Optimizing Immersion Silver Chemistries for Copper

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Abstract:

Immersion silver chemistry has been promoted as a final finish for solderability for several years now. There are different commercially available products that will deposit silver in a wide range of thicknesses. Some chemistries, because of their very aggressive nature can produce a thickness distribution within a circuit board of 20-30 millionths and higher on small pads versus large ground planes. A large difference in silver thickness will affect solder wetting times within the same board especially with SAC alloys. A large variation in silver thickness can be overcome in assembly. But it typically requires a more precise assembly process with a longer and or hotter soldering profile.

A study has been underway evaluating nitrate based immersion silver chemistry against other potential silver sources. The study evaluated several types of additives against PCB design. Data on thickness distribution, copper attack rate, and deposit porosity has resulted in new theories on how to control immersion silver deposits. Specific formulas have been found that provide a pore free deposit with minimal attack on electroless copper. A specific test vehicle was chosen that takes into account ground planes, isolated traces, interconnected pads and different metallization processes. Data on thickness distribution, copper attack rate, and deposit porosity has resulted in new theories on how to control immersion silver deposits. Specific formulas have been found that provide a pore free deposit with minimal attack on electroless copper.

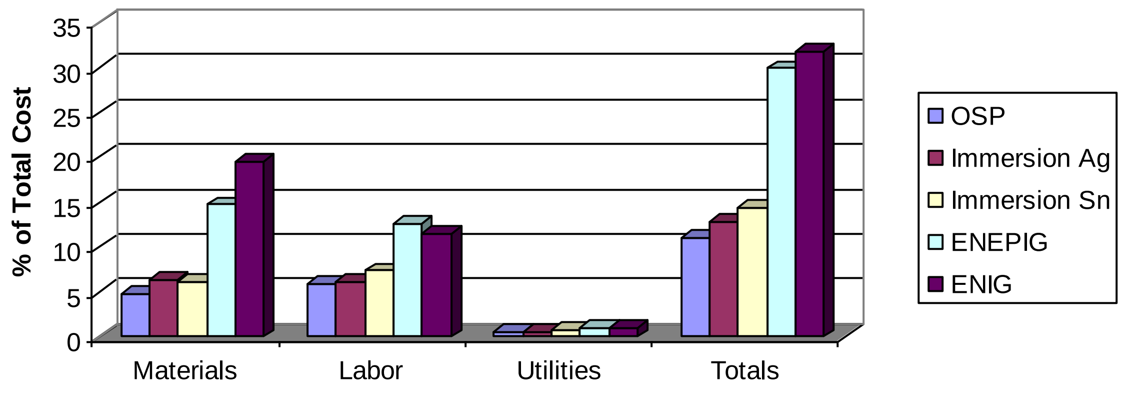
Introduction:

Protection of the copper surface from oxidation is the ultimate goal of all the numerous final finishes that are currently available on the market today. Technology changes due to increased functionality and environmental legislation has created the industry wide requirement for a lead-free flat co-planer surface. Global legislation finally caused the well prophesized change away from a well-known and understood hot air solder leveling process to electroless nickel immersion gold (ENIG) even for less complex product. ENIG, was chosen because it has a long, mostly successful history with a wide process window during assembly. In addition, a lot of work has been done over the years by several vendors to understand, predict and, for the most part, eliminate the phenomenon called black pad. However, there are two major reasons to continue looking at alternatives for ENIG:

- Solder joint strength
- Cost

From a metallurgy standpoint, a solder joint to ENIG forms on a nickel/phosphorus layer. This layer will have various amounts of phosphorus due to the electroless nickel vendor, fabricator's control parameters, and the attack rate of the immersion gold. Oxide free nickel is very solderable, but phosphorus is not. The end result with ENIG is lower solder joint strength[1] which becomes critical as the pitch goes down below 1mm especially on BGA and micro BGA designs. To the fabricator, this has translated into parts requiring selective ENIG, which adds to the fabricators process steps and ultimately their cost.

Chart 1: Proportional Cost HASL Alternatives



With the market price for gold at 20-year highs, ENIG is one of the most expensive surface finishes to apply. The gold deposit, even with limited thickness, becomes 70-80% of the cost to deposit ENIG. Chart 1 shows an approximation of process costs for several of the commercially available HASL alternatives. What's obvious is, organic solderability preservatives (OSP) and immersion plating chemistries provide cost benefits when compared to ENIG and electroless nickel electroless palladium immersion gold (ENEPIG).

In addition, numerous studies [2,3] have shown that immersion silver and OSP provide strong solder joints. In both these cases, the solder joint is formed directly on the copper surface. However OSP, while historically working well with eutectic solder, cannot provide the operating window in lead-free assembly that metallic coatings can. The big difference is that an OSP has to be penetrated and pushed off the copper surface while a metallic coating like silver or tin becomes part of the solder joint. OSP will limit solder flow and the ability to completely wet a pad or through hole.

The first generation immersion silver chemistries have become a second or third highest alternative to HASL. ENIG has the highest share with OSP and immersion silver fighting for second. Cost and solderability have been major factors in immersion silver achieving these market gains. However, high volume production with immersion silver has shown some issues that were not observed in the lab or during initial testing. Similar to the conversion to ENIG, the aggressive nature of immersion chemistry has to be controlled to provide consistency in production. Control of the immersion chemistry must start with an understanding of the chemical reactions during the immersion plating process.

Immersion Plating

Several factors must be understood when developing immersion silver chemistry. The ideal is to provide a consistent thin deposit that will be easily removed by the soldering operation. A thinner deposit has less impact on the solder joint alloy and will take less time to dissolve, which can be critical with the short liquidius time for some lead free solders. Consistency, especially thickness, within a PCB design will affect the solderability over the different pad geometries. This ideal immersion process would provide a wider window for assembly because of this improved consistency.

First, for an immersion reaction to occur there has to be a potential between the plated metal and the base metal that is being coated. Theoretically, the greater the potential, the more aggressive a replacement reaction becomes. (Table 1: Electrochemical Potential of Copper and Silver) However there are several other factors involved. Operating parameters such as pH, temperature, and solution flow will affect the transfer dynamics at the plating surface. Typically there is an increase in reaction rate as pH is lowered or temperature & solution movement are increased. In addition, additives can be used to complex either the base or the plated metal.

Table 1: Electrochemical Potential of Copper and Silver

Metal	Reaction	Potential (V)	Immersion Reaction	Immersion Potential (V)
Copper	$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.340	$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$	1.259
Silver	$Ag^+ + e^- \leftrightarrow Ag$	0.7996		

Complexants can be specific or at least selective for individual metals. If a complexant is chosen to tie up silver, it will slow the replacement reaction. On the other hand, a complexant chosen for copper can increase the replacement reaction and actually helps corrode the copper surface. In both cases, the dissociation factor of each complexant indicates how strong the attraction is to the metal. In designing an immersion silver process, the choice of complexant can be utilized to control the deposit rate and ultimately the consistency of the silver deposit.

However, very low pH can become the controlling factor for immersion silver plating overpowering the effect of other factors. By utilizing a low pH to drive the silver deposition, the initiation becomes very dependent on surface conditions. Variation in the copper, such as grain structure due to electroless versus electrolytic copper, or different wetting of the surface will create a different attack rate. In server cases, an immersion silver process can selectively remove electroless copper along the edge of traces and pads as shown in Figures 1 & 2. This notching effect, because of the high dissolution rate of copper will increase the measured silver thickness locally. It is unknown if the density of the silver deposit is changing at the same time.

Figure1: 200X notching after Ag Plate

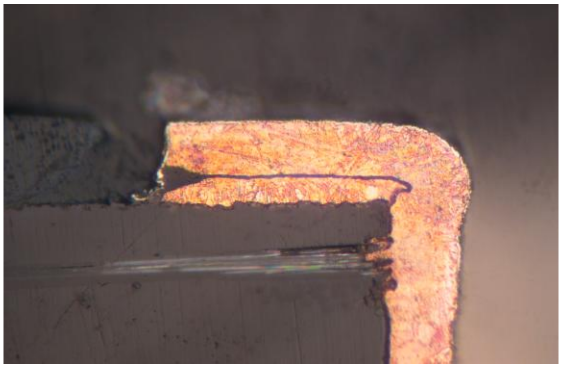
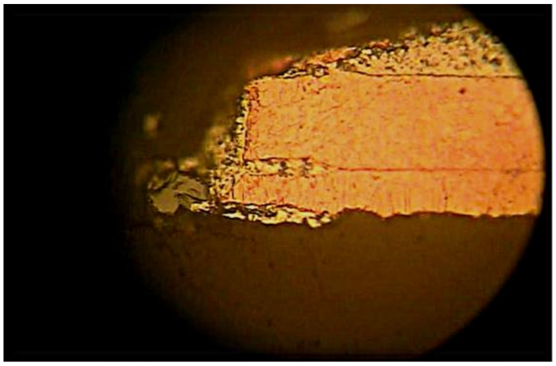


Figure 2: 400X Ag notch after soldering



This aggressive attack on copper is similar to the reaction that causes black pad with ENIG. To control black pad, the immersion gold chemistry was made less aggressive by increasing pH and the electroless nickel was made more chemically resistant by increasing phosphorus. The same principle applies to immersion silver. Controlling the deposition rate yields better deposit performance. With immersion silver the deposit rate can be controlled by increasing the pH in combination with a measured amount of a chemical to corrode copper and specific complexant for silver. This will yield a consistent deposit across PCB design features.

During development, another factor, the choice of silver salt, was also found to be critical. Silver is available in salts that can be dissolved in acid solutions. Cost and availability has resulted in the use of silver nitrate for most of the current formulas. Silver nitrate has two main issues.

- First nitrate in acid solutions increases the removal rate of copper as the concentration of nitrate increases and the pH of the solution changes. As silver is plated, nitrates build creating a changing condition and making pH control critical.

- Second, ionic silver has a very limited solubility in the presence of halogens. In silver nitrate solutions, chloride is usually limited to les than 10 ppm. Above 10 ppm, chloride has caused adhesion problems in most nitrate based immersion silver processes.

The solution is to utilize a pre-manufactured silver complex free of nitrates. Eliminating nitrates eliminates the need to control build up of this by-product. In addition, the use of a silver complex eliminates issues with halogen contamination and allows the ability to operate in an alkaline pH. The result after development work was complete was a nitrate free system that operates in a slightly alkaline pH.

Test Results New Immersion Silver Formula

Through statistical evaluation of several DOEs an immersion silver formula was developed utilizing a copper corrodant with a silver complex. The combination allows the process to operate at a slightly alkaline pH. The tests indicated that the specific choice of additives were key to obtaining good adhesion, uniform coverage, high tolerance to chloride, and minimal attack on electroless copper (notching).

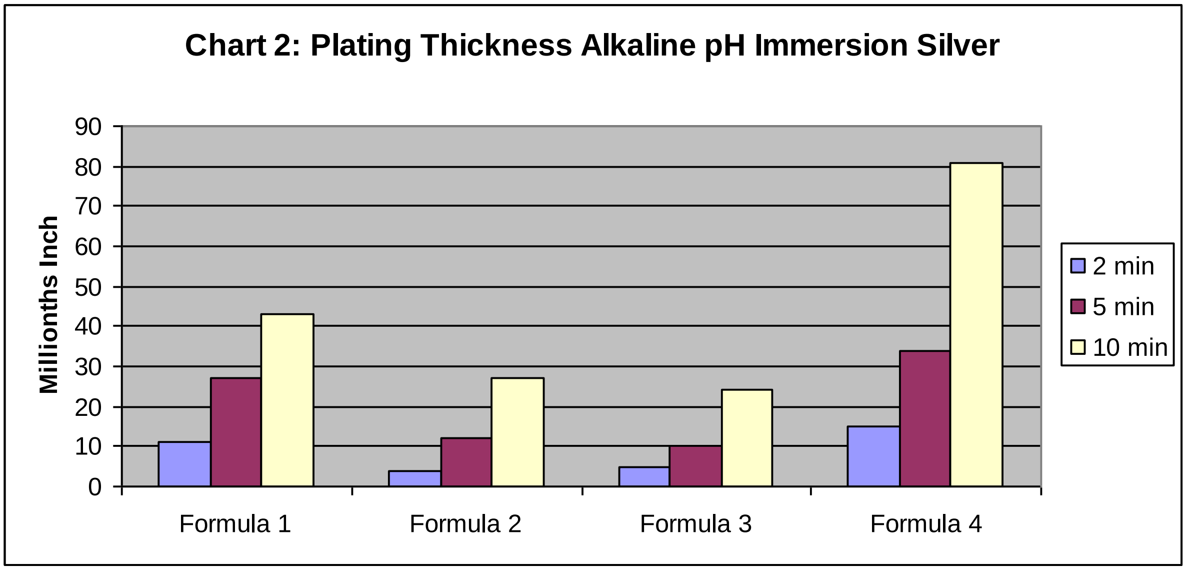
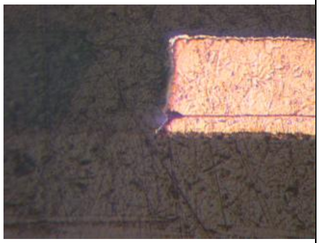
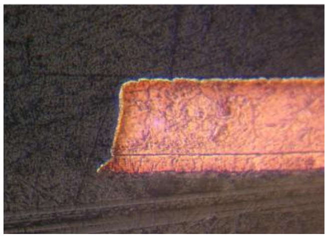
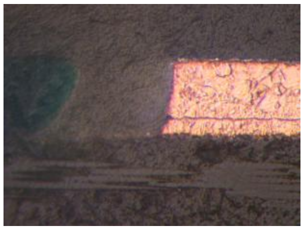
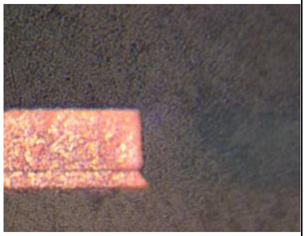
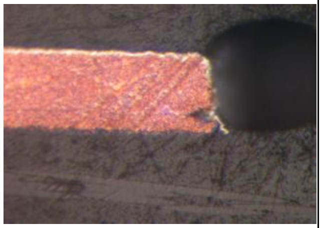
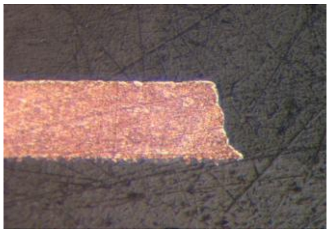
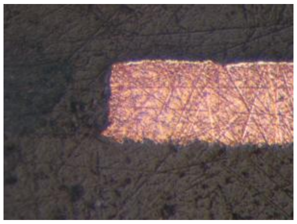
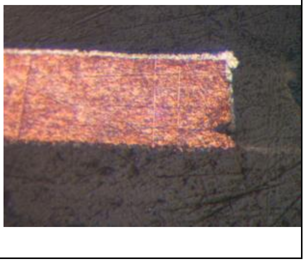


Chart 2: Plating Thickness Alkaline pH Immersion Silver

To look at worst case scenarios, the plating time was extended to 5 and 10 minutes in order to exaggerate the attack on electroless copper and insure there are no adhesion problems typical of long immersion times. (Chart 2) The formulas vary the concentration and specific choice of complexant and copper corroder. What's interesting is that as the plating thickness goes up, the attack on the electroless copper (notching) also increases. The plating thickness continues to climb with formulas 1 & 4 and the severity of notching also increases as shown below in table 2.

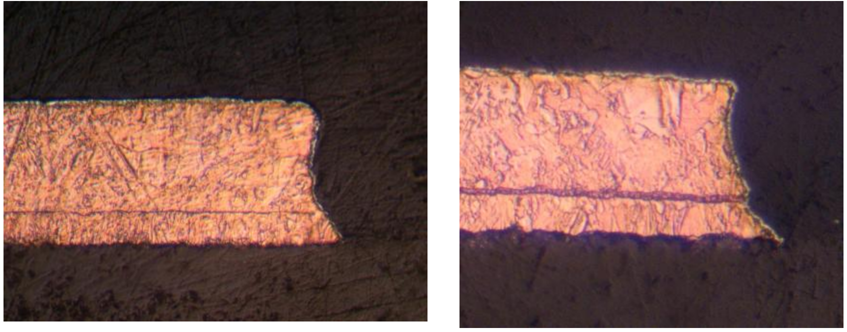
Table 2: Notching effect With Different Immersion Silver Formulas

	Formula 1	Formula 2	Formula 3	Formula 4
5 minutes				
10 Minutes				

Even though 5 & 10 minute immersion times are excessive, what they show is that since the formulas have no reducing potential, they are true immersion plating formulas and higher thickness is only possible by having copper available to drive the reaction. This indicates that there is porosity in the silver deposit in order to drive the plating reaction. An ideal process should be self-limiting but still provide quick initiation.

The initial testing also indicated, as expected, that more aggressive copper corroders and complexants were more prone to either excessive copper attack or tape test adhesion failures. Specific selection of additives was key to getting visual coverage in less than 15 seconds, good adhesion and no notching of sidewalls (Figure 3: 5 minute immersion alkaline nitrate free Immersion Silver).

Figure 3: 5 minute immersion in Alkaline, Nitrate –free Immersion Silver



Based on XRF measurements, the alkaline nitrate free process will deposit 10-15 millionths of silver in 2 minutes. The overall distribution of the thickness on a typical SMOBC PCB with BGAs is within 5-10 millionths. Most nitrate based systems have a range of 20 millionths and sometimes more. To evaluate the thickness distribution further, specific features on a full size production panel were measured after 2 and 5 minute immersion times. Typical immersion time for this process is 2 minutes, 5 minutes was also run to evaluate the self limiting nature of the new formula.

Chart 3: Average Immersion Silver Thickness Vs Pad Design & Plating Time

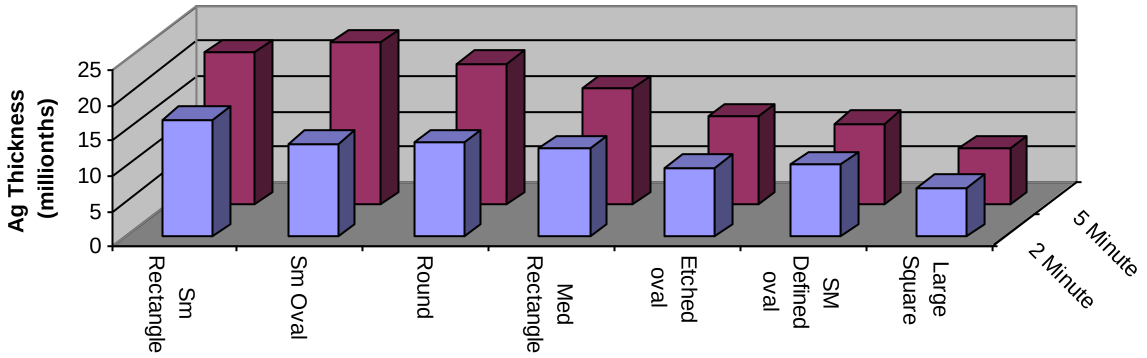
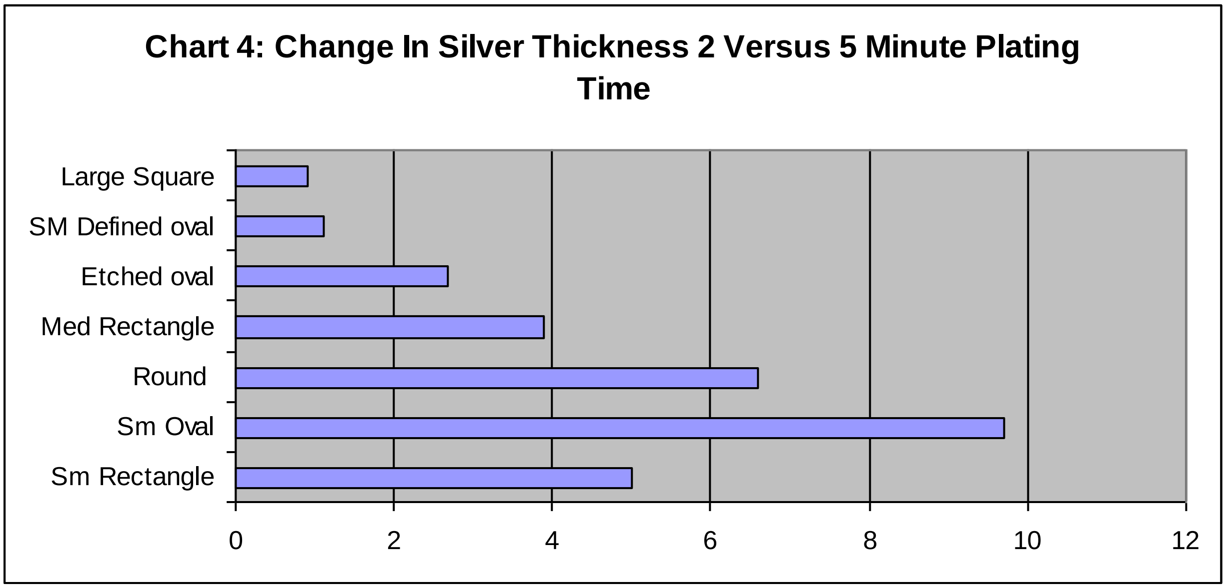


Chart 3 shows the average thickness on several types of features from small rectangular pads for quad flat packs to large squares for heat sinks on large BGA devices. The overall distribution on thickness for 2 minutes is approximately 10-15 millionths. By more than doubling the immersion time to 5 minutes, the thickness range does increase from about 5 to 10 millionths, however, the range is much tighter than earlier nitrate based immersion silvers. More consistent silver translates into more consistent soldering across different PCB feature sizes.

The thickness data in chart 3 also shows a trend some features show a bigger difference in thickness when plated for 2 versus 5 minutes. This difference is plotted in chart 4.



Smaller feature sizes as expected, do plate higher thicknesses. However, chart 4 shows that when immersion time is increased, the smaller features also have a higher differential in thickness. The surface area of the round, Sm oval and Sm rectangle pads are pretty similar but the Sm oval had the greatest change in silver thickness as immersion time was increased. Where the surface area and accuracy of the XRF should be similar with these three features, the Sm oval does have the highest ratio of perimeter to area, indicating that the sidewalls still influence the plating thickness. This may also be supported by the SM (solder mask) Defined oval yielding similar results to the Large Square. The Etched Oval is the same size as the SM Defined Oval but it had higher average thickness and greater difference with longer immersion time. The SM Defined oval has no sidewalls, whereas the etched oval sidewalls help drive the plating thickness. Additional work needs to be done in this area, but even with a controlled deposit rate from this nitrate free formula, it appears that the side walls still affect the plating thickness. If an immersion silver process is more aggressive, the differential in silver thickness between PWB geometries will only be greater.

An additional benefit of the new nitrate-free immersion silver is the tolerance to chloride. The key is the use of a manufactured silver complex allowing hundreds of ppm of chloride with no effect on the deposit or the plating solution. Existing silver nitrate based systems cannot tolerate more than 10 ppm of chloride. This high tolerance to chloride not only allows the use of city water prior to the immersion silver bath, but also eliminates one of the reasons for a pre-dip prior to plating.

Summary & Conclusion

A new immersion silver chemistry has been developed that replaces silver nitrate with a manufactured silver complex and operates in a slightly alkaline pH. The result is a process that initiates quickly on copper and provides a much more consistent silver thickness over different PWB geometries. The process is self-limiting and eliminates the aggressive attack on copper seen with nitrate-based systems. Based on this work, a theory has been developed on thickness distribution typically seen with immersion silver over different pad sizes. It appears that as the ratio of the perimeter of the feature to the surface area increases, the immersion silver thickness will increase as well. The problem is that with very aggressive immersion plating processes, the thickness distribution can be over 20 millionths and the attack can cause notching of the trace or pad sidewall.

The overall range in thickness with this new process is typically less than 10 millionths as measured by XRF. This provides a much more consistent surface which is extremely important with lead free soldering. During the assembly process the silver must be absorbed into the solder joint. Table 3 shows calculations for a % increase in silver based on the immersion silver thickness and the stencil thickness. Keep in mind that small pads/fine pitch will have the highest immersion silver thickness and for fine pitch typically the stencil thickness is lower yielding lower amounts of solder paste.

Table 3: Approximate weight % Increase of Silver in Solder Joint From Immersion Silver (Based on 90%Metal, SAC 305)

Silver Thickness (Inch)	**Stencil Thickness (Inch)**			
	0.005	**0.006**	**0.007**	**0.008**
5 Millionths	0.21%	0.17%	0.15%	0.13%
10 Millionths	0.42%	0.35%	0.30%	0.26%
20 Millionths	0.84%	0.70%	0.61%	0.53%
30 Millionths	1.27%	1.06%	0.90%	0.79%
40 Millionths	1.69%	1.41%	1.21%	1.06%

Based on these calculations, 30 millionths of immersion silver can change the weight % of silver in the solder joint by over 1%. With SAC alloys, typically the % silver is 3-4 so a thick immersion silver deposit can change the silver content by 25-30% of the total. As shown in table 4 a 1% shift in silver can change the liquidus temperature by as much as10 ^{0}C.

Table 4: Liquidus & Reflow Temperatures SAC alloys[4]

Alloy Composition	**Liquidus Temp. (°C)**	**Reflow Temp. (°C)**	**Melting Range$^{\#}$ (°C)**
Sn-3.0Ag-0.5Cu*	220**	238 – 248	
Sn-3.2Ag-0.5Cu	218	238 – 248	217-218
Sn-3.5Ag-0.75Cu*	218	238 – 248	
Sn-3.8Ag-0.7Cu	210**	238 – 248	217-210
Sn-4.0Ag-0.5Cu			217-219
Sn-4.0Ag-1.0Cu*	220**	238 – 248	217-220
Sn-4.7Ag-1.7Cu*	244**	237 – 247	217-220

By design, the new immersion silver process is impacted much less by PCB design. It offers the fabricator, a wider tolerance for chloride contamination and improved consistency of the silver deposit. To the assembler, this translates into a PCB that has the same soldering performance between boards and over the wide range of components used in today's advanced electronics.

References:

1) Johnson, R. W., Wang V., Palmer M., "Thermal cyclic fatigue of the Interconnect" SMI pg 59-69, 1998
2) Watanabe, Y., "PWB Surface finish process development to enhance the reliability of the solder joint strength" Advanced Packaging Materials: Processes, properties and Interfaces, 2001, pg 165-170
3) Rogers K., Hillman C., "The effects of Plating Materials, Bond Pad Size, and Bond Pad Geometry on Solder Ball Shear Strength" , CALCE Electronics Product and System Center
4) Siewert, T. "Properties of lead Free Solders, release 4.0" National Institute of Standards and Technology, Feb. 11, 2002