetting force are shown in Figures 6-9. Figure 10 shows a Box Plot of data of wetting force at 2, 5 and 10 seconds and indicates fairly consistent force at the various times. All data was combined and analysis of variance (ANOVA) was used to compare the number of reflows as a function of wetting time and wetting force. When a significant difference was indicated the Tukey test was used to identify which groups were significantly different. These results are shown in Table 7. In general 0, 1 and 2 reflows produced similar results while 4 reflows showed a significant difference.

Table 6 - Solderability with Tin/Lead Solder at 4 Reflows

Bath	**Durability Conditioning**	**Thickness (μ)**	**Wetting Time (sec.)**	**Wetting Force (μN/mm, 10 sec)**	**Solder Float (% Hole Fill)**
0	No	0.18	0.35	133	100
		0.35	0.27	150	100
	Yes	0.18	0.32	143	100
		0.35	0.31	143	100
3	No	0.18	0.34	167	100
		0.35	0.28	143	100
	Yes	0.18	0.35	160	100
		0.35	0.27	153	100

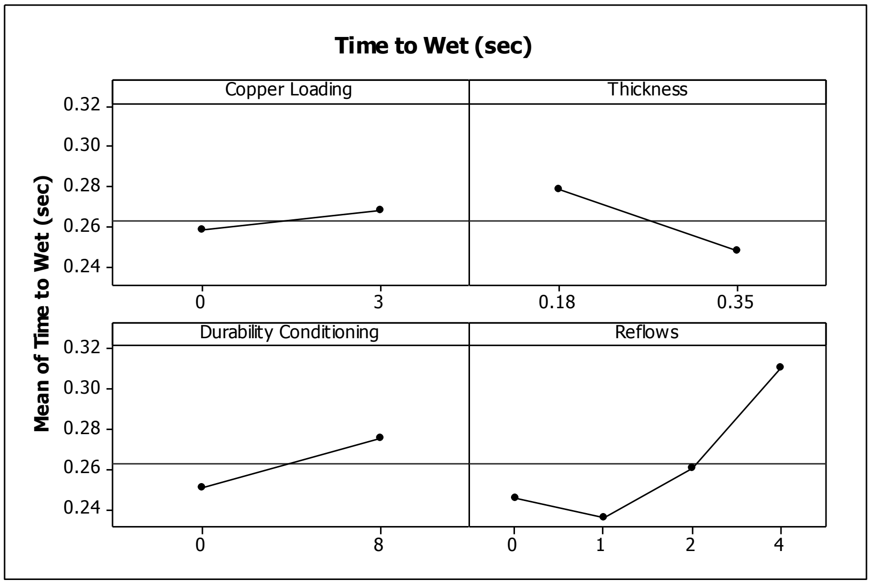


Figure 6 - Main Effects Comparison for Wetting Time

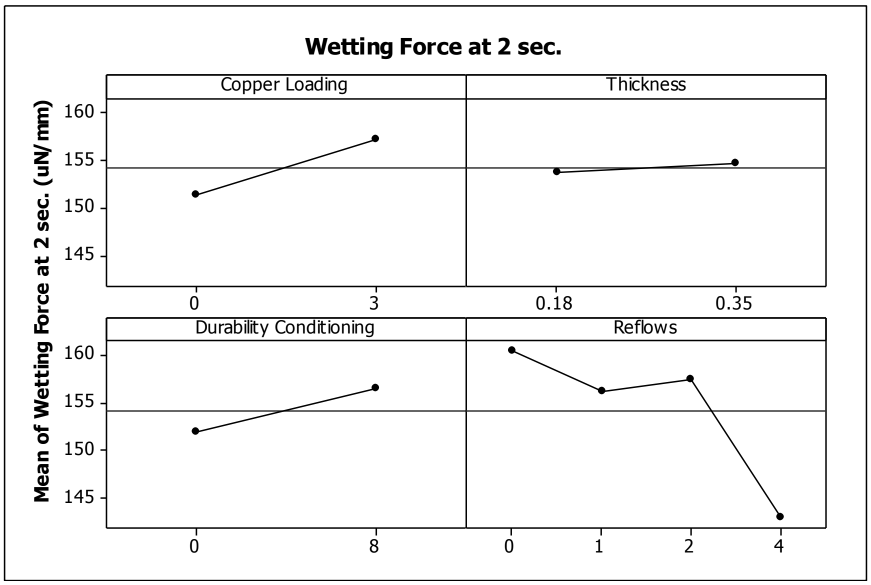


Figure 7 - Main Effects Comparison for Wetting Force at 2 Sec.

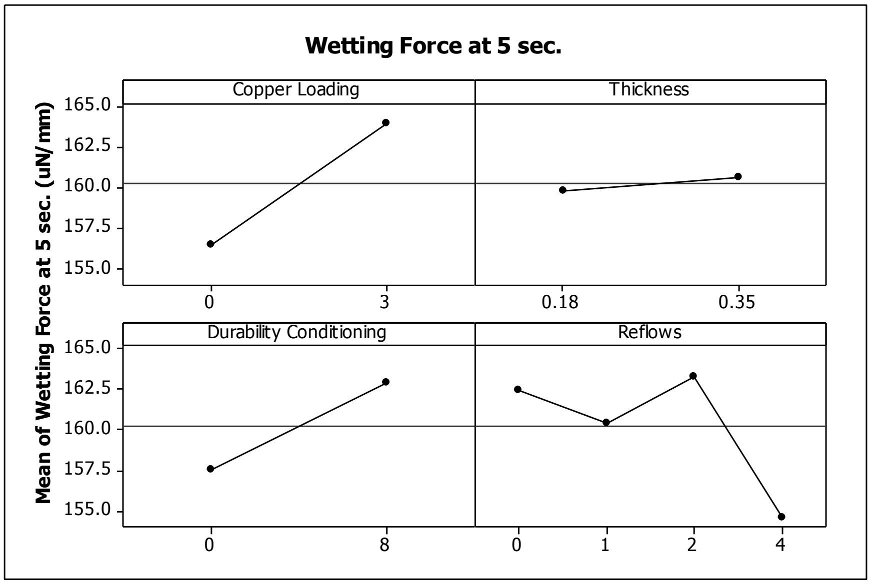


Figure 8 - Main Effects Comparison for Wetting Force at 5 Sec.

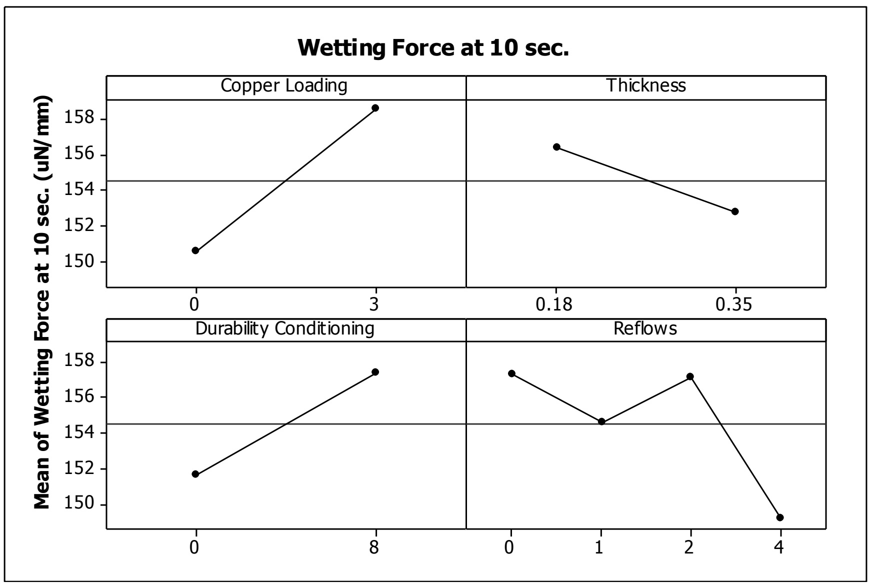


Figure 9 - Main Effects Comparison for Wetting Force at 10 Sec.

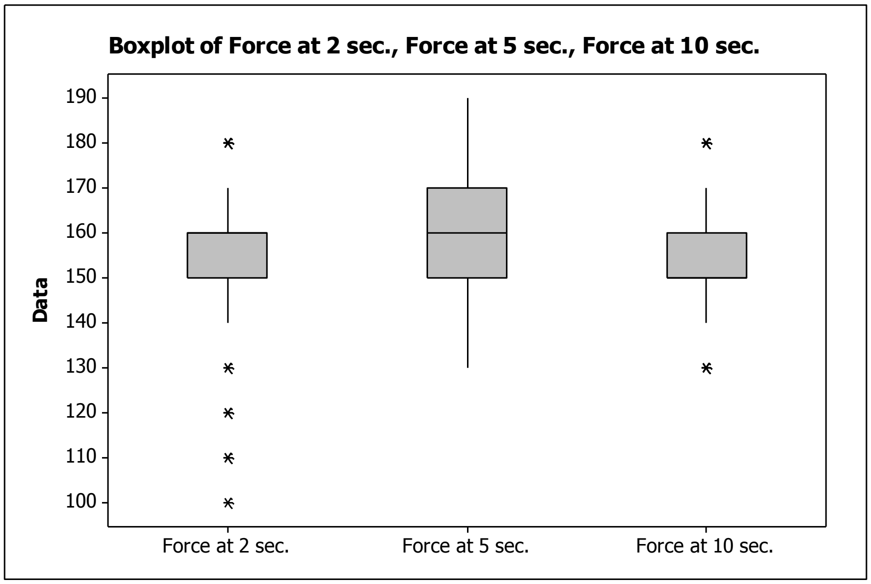


Figure 10 - Box Plot of Wetting Force at 2, 5 and 10 Sec.

Table 7 - ANOVA Comparing # of Tin/Lead Reflow Cycles vs. Solderability

Factor	**F Value**	**p Value**	**Tukey Comparisons – Differences in Reflows**
Wetting Time	15.03	0.000	4 vs. 0,1,2
Wetting Force at 2 sec.	7.89	0.000	4 vs. 0,1,2
Wetting Force at 5 sec.	2.80	0.044	4 vs. 2
Wetting Force at 10 sec.	2.54	0.061	none

Lead-Free Test Results

Similar data was generated for the lead-free testing. Table 8 shows a summary of results after 4 reflows. Wetting time, wetting force and % hole fill all show consistent and acceptable results. Main effects for wetting time and wetting force are shown in Figures 11-14. Figure 15 shows a Box Plot of data of wetting force at 2, 5 and 10 seconds and indicates and upward trend vs. time. All data was combined and analysis of variance (ANOVA) was used to compare the number of reflows as a function of wetting time and wetting force. When a significant difference was indicated the Tukey test was used to identify which groups were significantly different. These results are shown in Table 9. No differences were seen in wetting time. In terms of wetting force, 0 reflows was significantly different from other reflows at 2 and 5 seconds.

Table 8 - Solderability with Lead Free Solder at 4 Reflows

Bath	**Durability Conditioning**	**Thickness (μ)**	**Wetting Time (sec.)**	**Wetting Force (μN/mm, 10 sec)**	**Solder Float (% Hole Fill)**
0	No	0.18	0.65	220	100
		0.35	0.60	203	100
	Yes	0.18	0.60	227	100
		0.35	0.68	210	100
3	No	0.18	0.63	220	100
		0.35	0.66	207	100
	Yes	0.18	0.63	237	100
		0.35	0.72	203	100

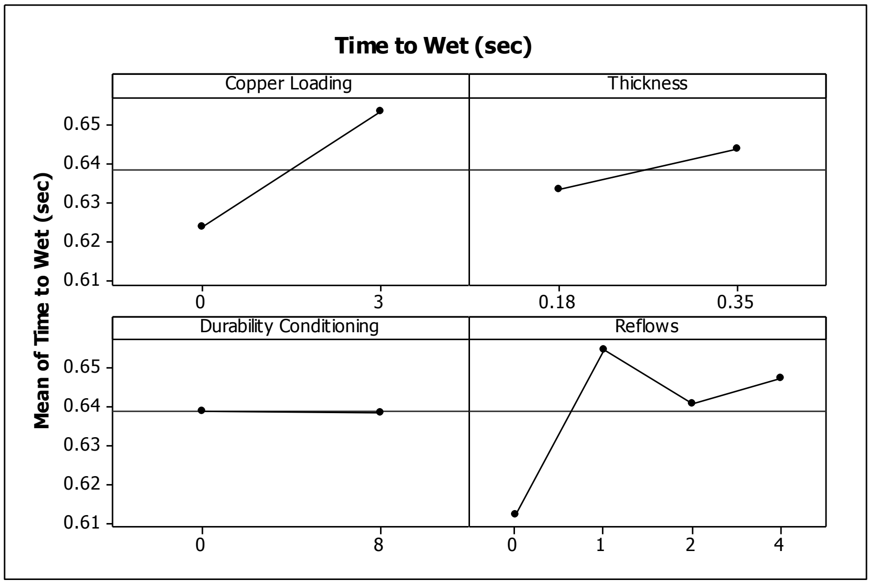


Figure 11 - Main Effects Comparison for Wetting Time

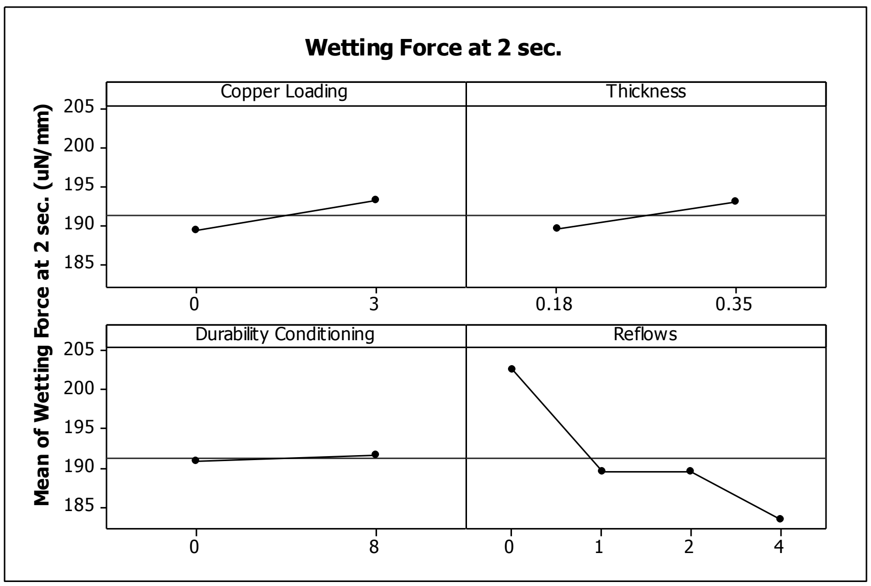


Figure 12 - Main Effects Comparison for Wetting Force at 2 Sec.

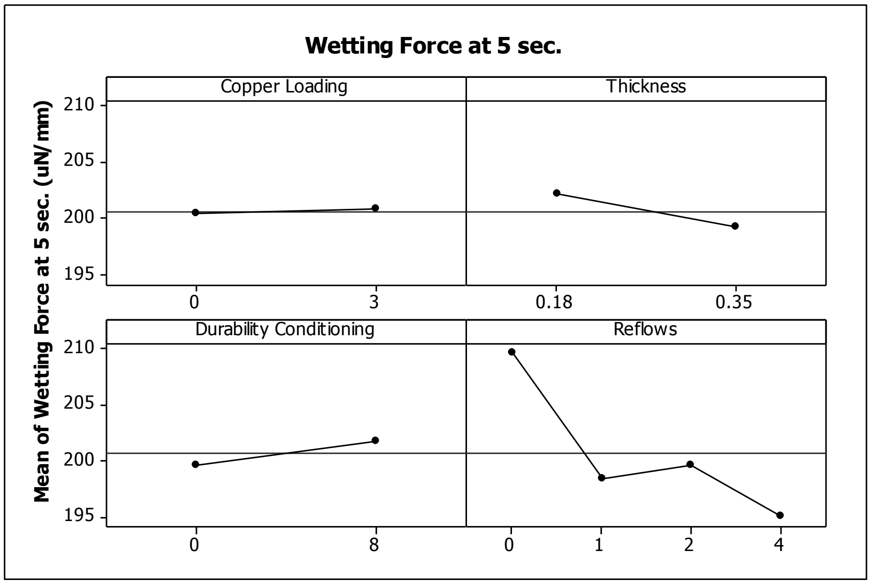


Figure 13 - Main Effects Comparison for Wetting Force at 5 Sec.

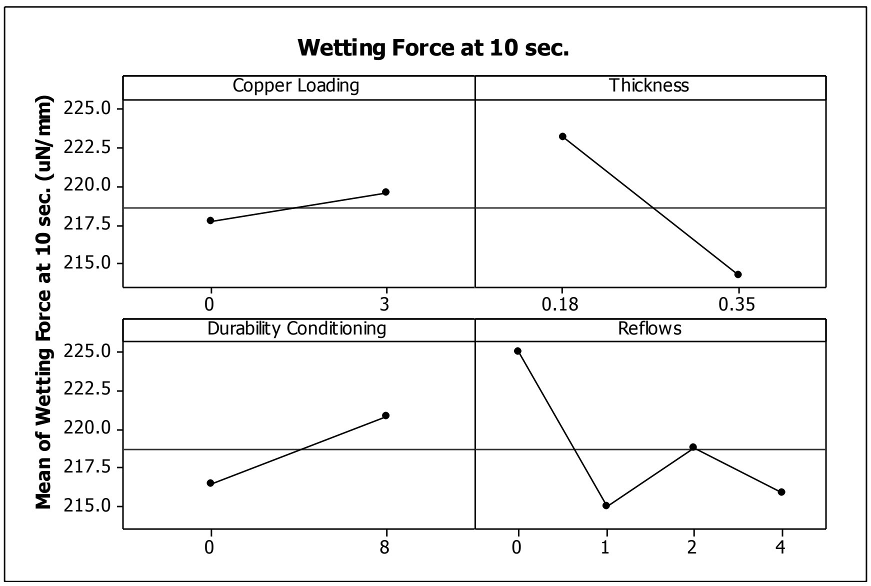


Figure 14 - Main Effects Comparison for Wetting Force at 10 Sec.

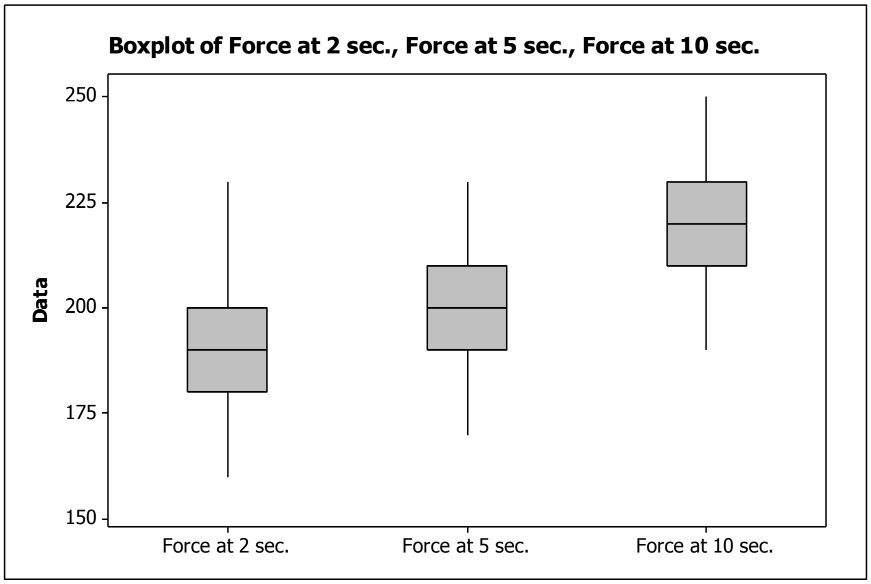


Figure 15 - Box Plot of Wetting Force at 2, 5 and 10 Sec.

Table 9 - ANOVA Comparing # of Lead-Free Reflow Cycles vs. Solderability

Factor	F Value	p Value	Tukey Comparisons – Differences in Reflows
Wetting Time	1.10	0.352	No differences
Wetting Force at 2 sec.	10.72	0.000	0 vs. 1,2,4
Wetting Force at 5 sec.	5.40	0.002	0 vs. 1,4
Wetting Force at 10 sec.	2.24	0.089	No differences

Summary and Conclusions

With OSP, a degradation of solderability was seen as thickness decreased and as the number of lead-free reflows increased. In most cases, the use of a peroxide-sulfuric etchant gave better results. Therefore when running multiple lead-free reflows it is important to make sure surface preparation and coating thickness are matched with the flux type and reflow oven settings.

The immersion silver process gave acceptable solderability with up to 4 reflows, both with tin/lead and lead-free solders. Copper loading of the silver bath, silver coating thickness and durability conditioning did not have a significant practical effect on solderability.

References

1. Aspandiar, Raiyo F., “Voids in Solder Joints, “Journal of the SMTA, Volume 19, Issue 4, 2006.
2. R.Michalkiewicz, “Report 48991 Bellcore GR-78 Core 13.2.7,” Trace Laboratories East, March 2001
3. R.Gordon, et al, “Evaluation of Immersion Silver Finish for Automotive Applications,” SMTA Int’l 2000 Proceedings
4. IPC-4553 Specification for Immersion Silver
5. Electrochemicals Internal Reports
6. IPC-J-STD 003B Solderability Tests for Printed Boards

Acknowledgements

The authors would like to thank Thao Pham and Mike Schanhaar for their work in completing the solderability testing.