Describing Key Coating and Process Characteristics of a Pb-Free OSP Process

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Abstract

Organic Solderability Preservatives (OSP) continue to attract significant attention as circuit board final finishes. They have evolved from simple and thin benzotriazole coatings to thicker and more complex substituted imidazole and benzimidazole based films. The driver for these changes is the demand for better protection of the copper surface, which is strengthened further by the harsh demands of Pb-free processing. Better protection of the copper surface is effected by a more thermally robust active ingredient: the organic compound. The thermal properties of the organic compound, though, are not the only characteristic of a good OSP coating. This paper attempts to describe the structure and composition of the organic film as well as the influence of the OSP coating process on achieving optimum performance in a Pb-free environment.

Introduction

Organic solderability preservative (OSP) is one of the preferred final finishes in the post-HASL era. The most attractive characteristics of OSP: low cost and ease of application give it a firm place in the market. The share of OSP finishes is expected to grow in the future.

OSP coatings and associated processes have evolved over the years. Organic substances with better thermal resistance were sought and more reliable processes to apply them were developed. This status quo is currently greatly challenged by the higher temperature Pb-free processing of circuit boards. Out of all final finishes, this challenge is arguably the greatest for OSP, which is the only non-metallic finish and by its nature least robust thermally. Approaches to overcome these challenges include selection of better organic substances, modifications of bath composition and process changes.

This paper discusses some attributes of state-of-the-art OSP coatings. The results of simple chemical analyses regarding composition of a "Pb-free" OSP coating are presented. This chemical composition is correlated with performance of the coating. In addition, thermal behavior of model substances is discussed with implications on mechanism of protection. Comments on preferred Cu surface preparation are also presented.

Experimental

Chemical Analyses. A set of 10 double-sided Cu panels of 5 x 5 cm size (50 cm^2) processed through an OSP process cycle was treated with 5% HCl. The resulting solution was used for the following analyses. UV/vis spectrophotometry (260 – 280 nm) was used to determine the average coating thickness and the corresponding azole content in the coating. Concentrations of metals were determined by flame atomic absorption spectrophotometry (FAAS). Anion concentrations were determined by ion chromatography (IC). Concentrations of molecular species such as acetic acid and organic additives were determined by high performance liquid chromatography (HPLC).

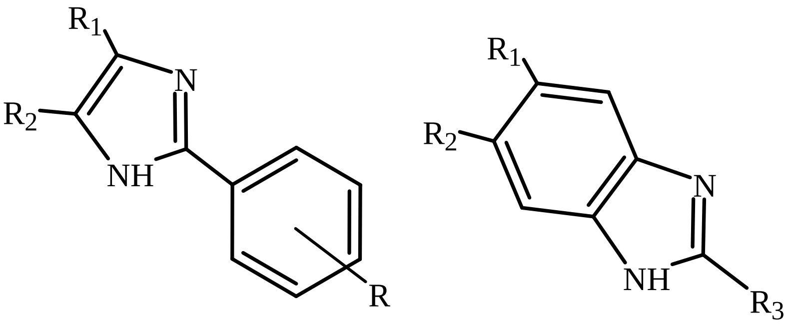
Thermal Analyses. Thermal behavior of the materials such as melting point and weight loss upon heating was examined and characterized using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) techniques in air. Sample size was approximately 10 mg.

Heat Reflows. Cu panels coated with OSP were reflowed in air to a peak temperature of 265 ºC with time in the oven for a single reflow lasting approximately 4 min.

Results and Discussion

What Is in The OSP Coating?

The essential component of OSP coatings is an organic compound, typically an azole. Progress to-date has allowed the selection of two types of azoles to be used for OSP: derivatives of 2-phenylimidazole (PhIM) and benzimidazole substituted at 2C (BZIM) [1, 2] (Figure 1).



PhIM BZIM

Figure 1 - Structures of Most Common Azoles Used in OSP

These compounds have been found to exhibit superior thermal stability and low volatility. In addition to these organic compounds, other chemical species are typically used in OSP baths and can co-deposit within the OSP coating, for example an organic acid present in the bath. OSP baths are typically acetic or formic acid based. Metal compounds are also used in formulas. It is, however, not obvious what chemical species are incorporated into the deposit.

We have performed a series of chemical analyses on coatings obtained on Cu panels from several OSP baths:

(1) A standard M-Coat Select HT bath which contains a benzimidazole compound (called BZIM hereafter), a metal compound 1 (the metal is not Cu), an organic additive and is acetic acid based,
(2) An experimental bath similar to (1) but with a different metal compound 2, and
(3) An experimental bath similar to (1) but without any metal compounds.

The results are presented in Table 1

Table 1 - The Results of Chemical Analyses of OSP Coatings Obtained from Different Experimental Baths (in µmoles/50 cm^2; i.e. per double sided 5 x 5 cm panel).

	(1) Standard HT Bath (with metal compound 1)	(2) Bath 2 (with metal compound 2)	(3) Bath 3 (without any metal compounds)
BZIM*	4.1	5.2	3.6
Metal compound 1	0.54***	-	-
Metal compound 2	-	0.27	-
Acetic acid/acetate**	0.91	0.97	0.97
Organic additive	1.1	2.4	1.4
Cu	3.3	3.0	2.9

* The BZIM values correspond to thicknesses of 0.26, 0.33 and 0.23 µm for (1), (2) and (3), respectively.
**The analysis did not allow the distinction between acetic acid and acetate.
***Similar measurements gave values around 0.3 µmoles/50 cm^2.

The following conclusions can be made based on these results:

A. The molecular ratios of BZIM to metal compounds are 7.6:1 and 19:1 for coatings (1) and (2), respectively. These ratios do not support a formation of a stoichiometric compound, or organometallic polymer between the metal and BZIM.

B. The coatings contain Cu. Cu was not deposited from the baths because the baths do not contain any Cu, but was stripped off the panel along with the coating. The ratios of BZIM to Cu may suggest a 1:1 or 2:1 ratio, and therefore a presence of a complex, but it is believed to be a coincidence. The OSP coating can be made thinner or thicker by changing the contact time. The concentration of Cu, however, is determined solely by a given pre-clean cycle, i.e. to what extent a native oxide is grown on the Cu surface. A similarly processed panel through a pre-clean cycle stopped before the OSP coating step showed 4.5 µmoles/50 cm^2, a comparable quantity.

C. Acetic acid (or acetate) and the organic additive were found in the coatings in similar quantities.

Solderability testing showed a superior performance of coating (1) over coatings (2) and (3), which were about the same. The standard BZIM HT bath shows excellent solderability (>95% PTH fill) after 4 Pb-free reflows with Kester 2220-VF flux and SAC 305 solder. Under the same conditions, the % fill for coatings (2) and (3) is only approx. 35%. This suggests that not any metal compound is equally good at making the coating effective. Acetic acid and the organic additive in the coatings are presumably inert and do not play any role in improving (or worsening) the solderability characteristics. However, the role of the organic additive is profound in formation of a coating of sufficient thickness, good appearance and also in improving the overall bath performance. This is especially important with the metal compound present in the bath.

The presence of a metal in OSP coatings deserves special attention. Salts of Cu, Fe and Zn have been mentioned by researchers from established OSP process suppliers and positive effects on coating protection were observed [3-5]. Recently, researchers from one supplier pointed out that the presence of Zn in the coating is equivalent to the formation of an organometallic polymer [5]. Such a polymer is very thermally stable [6] and its presence is suggested to explain a superior performance of OSP coatings containing Zn. We have not found any evidence supporting the existence of a polymer. OSP coatings are sometimes described as containing organometallic polymers but it is more applicable to thin azole coatings obtained from neutral and alkaline media [7]. Even then these coatings are more appropriately called strongly chemisorbed organic layers. Other arguments against the formation of a polymer within the OSP coating include: (1) there is no evidence of polymerization in the bath: it contains the same chemicals as the ones used to prepare it; and the coating process takes place under mild conditions unsuitable to form an organometallic polymer; a coating with a polymer would require a separate preparation of a polymer and applying it using a specific process such as dip coating [8], (2) OSP coatings strip easily with dilute acid, any organometallic polymer would be expected to be insoluble, therefore impossible to strip [6].

From our analyses, OSP coating is then a mixture containing BZIM, a relatively small quantity of a metal compound, acetic acid and an organic additive. They are bound by weak forces, i.e. without covalent bonding. It is interesting to note that the concentration of Cu is an order of magnitude higher than the concentration of the metal compound. It is unclear if Cu is present as a layer of CuO below the organic layer or it is contained within the layer, interstitially, as is the metal compound. We attempted to answer this question by using 2-propanol to strip the coatings because 2-propanol was expected to strip the organic coating but not the CuO layer. The results were inconclusive but they suggested the presence of Cu in both the OSP layer and the CuO layer underneath.

Studies of Thermal Behavior

The TGA/DSC curves of pure BZIM are shown in Figure 2.

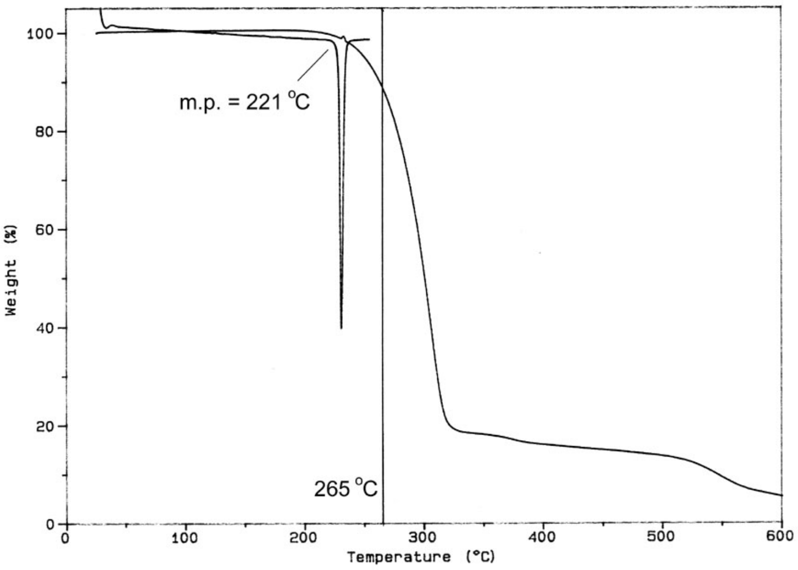


Figure 2 - TGA and DSC Curves for BZIM.

The graph shows that in bulk form BZIM melts at 221ºC and that its volatilization commences soon above the melting temperature. No decomposition is noticed and the evaporation is essentially complete at 320 ºC with the heating rate of 10ºC/min. in the experiment. Hence, if pure BZIM is coated on the Cu surface, it is susceptible to be evaporated off the surface unless it reacts with the base material which it can do at high temperatures. Also, the melting point of 221 ºC indicates that BZIM is apparently liquefied on the surface before the peak temperature of 265 ºC is reached. This may have a positive effect on improving coverage during reflow.

The inclusion of acetic acid and organic additives in the coating along with BZIM are expected to lower the melting point or cause softening of the coating at temperatures much lower than 221 ºC. In fact, entrained acetic acid and more volatile organic additives should boil off early. The effect of this evaporation on coating integrity and protection against oxygen is likely to be detrimental.

Similar experiments were carried out for 2:1 mixtures of BZIM:metal compound 2 and BZIM:metal compound 1 and the results are shown in Figure 3.

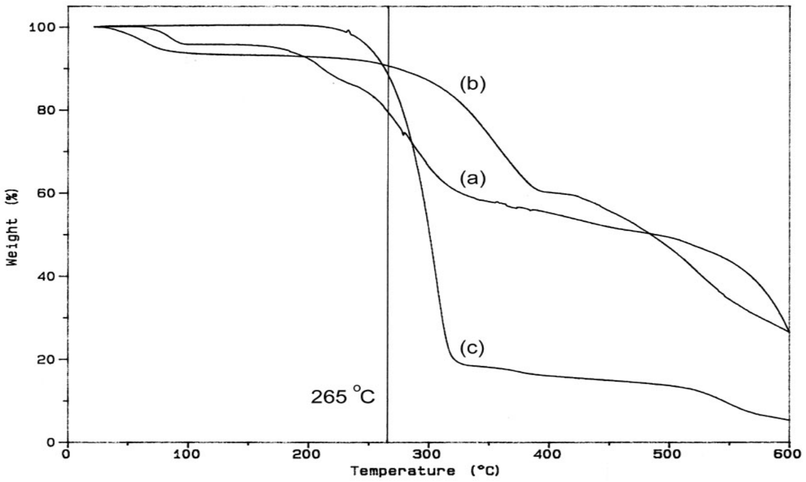


Figure 3 - TGA Plots 2:1 Mixtures of (a) BZIM:Metal Compound 2 and (b) BZIM:Metal Compound 1 with the TGA of Pure BZIM (c) Included for Comparison.

The TGA of 2:1 mixture of BZIM: metal compound 2 (a) shows that BZIM is volatilized in the same temperature range of 220 – 320ºC as pure BZIM (c). Some early weight loss is due to water of crystallization within the metal compounds used. The difference is that BZIM evaporates only partially from the mixture. At temperatures higher than 320 ºC (i.e. beyond that reached in Pb-free processing) a new compound between metal and BZIM is most likely formed. The TGA of 2:1 mixture of BZIM: metal compound 1 (b) shows weight losses shifted by about 50 ºC to higher temperatures, with the BZIM evaporating between 275 – 375 ºC. Again, a new compound is presumably formed between the metal and BZIM at high temperatures. Thus at 265 ºC the mixture of BZIM with metal compound 1 is least volatile. Our explanation of these observations is that by inclusion of metal compound 1 in the coating the volatilization of BZIM is delayed (or lowered).

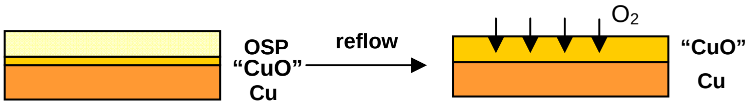
It is important to remember that (as shown above) the ratio of BZIM to metal compound in the actual OSP coating is not 2:1 but approximately 10:1. Our measurements with 10:1 ratios did not show differences in thermal behavior from the behavior of pure BZIM. Another limitation of this testing is that thermal behavior of bulk substances can differ significantly from the thermal behavior of OSP coatings on Cu surface.

What Happens During Reflow?

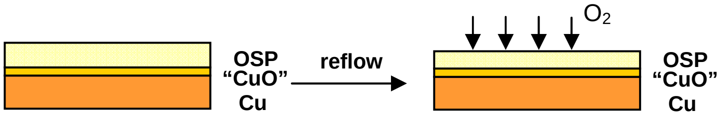
In most discussions about OSP coatings their low volatilities are equaled to their protective abilities. Is this always true? It is important that Cu is not oxidized, because this impacts solderability, and not just that the organic substance stays on the Cu surface.

There are several processes that can be envisioned to take place on a Cu pad covered with an OSP coating:

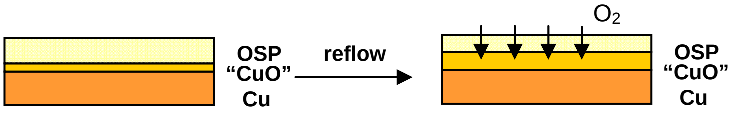
A. An organic compound (such as BZIM) is evaporated completely during reflow and Cu is exposed to oxygen.



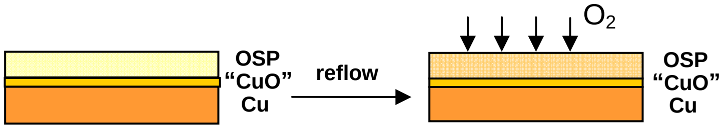
B. An organic compound evaporates but slowly enough to maintain protection.



C. An organic compound evaporates slowly (with sufficient thickness remaining) but is permeable to oxygen and does not protect well.



D. An organic compound reacts with metal in the coating (or Cu on the surface) to form a new substance which does not evaporate and protects Cu against oxidation (the type of reaction envisioned here is different from adsorption on the surface or electrostatic attractions with ions in the coating and is characterized by formation of a new, stable species with distinct covalent bonds). This substance would not evaporate and protect well against oxidation.



In these scenarios, the coating in A is presumed too volatile, the coating in B is what is viewed as desired, the coating in C is poor (but often misrepresented as A) and the coating in D is postulated by some as resulting from inclusion of metal compounds.

In order to determine which of these possibilities are likely, a simple experiment was carried out. Several 5 x 5 cm panels were processed through a bath with metal compound 1. These panels were then subjected to 0, 2, 4, and 6 Pb-free reflows and then stripped using 5% HCl solution. The solutions were analyzed for BZIM content using UV/vis spectroscopy and for Cu and M using FAAS. The results are shown in Figure 4.

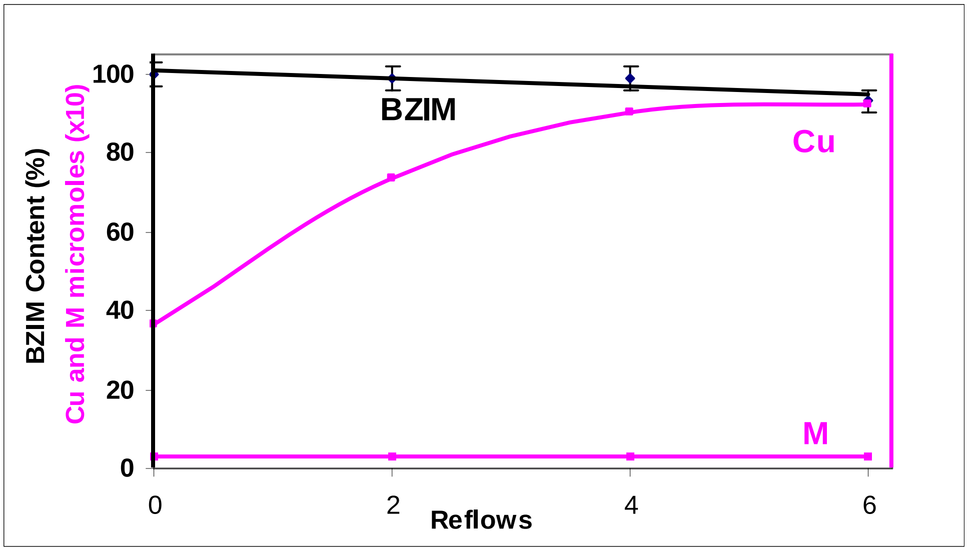


Figure 4 - Retention of BZIM with Multiple Reflows and Relative Cu and M Concentrations in the OSP Coatings.

The results show that virtually no BZIM was lost with reflows. Correspondingly, the concentration of M stayed unchanged at 0.3 µmoles/50 cm^2. The concentration of Cu increased steadily from the initial value of 3.5 µmoles/50 cm^2 to reach 8.8 µmoles/50 cm^2 after 6 reflows. The increase was faster with the first two reflows. Visually, the changes in appearance of the coatings were not significant.

These results indicate that volatility of BZIM with thermal excursions is not an issue. What is important, however, is the coating's resistance to oxygen permeability. It has been reported previously that OSP coatings obtained from acidic media, although thicker than the monolayer thin coatings obtained from neutral or mildly alkaline solutions, are often permeable to oxygen [7]. In the experiment above, 3.5 µmoles/50 cm^2 of Cu was contained within the OSP coating (and/or in a layer underneath). Upon thermal excursions, oxygen permeated through the coating oxidizing the underlying metallic Cu to CuO. The obtained result of 8.8 µmoles/50 cm^2 is the sum of the Cu concentration in the OSP coating and from the CuO contribution.

Our earlier experiments with previous generation OSP showed that those coatings tended to darken with reflows to a greater degree. This observation is also consistent with observations by others [10]. We suggest that the difference in OSP performance lies primarily in oxygen permeability of the coatings. The HT OSP coatings display better resistance to oxygen permeability and the inclusion of metal compounds plays a key role. The selection of a lower volatility organic is helpful for the overall protection but not sufficient.

It is also important to note that all of these coatings (as obtained and after reflows) could be stripped with 5% HCl. The UV spectra of BZIM in the stripped solutions showed no differences between as obtained coatings and coatings after reflows. The data suggest that BZIM did not undergo any chemical reaction to any significant degree upon heat treatments.

Concluding from these results, we reject cases A and D and choose B and C as describing HT and standard OSP coatings, respectively.

Conclusions

Chemical analyses of OSP coatings have revealed the presence of entrained species. In addition to an azole compound (such as BZIM) other species present in the bath are co-deposited. They include acetic acid, metal compounds and additives. A coating obtained from a bath containing metal compound 1 displays improved solderability upon Pb-free reflows. The presence of metal compound 2 is insufficient.

Comparable thermal analyses of model substances containing BZIM, BZIM: metal compound 2 and BZIM:metal compound 1 showed lowest volatility in the bulk form for the latter. However, although useful, the lower volatility may not be the most important property of the coating. Under Pb-free reflow conditions the coatings deposited on Cu pads show excellent retention of BZIM but also easily measurable increase in Cu content due to oxidation. The degree of oxidation, and therefore protection, is suggested to depend on the type of metal compound co-deposited in the coating.

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