"Behind the Scenes" of Effective OSP Protection in Pb-free Processing

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Abstract

Advancements and evolutions in printed circuit board manufacturing, design, and electronics assembly have driven new research on high temperature organic solderability preservative (HT OSP) surface finishes. More specifically, developments in OSP chemical processes are aimed at producing a durable finish which ensures that a board surface retains solderability through more challenging and harsh Pb-free assembly conditions. From this, it is clear that advancements in OSP processing and coating performance require a solid understanding of the mechanisms associated with coating formation and thermally driven degradation. This work examines and describes OSP structure and composition and how it is affected by heat treatments. Additionally, mechanisms of degradation of OSP are proposed along with possible strategies to remedy it.

Introduction

Organic solderability preservative (OSP) is one of the most common final finishes in the PCB industry today. In addition to its ever attractive characteristics of low cost and a relative ease of application, perceived or real issues with other final finishes contribute to OSP's appeal. For some fabricators OSP is the preferred final finish.

However, Pb-free processing is a challenge for OSP. Not only assemblers have been forced to optimize their soldering processes but also OSP vendors have reformulated their products in order to meet the challenge as well. In this paper, we attempt to examine the attributes and makings of a good high temperature (HT) OSP process and coating.

There are several of these attributes that one may wish to consider and several technical ideas or claims have been made. Under discussion are: type of azole, which is the primary chemical constituent of OSP, its volatility, its decomposition temperature, existence of an organometallic polymer between the azole and a metal other than copper. It may be hard to see how these correlate with better solderability. On the other hand, we have found out that some other properties and phenomena occurring in the OSP coating may be of greater importance.

Structure of OSP Coating

Molecular Network or Not?

It is common to present OSP structures as networks of azoles with copper in 1:1 ratio. It is unclear if modern OSP baths utilizing other metals (M) such as zinc or iron still form Cu-azole networks or M-azole networks. We have argued before that our OSP bath did not form such a network because chemical analysis of the coating showed a very different stoichiometry, approximately 1:10, M-azole. It is also chemically unlikely to obtain a Cu-azole network in excess of 2-3 layers in thickness, even though Cu-azole stoichiometry was found to be close to 1:1. This is because it would be a unique example of chemical self-assembly. More importantly, nobody has presented an experimental proof of existence of such a network.

What is chemically feasible then? It is said that a Cu surface to be coated with OSP needs to be rich in ionic Cu for coating to take place. In other words, azoles have a high affinity for oxidized Cu^{I}/Cu^{II} surface and not Cu^{0} metal. When such a surface is immersed in a typical modern acidic OSP bath the oxidized layer almost surely dissolves but perhaps not entirely. The undissolved part serves to chemisorb azole molecules from the bath; the dissolved ionic Cu may partially be incorporated in the coating and partially dispersed in the bulk of the OSP bath. This last process is observed experimentally: OSP baths do build up Cu with time.

Dynamic SIMS Measurements

We attempted an experimental confirmation of this structure and ran Dynamic SIMS measurement of an OSP coating looking at concentrations of carbon, oxygen and copper as a function of depth. Oxygen was of interest because it is reasonable to assume that the Cu^{I}/Cu^{II} layer contained oxide prior to OSP coating. It is not clear whether it is completely transformed into a Cu^{I}/Cu^{II}-azole layer or some oxide is retained at the interface.

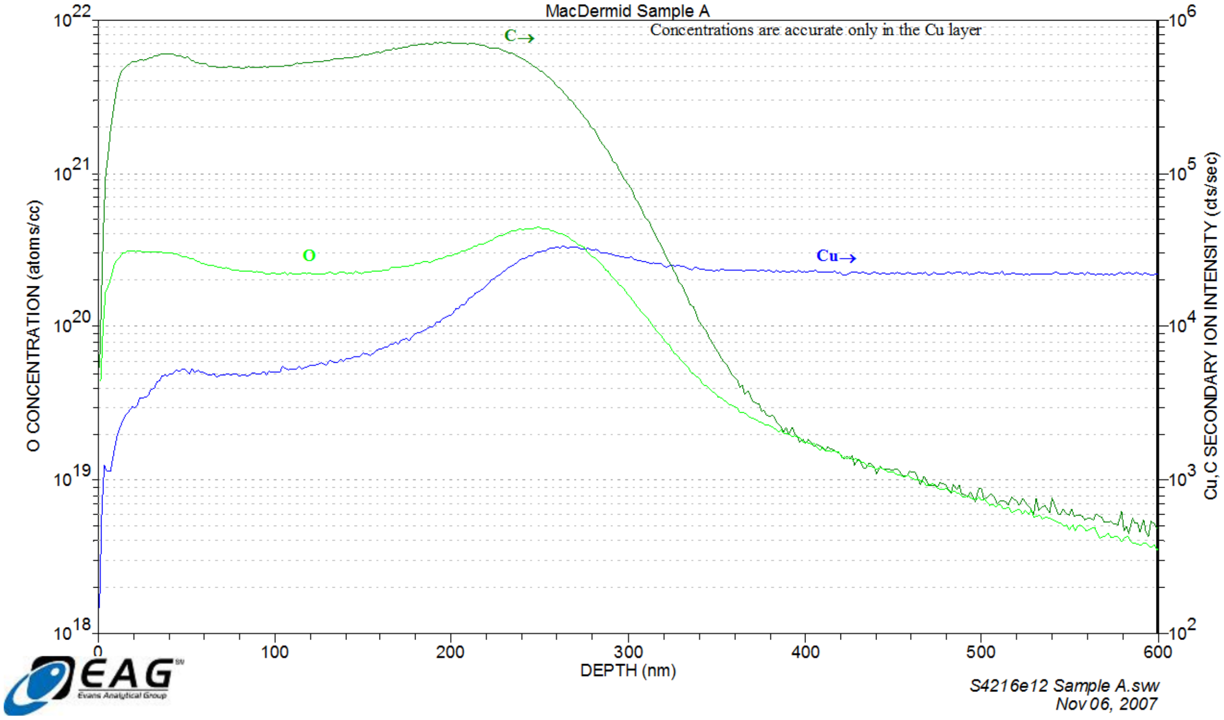


Figure 1. Profiles of C, O and Cu Concentrations Within As Coated OSP Layer Obtained by Dynamic SIMS.

The graph in Figure 1 shows that:

- the Cu concentration gradually decreases from the depth of approx. 0.26 µm (presumed OSP thickness); this means that the distribution of Cu within OSP is not uniform,
- there is a noticeable O rich layer at the Cu-OSP interface; this could be from Cu^{I}/Cu^{II} oxide or from an O richer additive deposited at that interface.

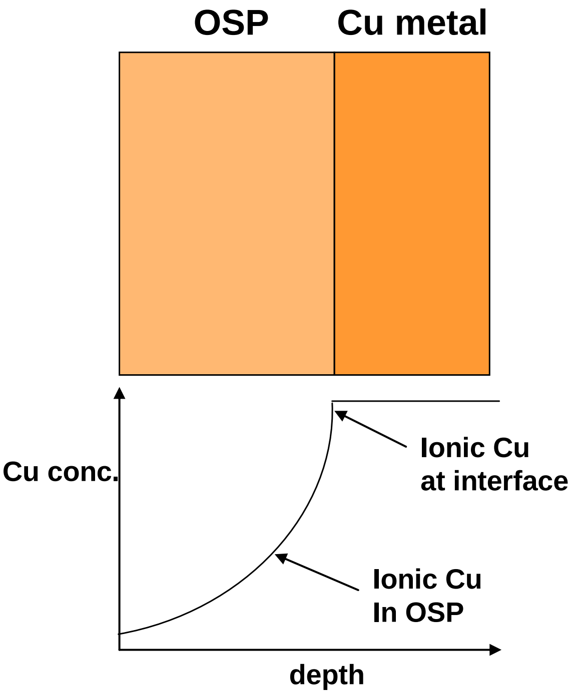
Stripping OSP with Organic Solvents

It is well known that OSP coatings can be stripped (dissolved) with dilute acids like 5% HCl or its mixture with alcohol. We investigated how well other solvents strip OSP and analyzed the stripped solution for azole and Cu concentration. The results (Table 1) are compared with the results obtained with the standard stripper, 5% HCl. This standard stripper is assumed to dissolve the entire OSP coating and all strippable (oxidized or ionic) Cu.

Table 1. Relative Amounts of Azole and Cu in OSP Stripped With Different Solvents.

Stripping Solvent	Azole (µmol/50 cm^2)	Cu (µmol/50 cm^2)
DMSO	7.2	1.5
DMF	7.2	2.1
M-Pyrol	7.5	2.4
IPA	5.9	0.90
5% HCl	7.0	3.9

Because the values of azole concentrations in organic solvent strippers except IPA are very similar to that from 5% HCl these organic solvents were able to dissolve the entire organic coating. However, the Cu concentrations in stripped organic solutions were significantly lower than for the 5% HCl stripper and it was the lowest for IPA. Our interpretation of the observed results is that the organic solvents used were not able to strip the Cu rich layer at the interface with Cu metal were the chemisorption took place. This layer presumably contains a very small amount of azole but is rich in Cu. Thus, we propose the following structure for OSP:



The organic layer is thought to contain a varied ionic Cu concentration at different depths and this concentration is presumably progressively lower from a high value at the Cu-OSP interface out to the surface. No data is available about concentrations of bath additives that are known to become entrained in the organic layer but it seems reasonable to assume that they are dispersed more uniformly, i.e. at constant concentration throughout the layer. The presence of ionic Cu within the OSP layer lowers its solubility in organic solvents. The weakest IPA solvent was able to dissolve a significant portion of the organic layer but not the interfacial Cu rich layer.

No-Flux Soldering of As Coated OSP

It is generally accepted that OSP coating is dissolved by flux during soldering implying that fluxing is essential. In our hands, a freshly coated OSP panel with through holes was wave-soldered without applying flux. A very good hole fill resulted. This result is surprising: while from other observations it is undeniable that flux is important, it is not necessary for soldering as coated OSP. This result suggests also that the interface of OSP and metallic Cu is largely oxide free because such oxide should hamper solderability.

Heat Treatments of OSP – What Happens?

Let us examine processes and phenomena that can occur when OSP coated Cu surface are heated during assembly.

1) *Azole Volatilization*. As previously reported, we see only a small % loss of azole (~10%) during reflows. With appropriate safety margin for thickness in OSP application, this is not a problem.

2) *OSP (Azole) Decomposition*. Again, as previously reported, we have not seen decomposition at temperatures below 260 ºC. In fact, a TG curve showed a clean transport into a vapor phase without exothermic events. Others reported results of thermal measurements suggesting a correlation between decomposition temperature and quality of an OSP coating. This correlation is unclear, especially if reported temperatures are well above 260 ºC, therefore not encountered in assembly and irrelevant.

3) *Reaction with Oxygen*. It is clear that oxygen has a negative impact. Samples processed under nitrogen solder better than those processed in air. It is not entirely clear though what is the responsible mechanism: oxidation of azole,

oxidation of metallic Cu under the organic layer or other reactions with OSP components including ionic Cu scattered in it. We have seen the evidence of some degradation of our azole heated in air (color change) but analytical techniques such as NMR and UV/vis hardly indicated any change. Oxidation of metallic Cu seemed a more detrimental process especially in light of reports that OSP coatings are permeable to some extent to oxygen and our previous report which appeared to confirm this. Looking for further proof we ran a Dynamic SIMS measurement of samples reflowed in air. A sample chosen was identical as the one described above.

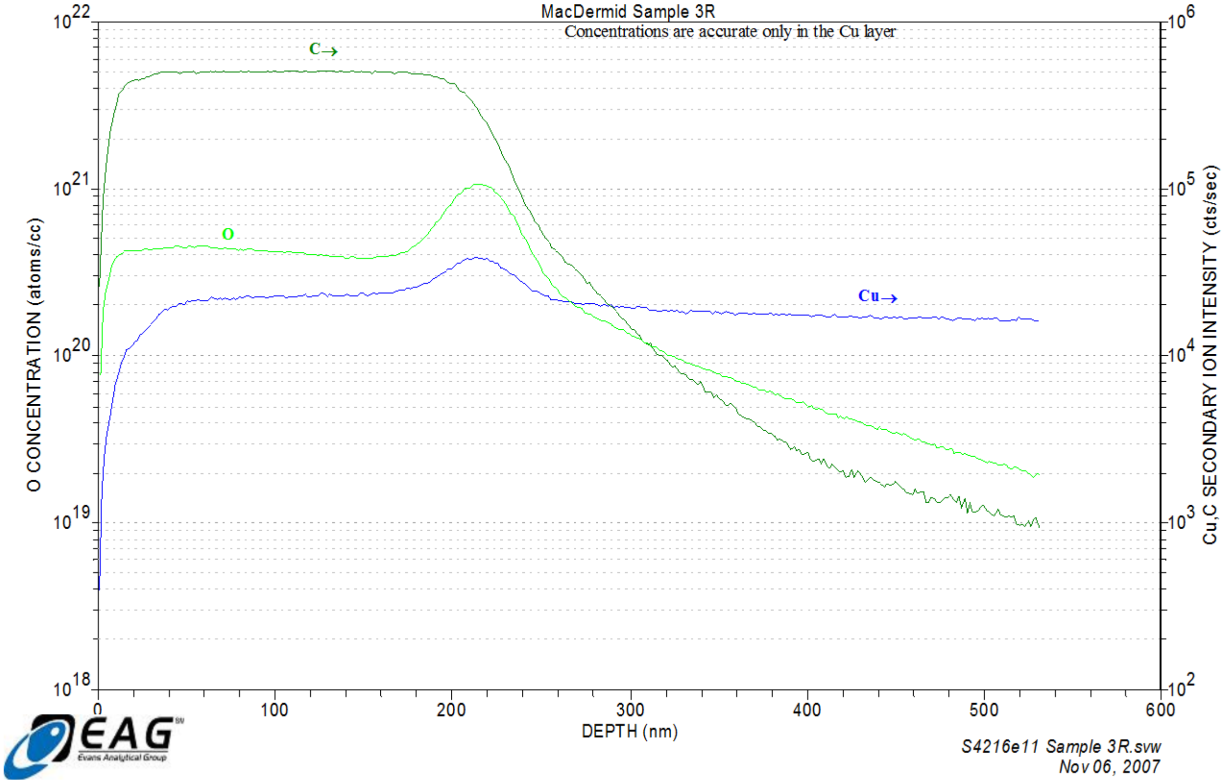


Figure 2. Profiles of C, O and Cu Concentrations within OSP Layer Reflowed Three Times Obtained by Dynamic SIMS

The graph in Figure 2 is best to compare to the one in Figure 1. Upon comparison it can be seen that:

- The oxygen peak at the interface of metallic Cu and the organic layer (~0.22 µm) is bigger; an estimated increase in O concentration is 2 times,
- The values of Cu concentrations within the organic layer are higher,
- The layers appear better defined and more compact, the perceived thickness is 0.22±0.02 µm compared to 0.26±0.04 µm for the unreflowed sample

This last observation of compacting can be well illustrated by overlaying carbon profiles for the unreflowed (A) and reflowed (3R) samples (Figure 3).

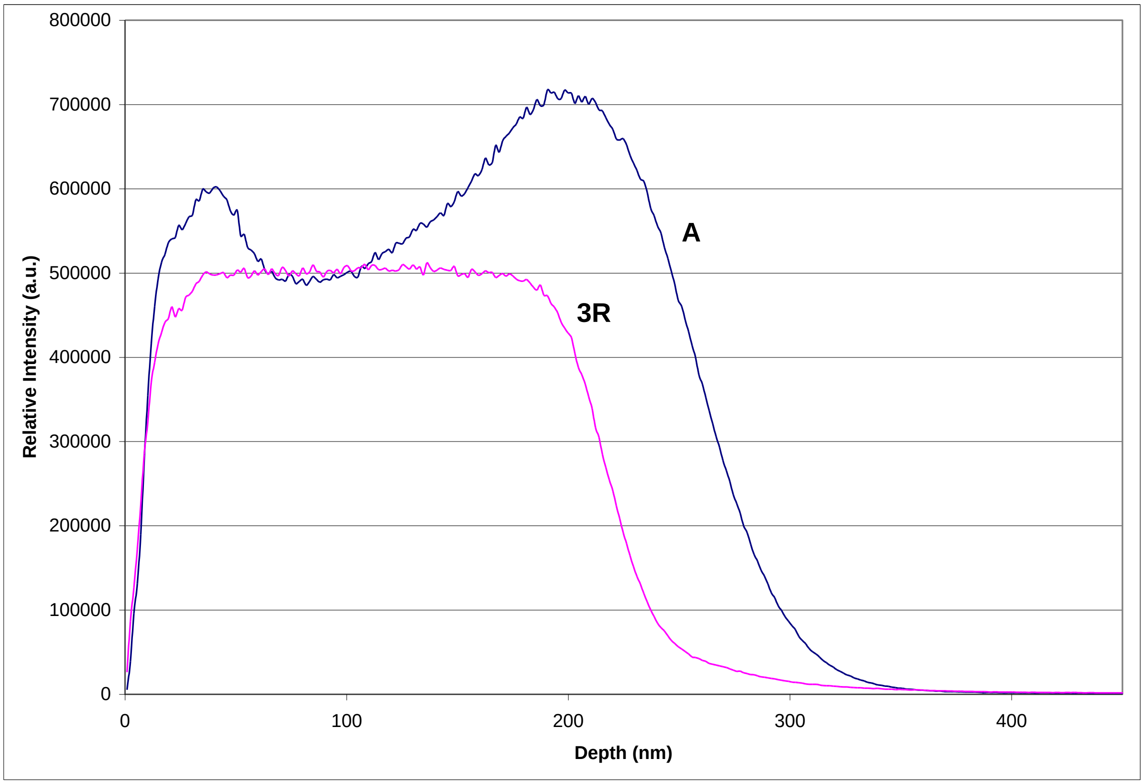
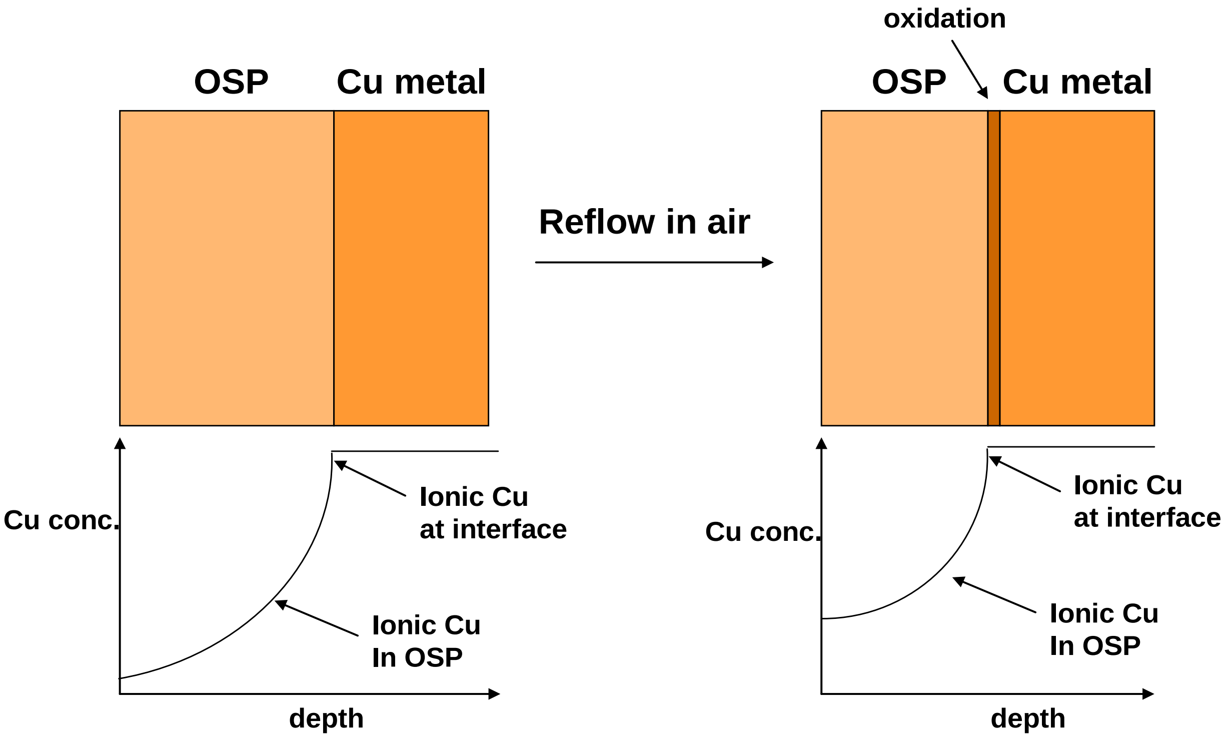


Figure 3. Comparison of C Profiles For Unreflowed (A) and Reflowed (3R) OSP Layers Obtained by Dynamic SIMS

The observations suggest that: 1) oxygen permeates the organic layer and oxidizes Cu at the interface, 2) ionic Cu migrates into the organic layer, and 3) there may be additional, purely physical phenomena occurring within OSP that can result in a repacked and harder coating.



- **Oxidation of interface**
- **Cu migration**
- **Compacting (hardening)**

4)
"Hardening" of OSP. It may be impossible to isolate physical, heat induced changes within OSP, from the changes resulting from oxygen impact. We attempted no-flux soldering of panels with through holes which were heated under nitrogen. No hole fill was observed indicating that heat alone (and not oxidation) was detrimental. We clearly see that OSP coatings reflowed in air are not strippable with organic solvents, and this may be caused by migrated ionic Cu, which "hardens" OSP. One can, however, speculate that azole molecules reorient themselves during heat excursions increasing intermolecular interactions between azole aromatic rings rendering the organic layer less soluble. Interestingly, if the organic layer is less soluble in organic solvents, it can be expected that fluxes used in soldering are less effective. Looking from a different angle, the role of fluxes in soldering becomes more important.

We believe that the first two processes, azole volatilization and decomposition, are insignificant. The latter two processes, oxygen permeation and oxidation of Cu metal, however, are more important. The difficulty in soldering OSP coated boards may be the result of oxide growth under the OSP, therefore being less accessible by flux that should normally remove the oxidation, and also the result of hardening of the organic layer, which will then be more difficult to penetrate by flux.

Summary - Strategies for Improving Solderability

Our results and observations suggest that solderability of OSP coated boards after heat excursions may be more difficult due to organic layer hardening and copper migration. These two phenomena suggest more specific strategies for chemical formulators:

1) *Azole Selection*. Within the families of imidazole and benzimidazole derivatives some compounds may be better. Of course, one needs to consider properties that make a compound suitable for formulation of an OSP bath, such as solubility, coverage, process window etc. In addition to these, however, some compounds may be less prone to hardening during heat treatments. For example, molecules of lower symmetry with geometrically obstructing substituents may undergo less compacting upon heat treatments.

2) *Additives.* These may play particularly useful roles. They can a) limit oxygen permeation through the organic layer, b) limit migration of Cu ions and c) limit compacting of OSP. We can thus think of additives as playing roles of oxygen scavengers and fillers. Alternatively, we can select additives based on their known or perceived direct impact on solderability/wetting.

3) *Synergize with Flux.* If flux is expected to dissolve OSP during soldering it may be useful to formulate OSP to work better with fluxes and optimize fluxes for OSP. It has been suggested that fluxing is very important for OSP and that some flux formulas may be more optimal for OSP.

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