A Superior Whisker-Reducing Immersion Tin Technology

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In order to maintain the solderability of printed circuit boards during storage, it is necessary to protect the Copper surface mount pads with a solderable surface finish. Immersion Tin is one of the materials used as a PCB surface finish. It is expected that the use Immersion Tin as a surface finish will grow substantially and become a high volume technology, especially in the course of the global switch to Lead-free processes following the Reduction of Hazardous Substances (RoHS) and the Waste Electrical & Electronic Equipment (WEEE) directives. Moreover, the further miniaturisation of structures and high volume production of PCBs require advanced alternative surface finishes.

With the growing global demand for Immersion Tin, the requirements placed on product and process technology are increasing significantly. Market leading OEMs require surface finishes with increased Tin thickness, improved solderability at multiple cycles and higher temperatures, enhanced surface flatness, fine pitch compatibility and – ever more important – limited whisker growth. Immersion Tin can meet these requirements and has proven its advantages with market leading PCB manufacturers.

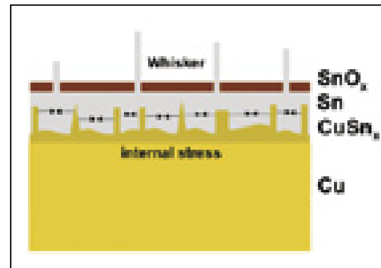


Figure 1 – Diagram illustrating whisker formation process

When talking about immersion Tin as a final surface finish for PCBs, whisker growth is a topic of concern. Ormecon International has spent a significant amount of time and resources investigating the whisker formation phenomenon and its prevention. Based on this experience, the company has developed a whisker-reducing immersion Tin product: Ormecon CSN FF-W. All chemicals used are Lead-free and halogen-free.

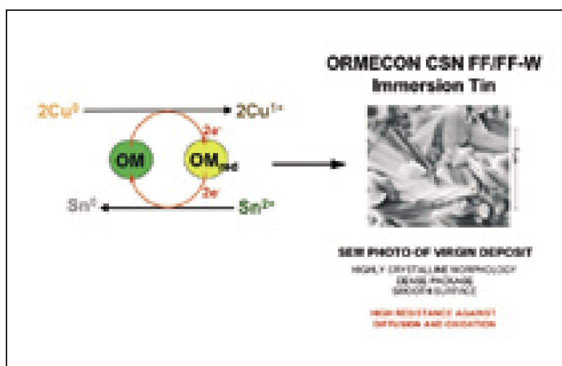
This product, as well as the already established Ormecon CSN and the recently introduced CSN FF, are based on the Organic Metal Polyaniline, which is responsible for a completely different deposition mechanism and Tin layer structure. This is due to the fact that the Organic Metal not only passivates the Copper (and later the Tin), but also exclusively forms Cu(I) cations and transfers electrons to the Sn(II) ions for the reduction and deposition, thus acting as a catalyst.

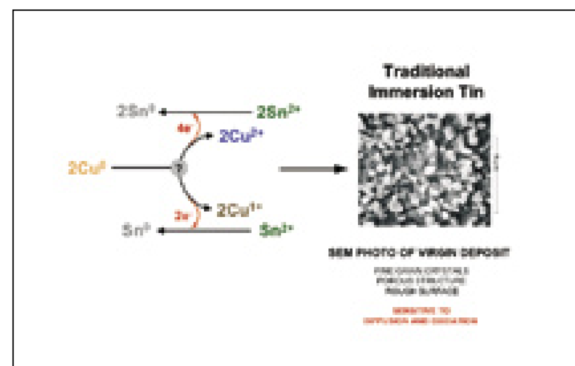
Whisker formation phenomenon and preventive actions

Whisker formation is a typical feature of metallic Tin. There can be two kinds of whisker phenomena: at the component itself and also at the Tin surface finish. Various factors can cause whisker formation. One key factor is internal stress. There are two stress categories:

- compressive stress, which drives the whisker growth, and
- tensile stress, which reduces the propensity of whisker growth.

Internal stress mainly develops during storage as a result of diffusion processes at the Cu-Sn boundary. With Tin plated over Copper, compressive stress is built up, because Copper diffuses much faster into Tin than Tin diffuses into Copper. With continuous diffusion over time, compressive stress increases in the Tin layer. Most often the presence of tin oxides prevents the stress from being released. However the tin oxide layer is never





Figures 2 and 3 – Ormecon Immersion Tin deposit reaction vs. standard immersion Tin reactions

perfect (defects are the norm) and when the internal stress becomes high enough, it will break through the defect in the oxide layer and a whisker can form to release the stress (Figure 1).

The products currently available on the market for whisker reduction are mainly based on reduced Copper-into-Tin diffusion because of the more compact nature of the Tin layer. Also whisker reducing effects are produced by a Silver layer on top of the Tin layer. Such products, however, do not satisfy some of the more stringent “whisker reduction” specifications. Some manufacturers require no whiskers with a length of more than 20µm and even less.

The Silver-topped Tin layer is relatively expensive, as it requires an additional process step and a significant amount of Silver. Therefore, a new Immersion Tin product and process technology for whisker reduction is necessary to meet all the requirements of the market leading OEMs and PCB manufacturers.

The new reduced whisker Tin layer

As in Ormecon CSN and Ormecon CSN FF, the pre-dip of the Ormecon CSN FF-W product contains the Organic Metal in aqueous dispersion, which catalyses the Tin deposition resulting in a very dense Tin layer with a big grain size morphology. Figures 2 and 3 show the difference between the Ormecon Immersion Tin deposit reaction compared to standard immersion Tin reactions.

The key benefits of the Ormecon deposit are:

• A large grain size Tin layer is thermodynamically more stable than Tin with a small grain size and it is less susceptible to re-crystallization. It is therefore more difficult to “squeeze” out a whisker from a large grain size Tin.
• A large grain size Tin layer furthermore reduces the speed of Copper diffusion, and thus less stress is produced compared to a rapid diffusion of Copper into a small grain size Tin.
• The big, flat Tin crystals of an Ormecon CSN FF / FF-W finish offer significantly less room (pores) for impurity inclusions compared to a small grain size Tin deposit. The small Tin grain size compared with the Ormecon large Tin grain size contains more pores (Figure 4).

However, as documented in Table 1, this is sometimes not sufficient. Therefore, Ormecon has completely changed the layer structure by adding an additional whisker inhibiting ingredient in the pre-dip process step. This can be selected from various metal ions. In the new product Ormecon CSN FF-W, Silver is used. Thereby a metal alloy nanolayer (10-20nm) containing Ag and Cu is formed on the Copper surface, again induced by the action of the Organic Metal catalyst. The subsequent Tin layer deposition is then carried out in a way that a new sandwich layer structure is set-up. There is a precisely defined Tin layer on top, followed by a broader intermetallic layer. All layers show a much smoother concentration gradient than in other types of Tin surfaces. Such a new sandwich layer construction has proven to have a superior characteristics in all respects. Based on Secondary Ion Mass Spectrometry (SIMS) (Figure 5), it was possible to prove that:

• Sn can be found at a much greater depth in the Cu layer (up to 3 µm or more) compared to standard immersion Tin products, where Sn can only be found up to about 1.5µm deep;
• Cu can be found directly at the surface (in very low concentrations) in contrast to standard products, where Cu is only present starting at a depth of about 0.8 to 1 µm;
• Ag is not present in the form of a separate layer, not even below the Tin layer (which was deposited after Ag deposition), but everywhere in the Tin-Copper and more deeper in the Copper-Tin alloy, with a maximum concentration slightly below the surface;
• the concentration of all three metals gradually changes with increasing depth.

The fact that Ag is not present in form of a separate layer eliminates the risk of Silver migration over time.

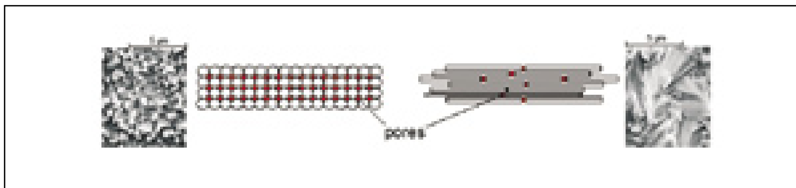


Figure 4 – Diagram of pores of small grain and large grain Tin finishes

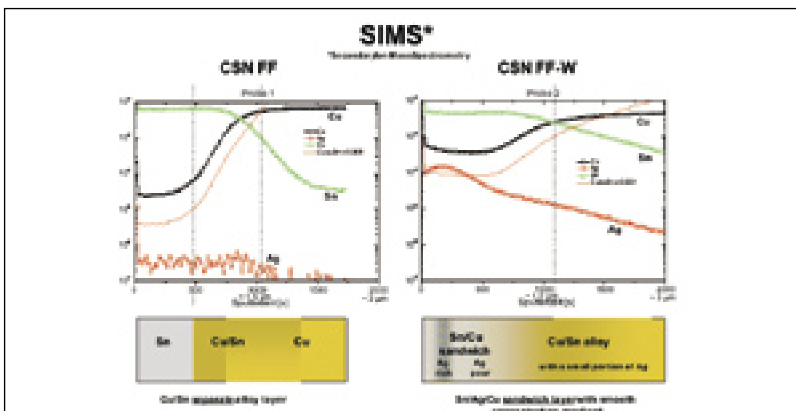


Figure 5 – SIMS results showing diffusion of Tin, Silver and Copper in various sandwich structures

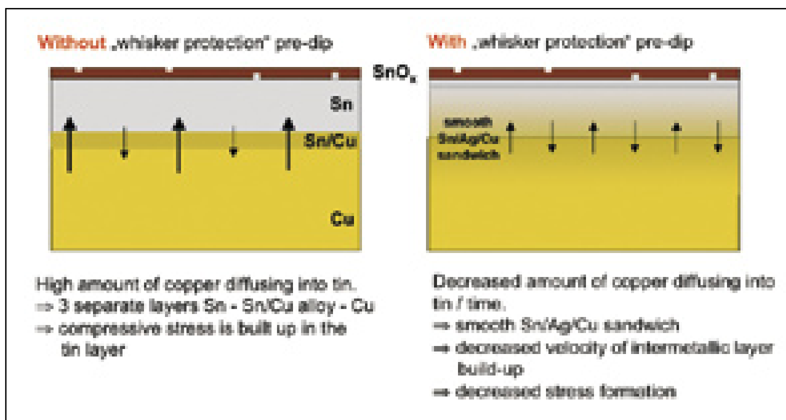


Figure 6 – Layer structure with and without the "whisker protection" pre-dip step

Figures 6 shows the difference in the layer structure resulting from the use of standard immersion Tin products and the new whisker preventing sandwich layer structure. The concentration gradient of both Cu and Sn is much less steep compared to the previous layer structures. Diffusion is dramatically reduced because of the fact that the concentration of Cu in Sn in the surface regions and of Sn in Cu in the deeper regions is relatively high to begin with. This fact, together with the ennobling effect of Ag and the Organic Metal, is also the reason for the extremely good solderability and ageing behaviour of the Immersion Tin layer.

Product	Storage time 7 weeks whisker size	Storage time 14 weeks whisker size
ORMECON CSN FF-W	No whisker	No whisker
ORMECON CSN FF	few 20 - 30 µm	Not measured
Product A	many > 100 µm	Not measured
Product B	many 20 - 30 µm	Not measured
Product C	several 20 - 30 µm	Not measured

Table 1 - Whisker formation with various Immersion Tin surface finishes

This new sandwich structure effectively reduces and even prevents whisker formation, as shown in Table 1, because less stress is induced due to the much lower diffusion of both Cu and Sn. This innovative process fulfils the requirements of several currently implemented OEM whisker reduction specifications. The product was introduced in 2004 with some high volume PCB manufacturers. The PCB manufacturers choosing to apply Ormecon Immersion Tin technologies can easily change between the standard immersion Tin product Ormecon CSN FF and the high-performance, whisker reducing immersion Tin product Ormecon CSN FF - W. The difference between such two products is only the pre-dip step.

Solderability

Due to the deposition process (using noble Organic Metal and noble Silver), the resulting Silver-containing sandwich composition and the compact and big crystal grain size structure, the ageing behaviour of this surface finish has proven to be superior. The diffusion rate of Cu into Sn at 155 °C is even lower (less than 3.3 nm/s) than in Ormecon CSN and Ormecon CSN FF (around 4.0 nm/s, which is significantly lower than with any other conventional immersion Tin technique). Oxidation is also strongly reduced. Consequently, after thermal ageing and / or multiple solder steps, the solderability is preserved to a superior degree. In particular:

- electrochemical analysis (GCM, SERA) shows remaining pure Tin is about 0.2 – 0.5 µm thick (depending on starting Tin layer thickness and ageing conditions);
- solder tests with a meniscograph show a wetting angle of less than 55° after ageing or multiple reflow;
- wave solder tests show complete solderability after thermal ageing and / or multiple solder steps (reflow).

For the electrochemical Tin layer thickness measurements (GCM or SERA), samples with comparable virgin Tin layer thickness were made: 0.58 µm for both Ormecon CSN FF and FF-W. After thermal ageing at 155°C for 4 hrs, a Tin thickness of 0.17 µm remains on the standard surface, whereas for the new FF-W, a thickness of 0.24 µm remains, corresponding to the lower diffusion rate.

Process description

Figure 7 shows the process technology of the two products. For an accurate process control, Ormecon International recommends the measurement of the layer thickness with the coulombmetric measurement system (GCM, SERA), before and after aging.

Figure 7 – Process technology for CSN FF and CSN FF-W