THIN IMMERSION TIN USING ORGANIC METALS

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ABSTRACT

With the international implementation of lead-free technologies/processes use of Immersion Tin usage as a PWB final finish is expected to grow substantially in the near future. With the world-wide growing demand for Immersion Tin, the demands towards the product and process technology consequently increase significantly. Market leading OEMs require the surface finish to have higher tin thickness, improved solderability at multiple heat cycles and higher temperatures, perfect surface flatness, fine pitch compatibility, etc. Modern Immersion Tin technology can serve such requirements and has proven over several years its superior product and process advantages at market leading PCB manufacturers. New technology using unique Organic Metal technology in the immersion tin process allows for thinner tin coatings without sacrificing performance. The catalyst and passivation effect of the Organic Metal leads to a large grain size with a low affinity for oxidation or whiskers and high process reliability. The ability of a thin immersion tin to achieve comparable performance to thick immersion tin results in significant improvements in process costs, yields and environmental impact.

Key words: immersion tin, Organic Metal, surface finishes, thin tin

INTRODUCTION

Classic thick immersion tin is used on an estimated 6% of all circuit boards produced globally [1]. (Fig 1)



Figure 1

Immersion tin growth has lagged behind other alternatives to HASL, but primarily because the major users have been in the automotive industry where lead free compliance was delayed. As the time to convert draws near, we expect to see immersion tin usage grow at the expense of the HASL process. Benefits of immersion tin include electrically conductive for in-circuit-test, color stability through harsh environments, co-planarity, mild thermal stress on board during application, halogen free, produces a visible coating, excellent solder joint strength and is well accepted for press fit applications. Concerns with immersion tin in lead free applications revolve around the need for tin thickness associated with many processes on the market. Thick deposits, greater then 1.0 microns allow for intermetallic growth over time, while leaving enough pure tin available to protect from copper oxidation. Increasing tin thickness can only be achieved through increased dwell times, which result in longer equipment, greater floor space requirements, greater facilities load, more soldermask attack, greater chance for whisker formation and more copper dissolution. With the use of Organic Metals in the immersion tin process, thin, more reliable coatings can be produced without sacrificing the benefits tin has to offer.

BACKGROUND

Organic Metal (OM) is an advanced form of conductive polymers which has metallic properties even though it is characterized as an organic compound. The material contains carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulphate (So) as elements and is synthesized and dispersed in the form of 10 nanometer (nm) small primary particles. A strong effect in the prevention of copper (Cu) oxidation was discovered many years ago (Figure 2). The material has been commercially used approximately 10 years for finishing printed circuit boards as a predip in standard immersion tin process. In this process, the organic metal is used as the Cu surface preparation predip prior to the immersion tin (Sn) deposition. [2]





ORGANIC METAL IN PREDIP

The use of Organic Metal in the predip does many things to improve the subsequent immersion tin deposit.

1. Passivation of the copper providing uniform surface to begin the tin plating.

2. Allows for even initiation of the tin deposit for excellent plating distribution.

3. Generates a large course crystalline deposit which slows copper diffusion

These attributes allow for the following benefits.

Uniform copper appearance as it enters the tin bath. This is not an obvious point if one has never plated before, but quite often the physical appearance of the copper entering a plating bath will be very much the same exiting a plating bath. By providing a bright uniform copper surface to the tin bath insures a bright uniform tin deposit as it exits the system. (Figure 3)



Figure 3

This unique attribute compensates for poor equipment designs, inefficient time ways and non-ideal plating conditions.

The Organic Metal also has the added benefit of uniform initiation of the tin plating deposit. This results in a very uniform thickness of deposit irregardless of feature size. Tables 1&2

Table 1

	Spots/pad	Horizontal				Vertical						
Pad Size		Tin Thickness [µm]	Standard deviation	Mean value [µm]	Cpk	Tin Thickness (µm)	Standard deviation	Mean value [µm]	Cpk			
XS	10	1,009	0,091			0,996 0,05	0,090					
S	10	1,007	0,060	1,010		0,99	0,059					
М	20	1.01	0,061		1,010	1,010	<u>81</u> 31 1,010		0,993	0.060		
L	20	1,012	0,081					1,70	0,995	0,090	0,994	3,32
XL	30	1,011	0,061			0,995	0,080					

Table 2

	Horizontal				Vertical			
Pad Size	Tin Thickness [µm]	Meanvalue [µm]	Standard deviation	Cpk	Tin Thickness [µm]	Meanvalue [µm]	Standard deviation	rd Cpk
S	1,162		0,10458		1,119		0,10071	
M	1,17	1,169	0,09360	1,58	1,135	1,132	0,11350	2,00
L	1,175		0,11750	0.000	1,141		0,09128	

Uniformity of coating will result in consistent soldering at assembly.

The third benefit of using Organic Metal in the predip is a unique grain structure which has many added side benefits. Figure 4



Figure 4

The larger more course grain structure results in slower copper diffusion with fewer grain boundaries for copper migration and contaminate inclusion. This results in a freer rinsing deposit, longer shelf life and better lead free assembly soldering,

Because of the strong affinity between copper and tin, interdiffusion occurs spontaneously even at room temperature through bulk, grain boundary and surface diffusion pathways, resulting in the formation of intermetallic compounds at the Sn/Cu interface as well as in the grain boundaries of tin coating. At room temperature, the primary intermetallic is η phase (Cu₆Sn₅) and grain boundary diffusion is significantly faster than bulk diffusion. This results in irregular growth of Cu₆Sn₅ in the grain boundaries of the Sn deposit. Cu diffusion into the grain boundaries of the tin deposit combined with IMC formation creates a compressive stress within the tin deposit. This compressive stress increases with time, and in the presence of surface defects or strain mismatch, creates conditions required to break through the oxide layer and form a whisker.[3] By reducing IMC growth rate and minimizing the grain boundaries, less stress and improved whisker reduction is realized.

Conventional methyl sulfonic acid based systems require hot rinsing with many stations to completely rid the surface of contamination. A standard line configuration may consist of a drag out rinse followed by a hot DI rinse followed by a second hot DI rinse in order to achieve acceptable ionic contamination values. Using Organic Metal predip in conjunction with a sulphuric acid based system requires fewer rinsing stations without heated water. In fact many lines consist of a single triple cascade rinse using ambient temperature water.

The course grain structure generated by Organic Metal predip also correlates to longer shelf life and improved soldering. Since there are fewer grain boundaries, there are fewer opportunities for copper migration to the surface. Copper oxides on the surface will result in a loss of soldering performance. The larger grain structure also retards the intermetallic growth formation. Tin coatings which use Organic Metal predip will typically have half the diffusion rate of conventional systems. Table 3

	Diffusion constant	Sn loss @ RT		
	for Sn @ RT	calculated for 1 month		
	[nm/s ^{1/2}]	[µm]		
Value for ImSn	0.160	0.26		
taken from [1, 2]				
	\frown	\sim		
Competitive Sn	0.144	0.23		
(no OM predip)				
ORMECON®				
CSN Classic	0.065	0.10		
(with OM predip)				
ORMECON [®]	\sim			
CSN Nano	0.058	0.09		

Grain Structure Improvement

Table 3

A lower diffusion rate of copper into tin means better soldering. As the intermetallic layer grows less free tin is available for protecting the substrate. Once the intermetallic layer breaks through to the surface of the pad, copper oxides will form and solderability will suffer. Some companies will promote a minimum of 0.2 microns of free tin are required for acceptable soldering [4]. Figure 5





With Organic Metals used in the system, acceptable soldering is obtainable with even less free tin, even down to 0.1 micron.

The use of Organic Metals in the predip lay the ground work for reducing the overall tin thickness. By using this material to initiate the reaction, it produces a tin coating that is more uniform in thickness and appearance while providing a grain structure more stable and less prone to solderability issues. By adding another process step, but still reducing the cycle time, we can then achieve a thinner coating with the same functionality as a thick coating.

ORGANIC METAL POST DIP

Use of different Organic Metal as a post dip provides protection of solderability through a very thin coating on top of the tin which passivates not only the tin, but any copper which may emerge from the intermetallic layer. This is a shift away from the conventional process which requires a minimum of 0.1 up to 0.2 microns of free tin above the intermetallic layer. The extra amount of free tin is required for copper protection embedded in the intermetallic layer. By adding an Organic Metal post dip, the need for free tin is negated. Excellent soldering results can be obtained with virtually no free tin available on the surface of the coating. Table 4

	Immersion Tin Process	Ormecon CSN Nanofinish
	1.2 µm	0.4 µm
Reflow Steps	Wetting Angle [°]	Wetting Angle [°]
0	15	8
1	25	35
2	30	40
3	45	50

Table 4

The ability to provide intermetallic protection means thin tin coatings can be used for soldering. A reduction of 60% of the tin thickness can be achieved and still produce a finish which is solderable and maintains its appearance through multiple lead free reflow cycles. A sign of the protection the Organic Metal post dip provides is colour stability of the thin immersion tin deposit. No discoloration is seen after 2 heat cycles, and only slight darkening is observed after paste is applied in the third heat cycle. Figure 6



Figure 6

This colour stability at a nominal 0.40 micron thick tin coating, is achieved through copper oxidation prevention. If copper oxides were present a brownish appearance would be seen. Copper oxidation states before and after reflow as compared to conventional thick immersion tin are similar. Figure 7



Figure 7

PROCESS CHANGES

With the use of Organic Metal in both the pre dip and the post dip portions of the line, significant changes can be made to the process to further improve board quality and production costs. The preclean and post clean portions of the line remain the same, but the tin plating cell dwell times and temperatures are changed. Table 5

Acid Cleaner	Acid Cleaner		
Microetch	Microetch		
• Pre Dip	• Pre Dip		
Immersion Tin Bath	Immersion Tin Bath		
(63 – 68 °C / 20 – 25 min)	(45 – 52 ℃ / 6 – 8 min)		
Rinse Aid	Post Dip		

Table 5

CYCLE TIME IMPROVEMENTS

By reducing the tin thickness to 0.40 microns significant improvements in cycle time can be achieved. A standard immersion tin process cycle time will vary from 32 to 38 minutes including pre and post treatments of the tin deposit. Cycle time will vary as the immersion tin bath ages. Older baths will require longer dwell times as Sn (IV) accumulates. Actual tin bath dwell times will range from 20 to 25 minutes to achieve 1 micron of tin thickness. By reducing the overall thickness to 0.4 microns, dwell times for the immersion tin step can be reduced to 6-8 minutes. This equates to a 67% reduction in plating time and an overall reduction of cycle time by 38%.

EQUIPMENT CONSIDERATIONS

The reduced cycle time has immediate improvement in equipment utilization. If a vertical line is being employed to produce immersion tin boards, throughput can immediately be increased by 38% without any additional capital expenditures. Even if a line is not fully utilized, improved cycle time will reduce labor costs as more work can be produced in shorter periods of time. If a horizontal line is being considered, reduced plating time significantly reduces the equipment length and costs. A standard 1.0 meter per minute line will be 42 meters long. By reducing the plating time to 6-8 minutes, the main plating chamber can be reduced in length from 20.4 meters to 8.2 meters. This results in a line which is significantly shorter and less costly. The new line configuration would now be less then 30 meters long.

ADDITIONAL BENEFITS

One of the major considerations to successfully running thick immersion tin is soldermask adhesion. Immersion tin baths are notorius for soldermask attack. When a company runs immersion tin, usually special process enhancements are made in the soldermask process to withstand the immersion tin bath chemistry. These changes can include chemical pretreatments which are expensive and add another layer of control and variability to the final product, increasing soldermask thickness which adds costs or running different masks for different finishes. These extra considerations add cost to the final product. By reducing dwell times in the tin bath, the need for extra soldermask improvements is eliminated. This will reduce cost and improve reliability of the final product.

Another benefit for reduced thickness is reduced chemical maintenance costs. Immersion tin coatings are generated by removing 2 copper atoms and replacing them with one tin atom. By reducing the tin thickness by a nominal 60%, we are also reducing the amount of copper generation by 60%. This means longer bath life at a more stable plating rate without adding extra equipment or chemical maintenance steps which only add costs and reduce efficiency.

CONCLUSIONS

The use of Organic Metals in the immersion tin process have many benefits. These benefits include enhanced tin grain structure, copper passivation, uniform plating initiation for excellent plating distribution. By incorporating Organic Metals into a post dip, improvements can be made in cycle time, operating costs, labor costs, equipment costs, floor space, product reliability and quality. Thin immersion tin coatings generated with Organic Metals are more efficient and produce the same reliability as thick immersion tin.

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REFERENCES

[1] Prismark Summary Report, PCB Final Finish, July 2009

[2] B. Wessling, Handbook of Conducting Polymers (T. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, eds.). Dekker, New York, (1998).

[3]Yung-Herng Yau, Cai Wang, Robert Farrell, PingPing Ye, Ed Kudrak, Karl Wengenroth and Joseph Abys, Properties of a Newly Developed Immersion Tin Coating, February 2008

[4] Sven Lamprecht, <u>Investigation of the Recommended</u> <u>Immersion Tin Thickness for Lead Free Soldering</u>, Atotech, 12/19/2003