

The Evolution of Organic Solderability Preservative (OSP) Process in PCB Application

K. H. Tong, M. T. Ku, K. L. Hsu, Q. Tang, C. Y. Chan and K. W. Yee

Dow Electronic Materials
The Dow Chemical Company
Hong Kong, China

ABSTRACT

The implementation of Restriction of Hazardous Substances Directive (RoHS) in 2006 has led to a requirement that soldering materials used in the fabrication of printed circuit boards (PCBs) should be lead-free. This change has raised the peak reflow temperature by 30 °C as compared with a tin-lead process. A protective surface finishing should be designed to maintain good solderability, by preventing the copper surface from being oxidized, both during storage after PCB fabrication and during exposures to soldering temperatures. Organic solderability preservative (OSP) is considered as a preferred low cost surface mount technology (SMT)-compatible non-metallic surface finishing method, due to the excellent surface co-planarity of the coated pads. However, the protectiveness of some commercial available OSPs is still poor and their solderability performances are always deteriorated after the multiple lead-free reflow cycles.

This article presents experimental data to illustrate the newly developed OSP coating in terms of thermal resistance, copper diffusion suppression and solderability.

INTRODUCTION

Printed circuit boards (PCBs) require electronic components to be attached to surface pads or through holes by a soldering operation. Leaded components can be inserted into through holes followed by a wave soldering operation, or surface mount (SMT) components can be attached to surface pads using screened solder paste, followed by reflow soldering. For SMT assembly operations, a minimum of two reflow cycles are required, in order to attach component both to the front and back of the PCB. For more complex assemblies, additional reflow operations may be required to attach additional components or to carry our repair operations.

The copper surfaces of the PCB pads to which components will be mounted are typically coated with a protective finish (metallic or non-metallic). Such protective finishes are designed to maintain good solderability, by preventing the copper surface from being oxidized, both during storage after PCB fabrication and during exposures to soldering temperatures.

Over the past twenty years, Organic Solderability Preservative (OSP) processes have maintained the largest share of the printed circuit board (PCB) final finish market due to their low cost, suitability for SMT solderability applications (due to the thin, uniform surface film), simple process equipment and capability for continued performance improvement based on incremental modifications of the original active species [1].

OSP used in the PCB market are predominantly based on azole compounds, such as benzotriazoles, imidazoles, benzimidazoles and their derivatives [2] (Figure 1). All these N-heterocyclic compounds adsorb on copper surfaces, via the formation of coordination bonds with copper atoms and have the capability to form thicker films through formation of copper (I) – N-heterocycle complexes. OSP film formation needs to be copper-specific, with much lower rate of film formation on gold or other surfaces, in order to prevent contamination of these substrates during the film formation process on copper.

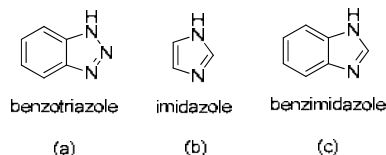


Figure 1. Structures of azole compounds used for OSP (a-c)

The ability for OSP processes to continue to evolve, generation by generation, to meet increasingly stringent performance requirements resides in the diversity of derivatives of N-heterocyclic compounds that have been synthesized. At the present time, azole compounds for OSP processes have gone through at least four generation, as described in Figure 2.

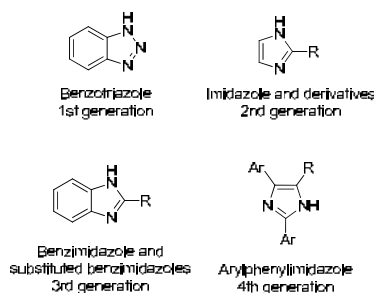


Figure 2. Representative structures of different generations of OSPs

A copper tarnish prevention product, based on benzotriazole, was first used as an OSP in the 1960's [3]. The thickness of the benzotriazole film formed on copper is low, usually less than 10 nm. In addition, the decomposition temperature of the benzotriazole-copper complex is reported to be very low (around 75 °C) meaning that the coating might only allow one or perhaps two thermal reflow cycles. In addition, this type of formulation does not provide any coating selectivity between copper and other metal surfaces such as gold.

Second generation OSP products [4] using alkyl substituted imidazoles as the active component, were introduced in 1977. These

materials formed OSP films with thicknesses above 200 nm, but had relatively poor stability at higher temperatures.

The third generation, substituted benzimidazoles, formed by fusing a benzene ring to the imidazole ring, was first applied for use as the active component in OSP products in 1990 – 1991 [5], although the use of that class of compounds for copper corrosion protection was described earlier by AT&T [6]. Other benzimidazole-based active materials have been widely used as the main component in many commercial products [7,8]. Benzimidazole derivatives form films on copper very efficiently, with thickness varying from 10 to 100 nm. The coating thickness can be further increased to as much 500 – 600 nm by addition of appropriate metal ions to the working solution.

Typical film thickness for the commercial available OSP coatings is around 200 to 350 nm. However, such formulations still lead to film formation on gold surface. The thermal resistance of these coatings is substantially better than the earlier products, with film decomposition beginning around 250°C.

The shift towards lead-free soldering in the PCB assembly industry that had emerged in Japan in the 1990's was accelerated by the requirements of the 2003 RoHS Directive [9,10]. This change raised the required peak reflow temperature by 30 °C as compared with a tin-lead process.

Driven by these requirements, a fourth generation of OSP was developed, based on the use of aryl phenyl imidazoles as the active components [11,12]. The thermal resistance of these organic-copper complexes is significantly higher, with decomposition temperature beginning around 350 °C. This leads to extremely high film stability on copper, at thicknesses in the range of 100 to 300 nm.

Several different approaches have been used by suppliers to reduce OSP film formation on gold surfaces. In 2003, the use of a benzimidazole derivative containing predip composition which accelerates subsequent OSP film formation on copper surfaces was patented [13]. The accelerated film formation allows the use of lower concentrations of active material in the main OSP bath; thus reducing the film formation on gold surfaces. Approaches based on modifications to the main bath formulation have also been found to be effective with commercial products based on the use of an iron additive [14].

In order to develop a new generation of OSP, a new series of N-heterocyclic compounds, with higher thermal stability and better coating selectivity, have now been applied to OSP applications.

EXPERIMENTAL

Samples Preparation

A standardized test panel design was used for the OSP process characterization in our study. The substrate has different pad sizes and it is designed for SMT assembly simulation test. It also has 1 × 20 mm² strip pads features suitable for solder spread test and 0.47 mm diameter BGA pad features suitable for ball shear test.

The new OSP samples (OSP-N) were prepared in the pilot line. Prior to the coating process, standard copper surface cleaning and etching steps appropriate for OSP were carried out.

Coating Thermal Resistance

The solderability performance of protective coatings was often assessed by visual inspection of the copper appearance after baking or reflow cycling. Discoloration is normally attributed to oxidation of copper due to inadequate surface protection. Samples were passed through a lead-free IR solder reflow cycle for five and nine times under atmospheric condition without purging any nitrogen gas. Following treatment, the sample appearance was recorded and compared with the corresponding as-received samples. X-ray Photoelectron Spectroscopy (XPS) was employed to analyze the elemental surface composition after thermal treatment. Two commercial OSP samples (OSP-A and OSP-B) were prepared in production lines and their coating thermal stability was compared with our new OSP coating.

SMT Assembly Simulation Test

In order to obtain information about the performance of the coatings in reflow assembly conditions, an assembly simulation test was performed.

Kester EM 907 (SAC 305, ROL0) solder paste was screen printed onto panel surface and then reflowed in a production reflow oven with a lead-free reflow profile under atmospheric condition. The reflow cycle peak temperature was 255 °C. The screened pattern consisted of a number of arrays with two different sizes of rectangular features (1×4 mm² and 1×2 mm²). The percentage of features which exhibited good solder wetting to the substrate were assessed visually and recorded. In addition to an as-plated sample, other panels were baked at 150 °C for 4 hours before solder paste printing.

Solder Ball Spread Test

The wettability of the OSP deposits was evaluated using Solder Ball Spread Test.

Prior to attachment of 0.63 mm diameter SAC305 (tin / silver 3% / copper 0.5%)¹ lead-free solder balls, Alpha WS 609 (ORH0) flux gel was applied to the 1 × 20 mm² strip pad surfaces. The panel was processed through a reflow oven using a lead-free profile with peak temperature of 260 °C under atmospheric condition and the spread length of the solder ball was recorded. In addition to an as-plated sample, other panels were exposed to different pre-conditioned processes before ball attachment.

Ball Shear Test

The strength of solder joints formed on the OSP deposits was evaluated using Ball Shear Test.

Prior to attachment of 0.63 mm diameter SAC305 (tin / silver 3% / copper 0.5%)¹ lead-free solder balls, Alpha WS 609 flux gel was applied to the pad surfaces. To form the bond between the copper surface and solder, the panel was processed through a reflow oven using a lead-free profile with peak temperature of 260 °C under atmospheric condition. In addition to an as-plated sample, other panels were exposed to different pre-conditioned processes before ball attachment.

A Dage 4000 Bond tester was used to evaluate solder ball shear force. The test speed and shear height were set at 200 μm/s and 100 μm

¹ Sharemate Technology (Dongguan) Co. Ltd.

respectively. The shear force and the fracture interface location were recorded for each location tested.

Coating Selectivity

For applications in which OSP is applied to substrates that already have other surface finishes such as ENIG applied to some pads, it is necessary that the OSP have good selectivity to deposit only on copper and not on the other surface finishes. This prevents formation of organic films on the other surface finishes that might interfere with their functionality [15].

Test substrates were prepared with ENIG process² (Ni thickness: 5 μm; Au thickness: 0.05μm) and then proceeded to OSP process. Following the treatment, the sample appearance was recorded and compared with the corresponding as-received ENIG samples.

RESULTS AND DISCUSSION

Table 1 shows that, for copper coated with the newly developed OSP coating (OSP-N), discoloration was insignificant after 5× and 9× thermal reflow cycles. For commercial products like OSP-A and OSP-B, significant discoloration was found after 5× and 9× reflow cycles. The change of color indicated that oxidation had occurred on the copper surface.

	OSP-N	Commercial Product OSP-A	Commercial Product OSP-B
As-plated			
After 5x reflow			
After 9x reflow			

Table 1. Surface appearance of different OSP Coatings under as-is, 5× and 9× thermal reflow cycles.

Solderability is mainly determined by the surface oxidation and the activity of the applied flux. Therefore, XPS is always a good indicator to evaluate the oxygen and copper contents change in the coating caused by thermal reflows. In Table 2, OSP-N shows excellent barrier against oxygen permeation and copper diffusion and low oxygen and copper content increase in the coating after the thermal reflows. This could be the reason why insignificant discoloration was found in OSP-N coating after the reflow cycles. For commercial available products like OSP-A and OSP-B, significant amount of oxygen and copper were found in their coatings after the thermal reflows, implying that the protectiveness of these coatings were insufficient.

² TM Trademark of The Dow Chemical Company (“Dow”) or an affiliated company of Dow DURAPOSIT™ SMT 88 Electroless Nickel / Interconnect Technologies AUROLECTROLESS™ SMT 520 Immersion Gold / Interconnect Technologies

SMT assembly simulation test was used to evaluate the solderability of OSP coatings. Table 3 summarizes the test results. Excellent solder coverage both in as-plated and aged samples was observed. Besides, the solder ball spreadability was compared between as-plated and different pre-conditioned samples and the test results were summarized in Figure 3. It was showed that the spreadability was good and there was no significant difference against aging.

	OSP-N		Commercial Product OSP-A		Commercial Product OSP-B	
	5× reflow	9× reflow	5× reflow	9× reflow	5× reflow	9× reflow
Thermal Reflow	5× reflow	9× reflow	5× reflow	9× reflow	5× reflow	9× reflow
Oxygen Content	0.2	1.1	3.3	3.3	2.8	3.7
Copper Content	0.2	2.9	10.9	8.6	3.7	4.1

Table 2. Weight percentage change of oxygen and copper contents by different thermal reflows

	Solder Coverage Photos (1x4 mm, 84 pads; 1x 2mm, 150 pads)	Solder Coverage (%)
As-plated		100
After 5x Reflow		100
After 9x Reflow		100
Baking 150°C 4hr		100

Table 3. SMT assembly simulation test on OSP-N

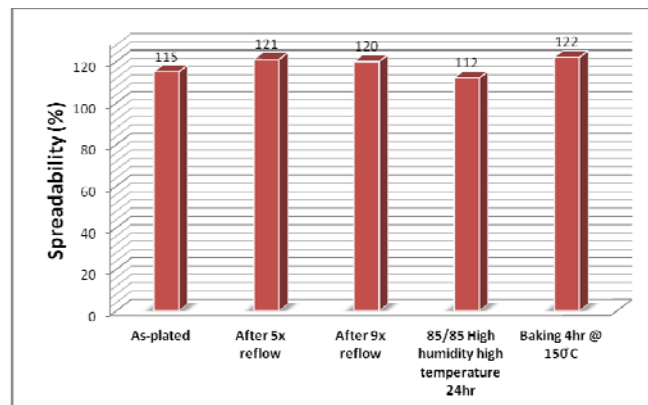


Figure 3. Solder ball spread test on OSP-N

Ball shear test were performed to measure the solder joint performance of the OSP deposits. Thirty measurements were made for each ball shear test conditions. Figure 4 shows the average shear forces obtained from as-plated samples and samples exposed to different pre-conditioning conditions. The values of force were high and no significant change in shear force was observed for as-plated and different pre-conditioned samples, implying that the quality of the deposits was good.

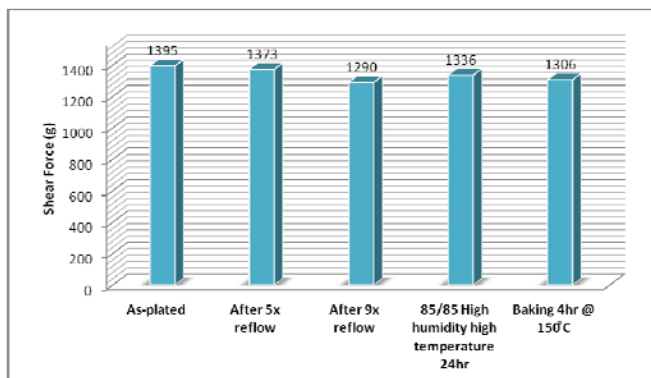


Figure 4. Shear force results for ball shear test on OSP-N

The fracture mode was also recorded during the ball shear tests. In all cases, the failures occurred within the solder, rather than in the IMC layer at the solder joint interface, showing that all the samples had good solder joint formation with SAC305 alloy. Figure 5 shows the microscopic images of sheared pads for as-plated and pre-conditioned samples.

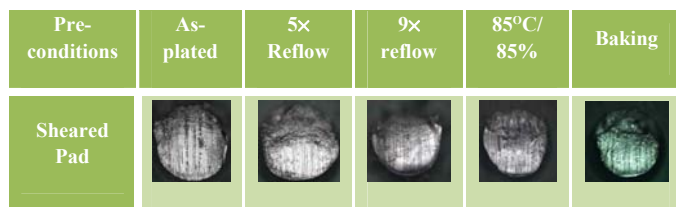


Figure 5. Microscopic images of sheared pad for as-plated and pre-conditioned samples

Coating selectivity of the new OSP process was good and no appearance change was found on the ENIG surface after OSP process. Figure 6 showed the results of the coating selectivity. Golden appearance was observed after OSP-N process.

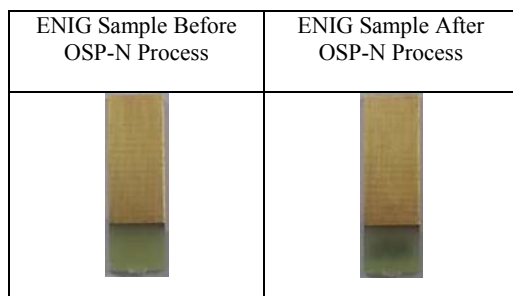


Figure 6. Results of coating Selectivity test on OSP-N

CONCLUSION

As the assemblies become more complex, additional reflow operations may be required to attach additional components or to carry our repair operations. A novel organic solderability preservative process with good protectiveness on the copper surface is needed in the industry. Our new OSP coating is a good oxygen barrier and demonstrated excellent thermal resistance and solderability after multiple lead-free thermal reflow cycles and different aging conditions. It has been proven to have good coating selectivity and compatible to selective ENIG process.

REFERENCES

- [1] "The evolution of organic solderability preservative (OSPs) from a temporary protectant to a leadership position in surface finishing chemistry", M. Carano, *Circuit World*, 37(2), 12 – 19, **2011**.
- [2] "Copper corrosion inhibitor: a review", M. M. Antojjevic and M. B. Petrovic, *International Journal of Electrochemical Science*, 3, 1-28, **2008**.
- [3] "Application model for organic solderability preservative", G. M. Wenger, D. A. Machusak and J. L. Parker, *Soldering and Surface Mount Technology*, 7(2), 6-9, **1995**.
- [4] "Method of rust preventing for copper and copper alloy", N. Sawa, M. Hoda, Shikoku Chemicals Corporation, US 3,933,531, **1976**.
- [5] "Process for surface treatment of copper and copper alloy", M. Kinoshita, T. Murai, T. Yoshioka, Shikoku Chemicals Corporation, US 5,173,130, **1992**.
- [6] "Copper corrosion inhibitor", N. Hobbins, R. Roberts, Bell Telephone Laboratories, US 5,395,294, **1983**.
- [7] "Composition and process for treatment of metallic surface", W. Adams, C. Newcomer, G. Larsen, MacDermid Inc., US 5,362,334, **1994**.
- [8] "Composition and process for treatment of metallic surfaces", P. Kuskansis, MacDermid Inc., US 5,376,189, **1994**.
- [9] DIRECTIVE 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment.
- [10] "Implementing Lead-free Electronics", J. S. Hwang, McGraw-Hill Professional, **2004**.
- [11] "Agent for treating surfaces of copper and copper alloys", H. Hirao et al., Shikoku Chemicals Company, US 5,560,758, 1996.
- [12] "Method for forming a protective chemical layer on copper or copper alloys", H. Hirao et al., Shikoku Chemicals Company, US 5,560,785, **1996**.
- [13] "Process for selective deposition of OSP coating on copper excluding deposition of gold", K. F. Wengenroth, Enthone Inc., US 6,524,644 B1, **2003**.
- [14] "Surface treating agent for copper or copper alloy", H. Hirao, K. Kikukawa, US 5,795,409, **1998**.
- [15] "New trends for PWB surface finishes in mobile phone applications", C. W. Nielsen, A. A. Rasmussen, *Pan Pacific Symposium Conference Proceedings*, **2006**.