Novel High Temperature Resistant OSP Coatings for Lead-free Processing

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Abstract

In order to meet the growing requirement of eliminating lead from electronics, the printed wiring board (PWB) industry is migrating from hot-air-leveled solder (Sn/Pb) to lead free compatible alternative final finishes. Among the available alternatives which include organic solderability preservative (OSP) immersion silver, immersion tin and electroless nickel/immersion gold, the OSP type coating is considered to be one of the leading candidates because of its excellent solderability, ease of processing and low cost.

This paper uses Gas Chromatography-Mass Spectroscopy (GC/MS), Thermogravimetric Analysis (TGA), and X-ray Photoelectron Spectroscopy (XPS) to characterize the relative thermal properties of a novel high temperature (HT) resistant OSP coating. The GC work performed in this study clearly shows the key organic components in the HT OSP coating that affects solderability. The GC work also shows the alkyl benzimidazole-HT used in HT OSP is of the lowest volatility. The accompanying TGA data also illustrates that the HT OSP coatings have a higher decomposition temperature compared to existing industry standard OSP coatings. The XPS shows that HT OSP has only about 1% increase of oxygen content after five lead-free reflow cycles. In combination, these improvements are assessed relative to the industry needs to meet the performance challenges of lead free soldering.

Introduction

OSP coatings have been used in the printed wiring board industry for many years. They are based on the reaction of azole derivatives with transition metals, such as copper and zinc, to form thin organometallic polymeric coatings. Very extensive academic research [1,2,3] has been conducted to reveal the corrosion inhibition mechanism of azole compounds on metals. G.P. Brown [3] successfully synthesized organometallic polymers of benzimidazole with copper (II), zinc (II) and other transition metals and specially characterized the unusually high thermal stability of poly (benzimidazole-zinc) by using TGA. TGA data from his work shows that poly (benzimidazole-zinc) has a decomposition temperature as high as 400^{o}C under ambient atmosphere and as high as 500^{o}C under nitrogen atmosphere, while the decomposition temperature of poly (benzimidazole-copper) is only 250^{o}C. The recently developed novel HT OSP is based on the poly (benzimidazole-zinc) chemistry, which offers superior thermal stability.

OSP is mainly composed of organometallic polymer with small molecules such as fatty acids and azole derivatives entrained in the coating during deposition. The organometallic polymer provides the necessary corrosion resistance property, adhesion to copper and surface hardness. In order to withstand the lead-free assembly processes, the decomposition temperature of organometallic polymer has to be higher than the melting point of lead-free solders. Otherwise, the backbone of OSP would be degraded after passing through lead-free assembly processes. The decomposition temperature of OSP largely depends on the nature of the organometallic polymer. Keep in mind that there is another key factor that affects protection of copper from oxidation: the volatility of azole derivatives which,of course, include benzimidazole derivatives and phenyl imidazole derivatives. During the lead-free reflow process, the small molecules in the OSP coatings evaporate, which definitely causes some loss of protection of copper from oxidation as well. In order to scientifically characterize the thermal resistance of OSP, GC/MS, TGA, and XPS were used.

Experimental

1. GC/MS Study

Test samples of OSP materials were obtained by scraping approximately 0.74-0.79 mg of the OSP coatings from copper panels. These test panels were coated respectively with: a) the new HT OSP; b) the industry standard OSP and, c) another commercially available OSP.. Neither the panels nor the coating material samples were processed through any assembly reflow processes prior to GC/MS testing. A H/P 6890 GC/MS was used in syringeless injection mode (see Figure 1), which is also called Direct Dynamic Thermal Desorption mode. The Syringeless Injector gives the capability to perform thermal desorption of solid samples directly within the injection port of a gas chromatograph. The Syringeless Injector transfers the sample, contained within a glass sample vial, into the injection port. Carrier gas continuously sweeps volatile compounds from the sample into a capillary column for collection and separation. Positioning the sample in close proximity to the capillary column results in highly efficient and reproducible thermal desorption. After sufficient sample has been transferred the sample is expelled up and out of the injection port, where it can be removed or reinjected. The GC column used is a Restek RT-1 GC (0.25 mm ID x 30 m, 1.0 µm film). The GC oven temperature program applied was 35°C to 325°C at 15°C/minute with 2 min. hold at 35°C. Thermal desorption was at 250°C for 2 minute splitless. With this device, the sample is heated in the injection port, in this case at 250°C. Volatiles are continuously transferred into the column by helium flow, where they are trapped by using liquid nitrogen cooling of the head of the column. After the heating period, the sample vial is forced out of the injection port with gas pressure. Identifications were made by mass spectra of the whole mass range (from 10-700 daltons). Retention times were determined for each compound.

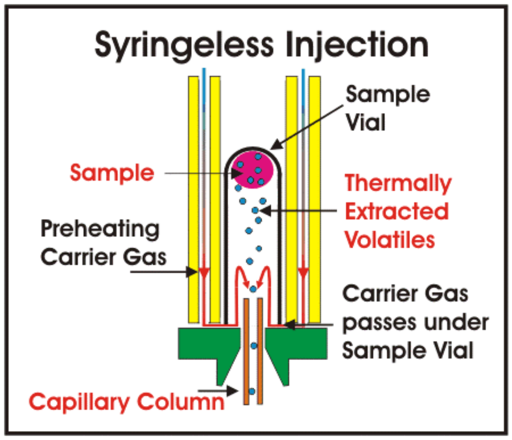

Figure 1: Syringeless Injection

2. Thermogravimetric Analysis (TGA) Study

Test samples of OSP material were obtained by scraping approximately 17.0 mg of the coating material from copper panels. The panels were also coated with the new HT OSP; the industry standard OSP, and other commercially available OSP product. Neither, the panels nor the coating material samples were processed through any assembly reflow processes prior to TGA testing. The TGA was run in nitrogen atmosphere with TA Instrument 2950TA. The working temperature holds at room temperature for 15 minutes, then elevates to 700°C at the rate of 10°C/minute.

3. X-ray Photoelectron Spectroscopy (XPS) Analysis

X-ray Photoelectron Spectroscopy (XPS) also called Electron Spectroscopy for Chemical Analysis (ESCA) is a chemical surface analysis method. XPS measures the chemical composition of the outermost 10-100 Å of a sample. Copper panels were coated with HT OSP and industry standard OSP, then passed through five lead-free reflow cycles. The XPS analysis of HT OSP before and after five lead-free reflow cycles, and industry standard OSP after five lead-free reflow cycles were conducted with VG ESCALAB Mark II. The VG ESCALAB Mark II Operating Conditions are listed as follows:

Source: Twin anode, Al Source
Anode Voltage: 12kV
Filament Current: 5 A
Emission Current: 24 mA
Operating Pressure: 6 x 10E-8 Torr
Data acquisition:
Binding Energies: 1100eV to 0 eV
Step Size: 1eV
Dwell Time: 100ms per step
Sweeps: 20
Pass Energy: 60eV

4. Through-Hole Solderability Testing

Through-Hole Solderability was tested using Solderability Test Vehicles (STVs) (see Figure 2 below). A total of ten STV arrays (four STVs per array) were coated to a thickness of approximately 0.35 microns. Five arrays were coated with the HT OSP, and five were coated with the industry standard OSP, using conveyerized horizontal processing. Afterwards, the coated STVs were subjected to a series of high temperature, lead-free reflow cycles in a solder paste reflow furnace. The reflow series consisted of 0, 1, 3, 5 or 7 consecutive reflow cycles per test condition, all under an air atmosphere. Four STVs (1 array cut into individual test coupons) from each coating set was processed per reflow test condition. Following reflow conditioning all STVs were processed through a high temperature, lead-free wave soldering process. Through-hole solderability was measured by inspecting each STV and counting the number of properly filled through-holes. The acceptance criteria are that solder fillet must fill to the top or the knee of the plated through hole and can also extend to the top of the topside pad.

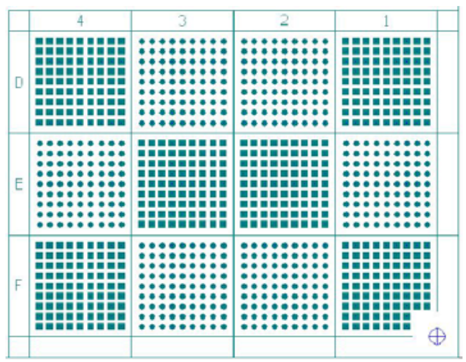

Figure 2: Through-Hole Solderability Test Vehicle
1196 through holes per solderability test vehicle (STV)
•10 mil holes-Four grids, 100 holes each grid, square and round pads
•20 mil holes-Four grids, 100 holes each grid, square and round pads
•30 mil holes-Four grids, 100 holes each grid, square and round pads

5. Solderability by Wetting Balance

Solderability was also evaluated by wetting balance testing. The wetting balance coupons were coated with HT OSP and treated with up to 7 lead-free reflow cycles, T_{peak} =262 °C. The reflows were conducted in air by using a BTU TRS combination IR/convection reflow oven. The wetting balance tests were conducted per IPC/EIA J-STD-003A section 4.3.1 [4] using a “Robotic Process Systems” automated wetting balance tester with EF-8000 flux, a no-clean flux and SAC 305 alloy solder.

6. Solder Joint Strength Tests

The solder joint strength was measured by shear test. Test boards of BGA pads (0.76 mm diameter) were coated with HT OSP at a thickness of 0.25 and 0.48 microns and subjected to three lead-free reflow cycles with peak temperature of 262°C. Solder balls composed of SnPb and SAC 305 alloys (0.76 mm diameter) were soldered onto the pads with matching solder pastes. The solder ball was sheared off at 200 μm/second by using a Dage PC-400 bond tester as shown in Figure 3.

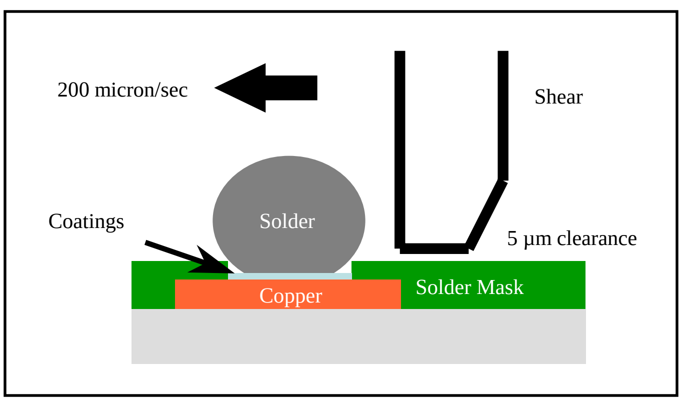

Figure 3: Schematic Diagram of Shear Test

RESULTS AND DISCUSSION

1. GC-MS Analysis

The GC-MS is a very useful tool that can be used to monitor the evaporation behavior of the organic ingredients in OSP coatings. Various azole derivatives including imidazole derivatives and benzimidazole derivatives are used in various OSP products in the industry. The alkyl benzimidazole used in the HT OSP, alkyl benzimidazole used in the STD OSP and the aryl phenylimidazole used in other OSP coatings were evaporated during heating in a GC column. The azole derivatives that co-polymerize with metals cannot be detected by GC/MS because the organometallic polymer does not evaporate. Therefore, GC/MS only detects the azole compounds that do not react with metals and other small molecules. Normaly, the molecule that has lower volatility has longer retention time under exactly same heating and flow conditions in a GC column. The Figures 4-6 show that the three OSP coatings contain same fatty acid, different azole derivative, and some other impurities. The alkyl benzimidaole-HT peak, the alkyl benzimidaole-STD peak, the aryl phenylimidazole peak appear in 20.5, 19.0, and 19.0 minutes respectively. The relative retention times clearly indicate the volatility of imidazole and benzimidazole derivatives used in three OSPs (see Figure 7).

The alkyl benzimidazole-HT has the lowest volatility during heating and flowing in GC column. The alkyl benzimidazole-STD and the aryl phenylimidazole have very close retention times and volatility. GC-MS shows that HT OSP has least impurities as well. Organic impurities in OSP coatings cause some loss of solderability and discoloration during reflow processing. Therefore, in this respect, the HT OSP is superior to industry standard OSP and other OSP coatings.

Koji Saeki [5] reported that the polymerization on the surface of OSP should be weaker than that on the bottom because of less density of copper ion. It is believed that unreacted azole derivative molecules exist in the upper layer of OSP. During reflow processes, more copper ions would migrate from bottom to upper layer. These unreacted, more thermally resistant, azole derivative molecules in the upper layer would have more opportunity to react with copper ion and prevent the copper from oxidation by air. It is surmised that the alkyl benzimidazole-HT used in HT OSP has a lower volatility and has more possibility to react with copper ions migrating from the bottom layer, thus reducing the possibility of copper oxidation during reflow processing. X-ray Photoelectron Spectroscopy can show copper ion migration from the bottom layer to the upper layer, which will be discussed later.

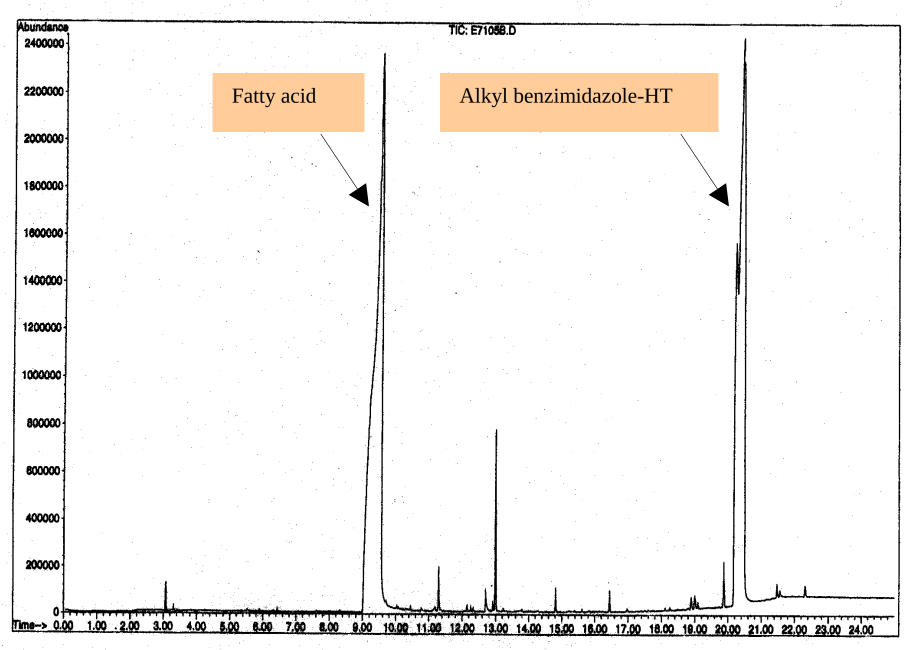

Figure 4: HT OSP before lead-free reflow

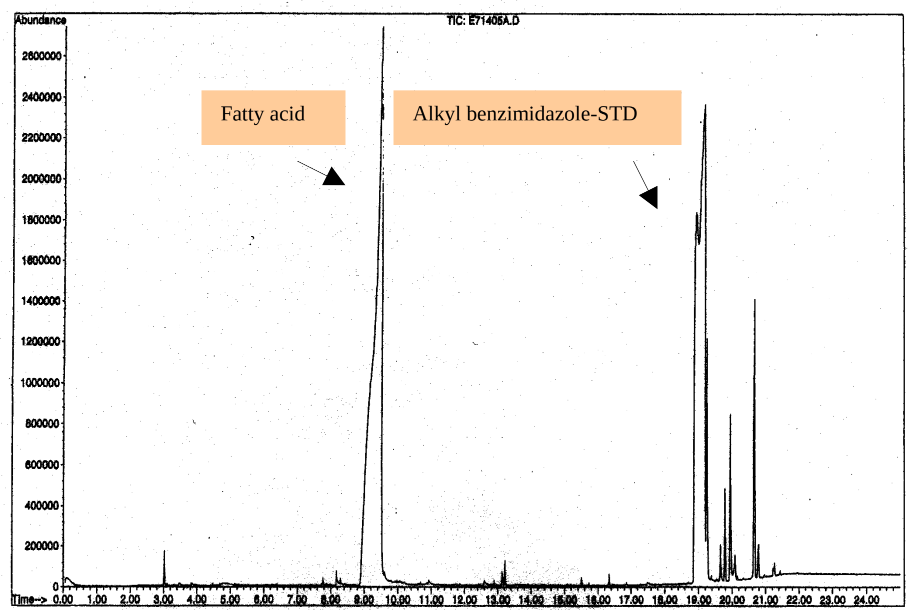

Figure 5: Industry standard OSP before lead-free reflow

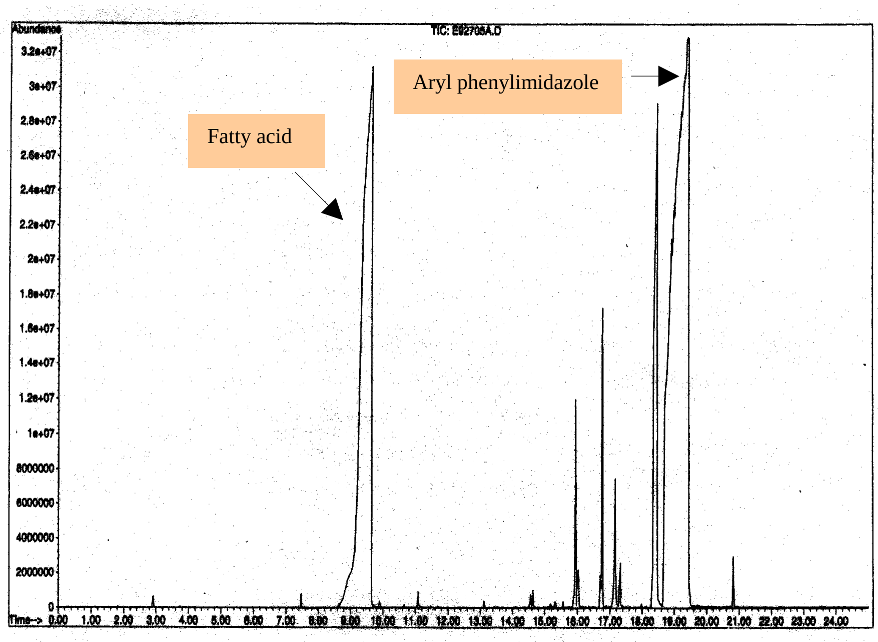

Figure 6: Other OSP before lead-free reflow

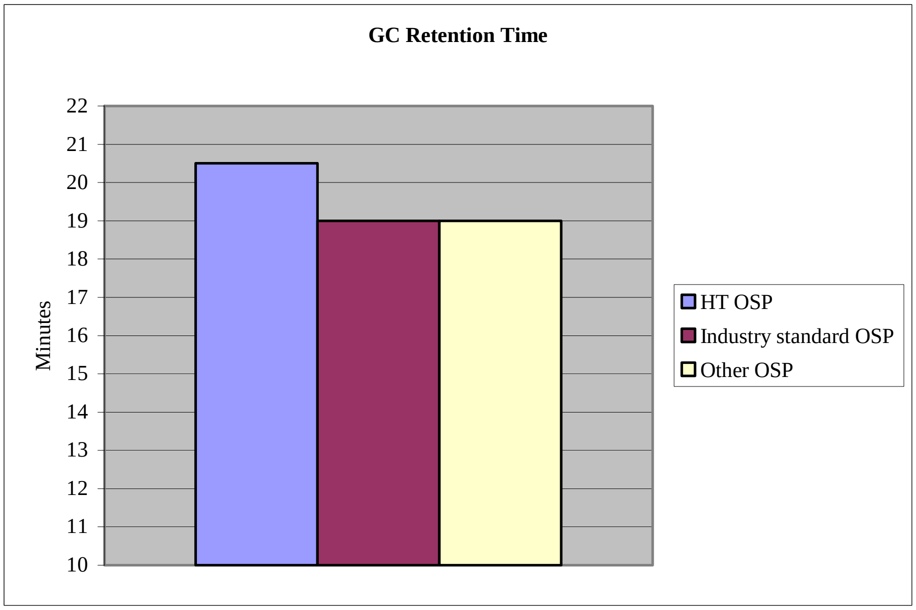

Figure 7: Retention time comparison

2. Thermogravimetric Analysis (TGA)

The TGA measures weight changes in materials with regard to temperature and allows for the effective quantitative analysis of mass changes. In our case, TGA is also an ideal method to reproduce the evaporation and decomposition behavior of OSP coatings during the first lead-free reflow process in nitrogen atmosphere.

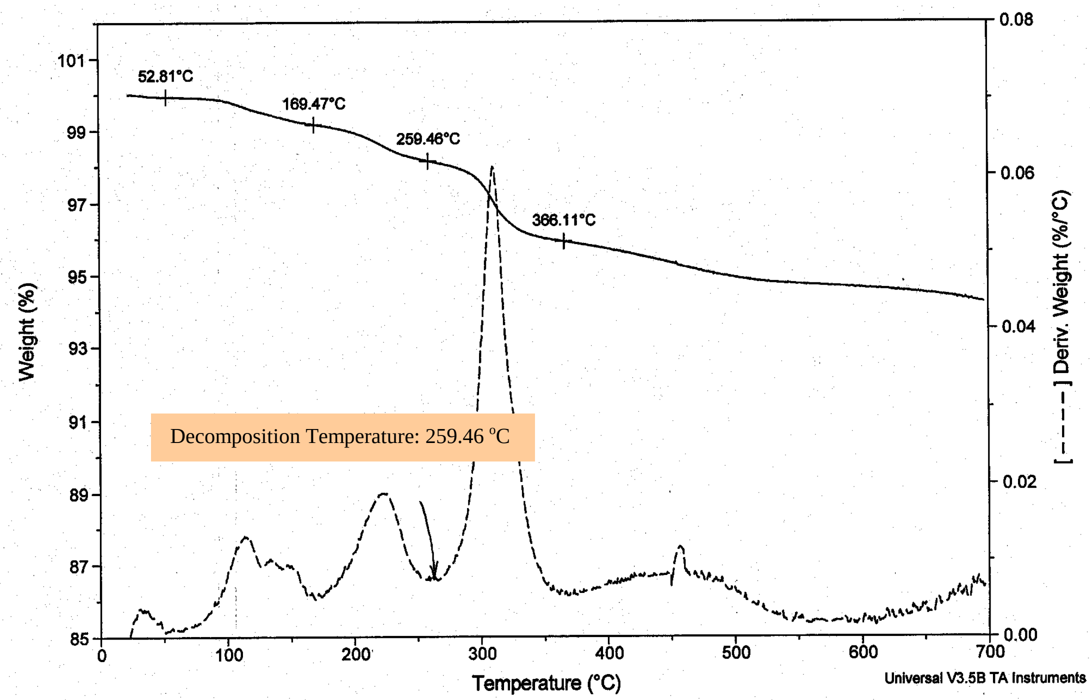

Figure 8: TGA of industry standard OSP

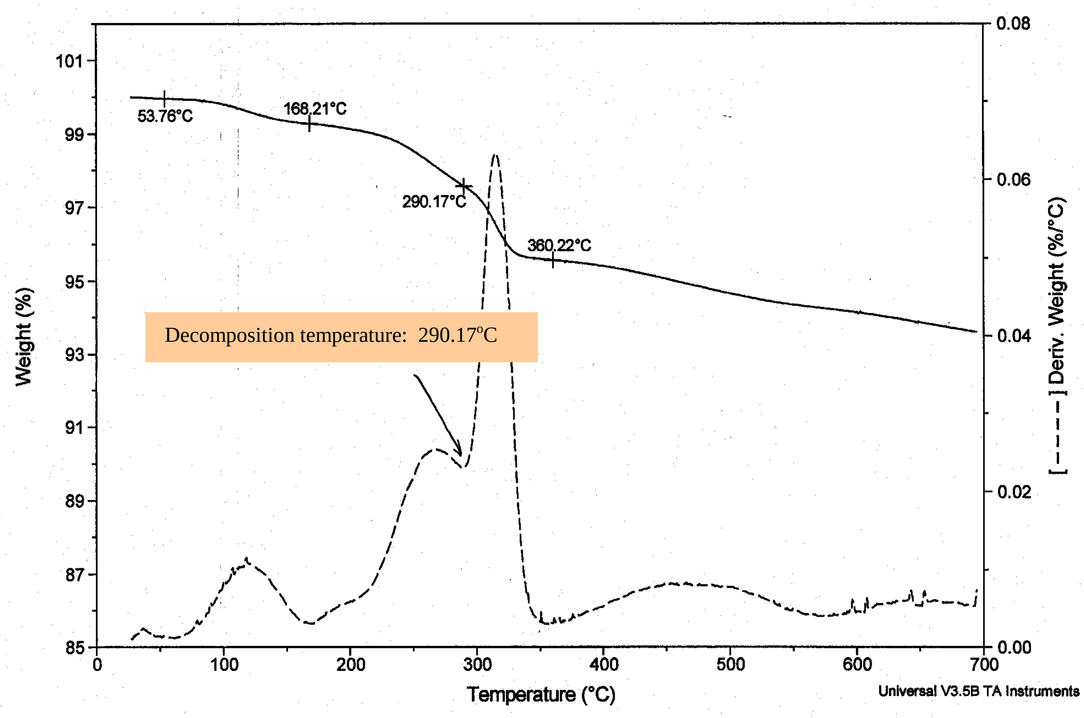

Figure 9: TGA of HT OSP

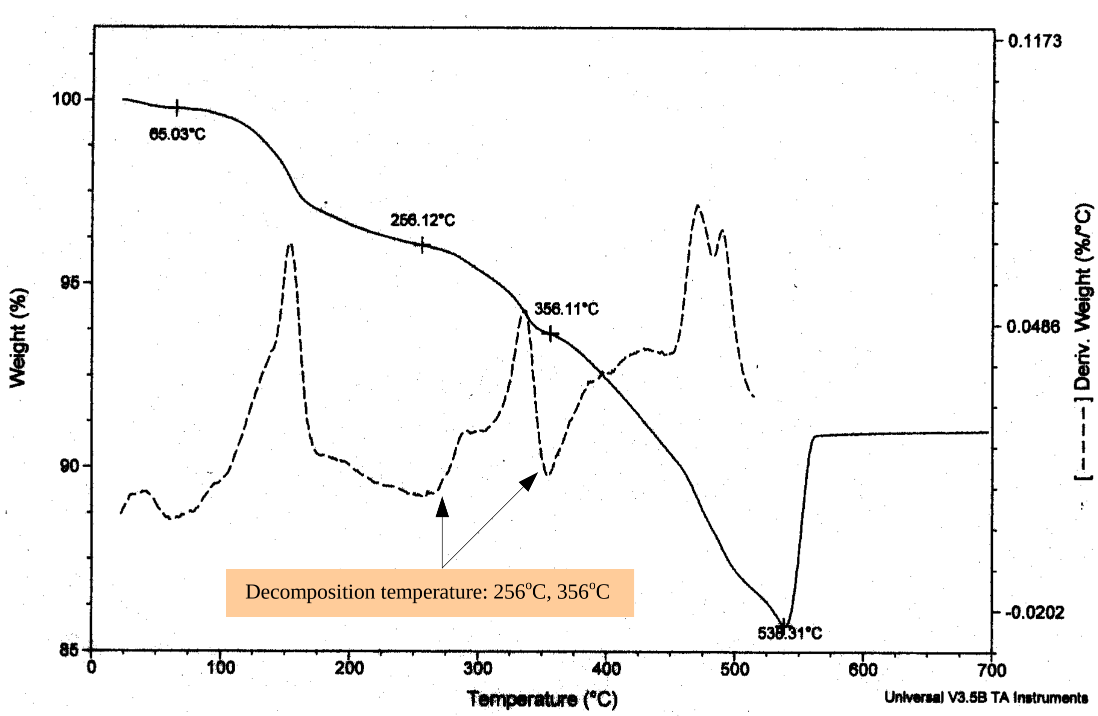

Figure 10: TGA of the other OSP in the market

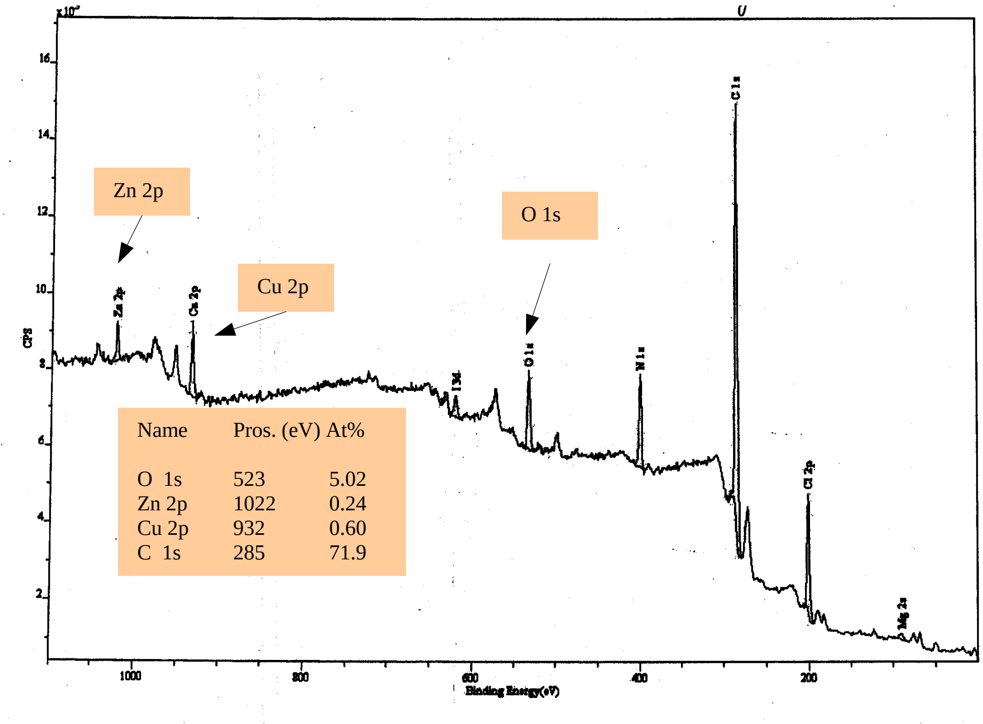

Figure 11: XPS of HT OSP before lead-free reflow

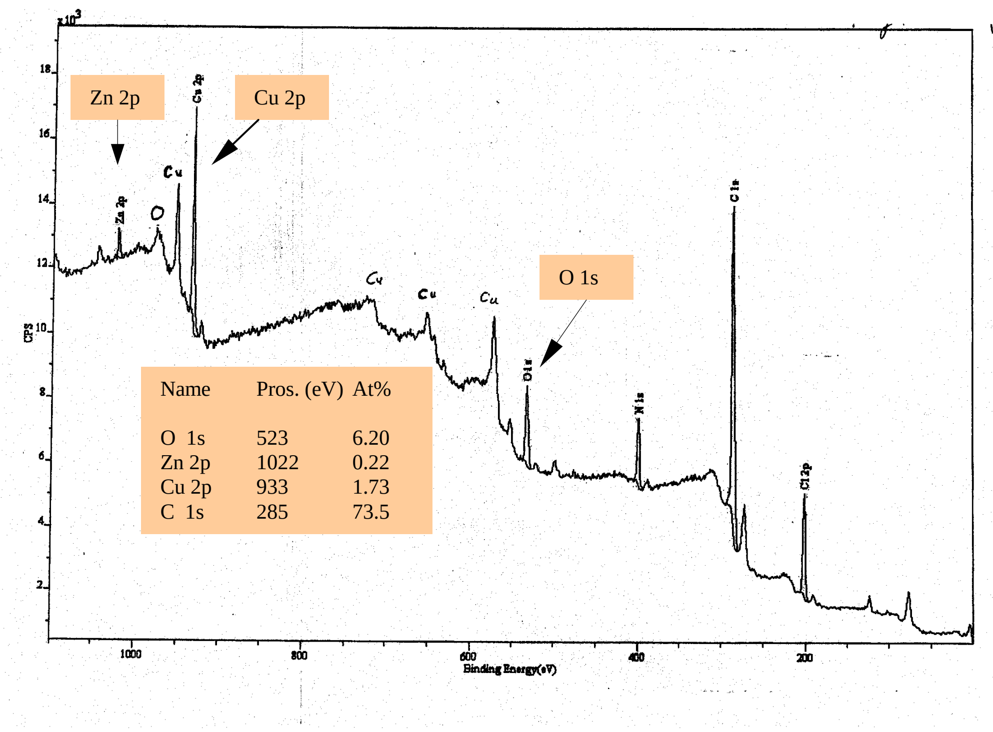

Figure 12: XPS of HT OSP after five lead-free reflow cycles

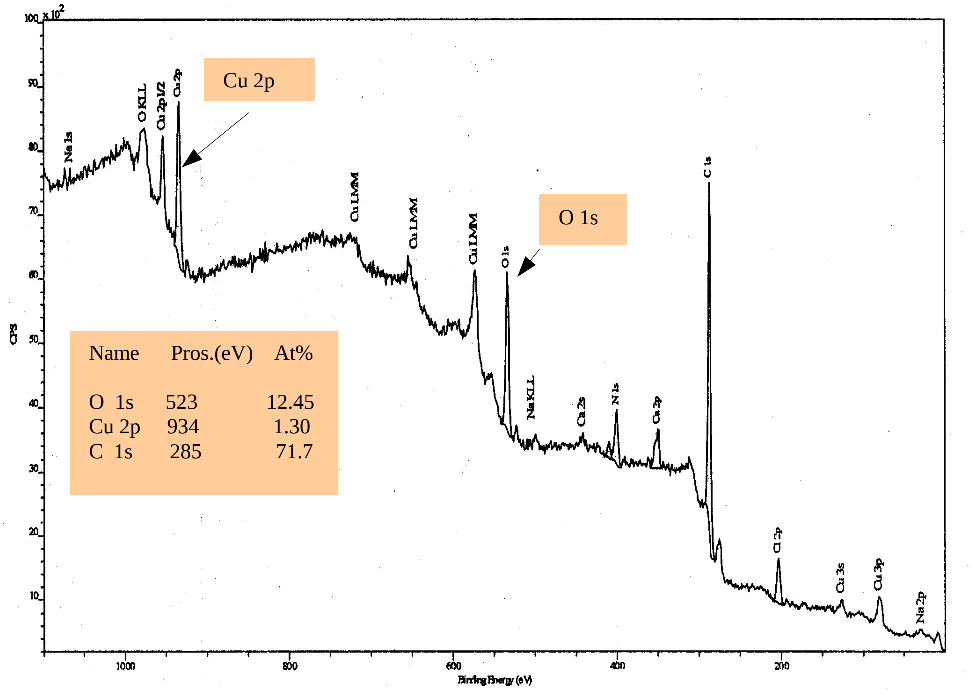

Figure 13: XPS of industry standard OSP after five lead-free reflow cycles

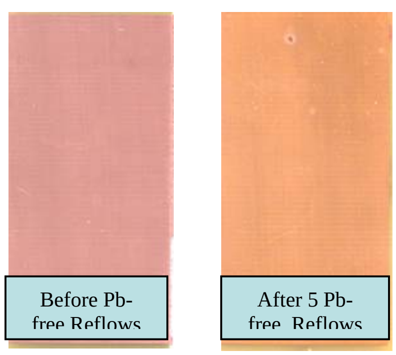

Figure 14: Industry standard OSP

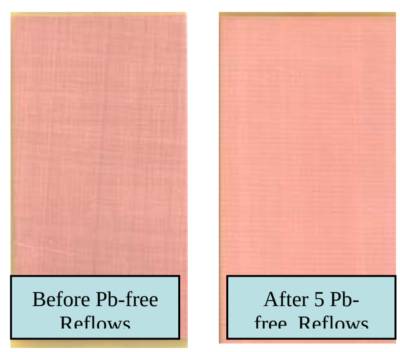

Figure 15: HT OSP

Figures 8 and 9 clearly show that the industry standard OSP has a decomposition temperature of 259°C and HT OSP has a decomposition temperature of 290°C. HT OSP has a higher decomposition temperature because it is based on poly (benzimidazole-zinc) chemistry that has a decomposition temperature of 400°C. However, the actual decomposition temperature of HT OSP is not as high as 400°C because copper co-deposits in the HT OSP coatings. The decomposition temperature of the industry standard OSP is only 259°C because it is based on poly(benzimidazole-copper) chemistry. Interestingly, the other OSP has two decomposition temperatures, which are 256°C and 356°C (see Figure 10). This OSP may contain iron[6] and the stepwise decomposition may possibly be the attribute of poly (aryl phenylimidazole-iron). TGA results from F. Jian and his associates show that poly (imidazole-iron) also has two decomposition temperatures of 216°C and 378°C[7]. Therefore, HT OSP has the highest decomposition temperature and higher thermal resistance compared to the industry standard OSP, and the other OSP coatings in market.

3. X-ray Photoelectron Spectroscopy Analysis
X-ray Photoelectron Spectroscopy utilizes photo-ionization and energy-dispersive analysis of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample. The binding energy peak of oxygen (1s), copper (2p) and zinc (2p) in XPS appear at 532-534 eV, 932-934 eV, and 1022 eV respectively. This technique can provide a quantitative analysis of the surface compositions of the outermost 10-100 Å of a sample. Figure 11 shows that HT OSP has 5.02% of oxygen and 0.24 % of zinc before lead-free reflow process. Figure 12 shows that HT OSP has 6.2% of oxygen and 0.22% of zinc after five times lead-free reflow cycles. Therefore, HT OSP has only 1.2% of increase of oxygen content after 5 lead-free reflow cycles and the zinc content remains unchanged after five lead-free reflow cycles. However, copper content increases from 0.60% to 1.73% after five lead-free reflow cycles. The possible reason of copper ion increase is the copper ion migration from bottom to the top layer during reflow cycles.

E. K. Chang and his associates [8] also conducted surface analysis of the industry standard OSP by using X-ray Photoelectron Spectroscopy. It was reported the oxygen content is about 5.0% without passing through any reflow process, which then increases to 9.1% and 11.0% after one and three conventional SnPb reflow cycles in air atmosphere respectively. From their work, it was also reported that the oxygen content increases to 6.5% after one reflow cycle in nitrogen atmosphere. Figure 13 shows that the oxygen content increases to 12.5% after five lead-free reflow cycles. Therefore, the industry standard OSP has about 7.5% increase of oxygen content after five lead-free reflow cycles, which is much more than HT OSP.

Solderability is largely determined by the degree of oxidation on the joining surfaces and the aggressiveness of the applied flux. Therefore, the oxygen content determined by XPS is a very effective indicator of the thermal resistance of OSP. HT OSP exhibits excellent thermal resistance compared to the industry standard OSP.

Discoloration tests show that HT OSP has almost no discoloration after five lead-free reflow cycles (see Figure 14), while industry standard OSP has significant discoloration after five lead-free reflow cycles (see Figure 15). The discoloration results are consistent with the XPS results.

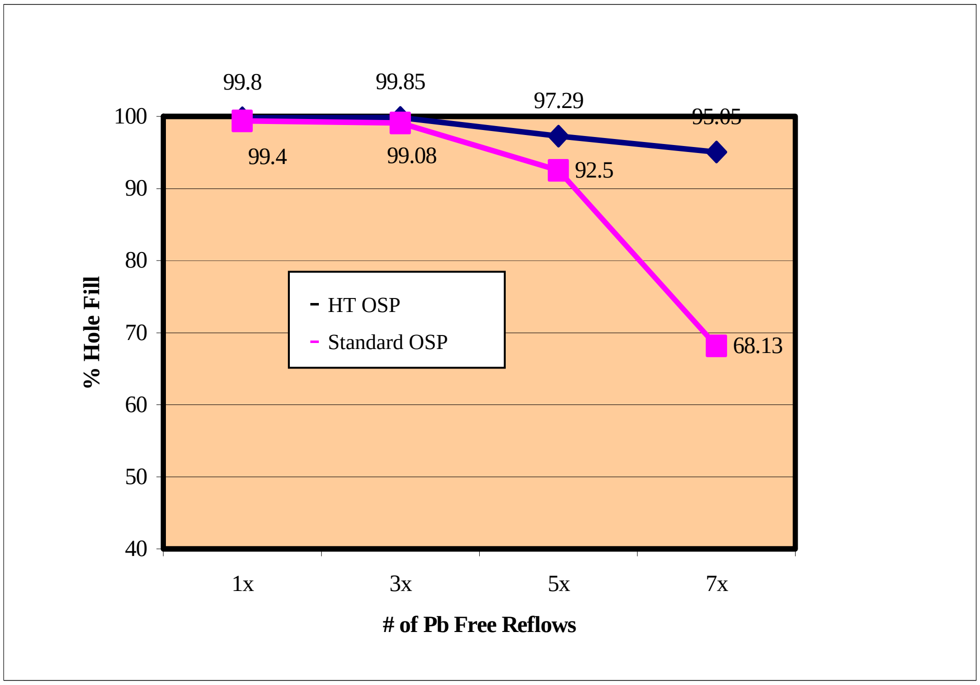

Figure 16: Through-Hole solderability of HT OSP
and industry standard OSP (LS 500A flux, SAC 305 solder)

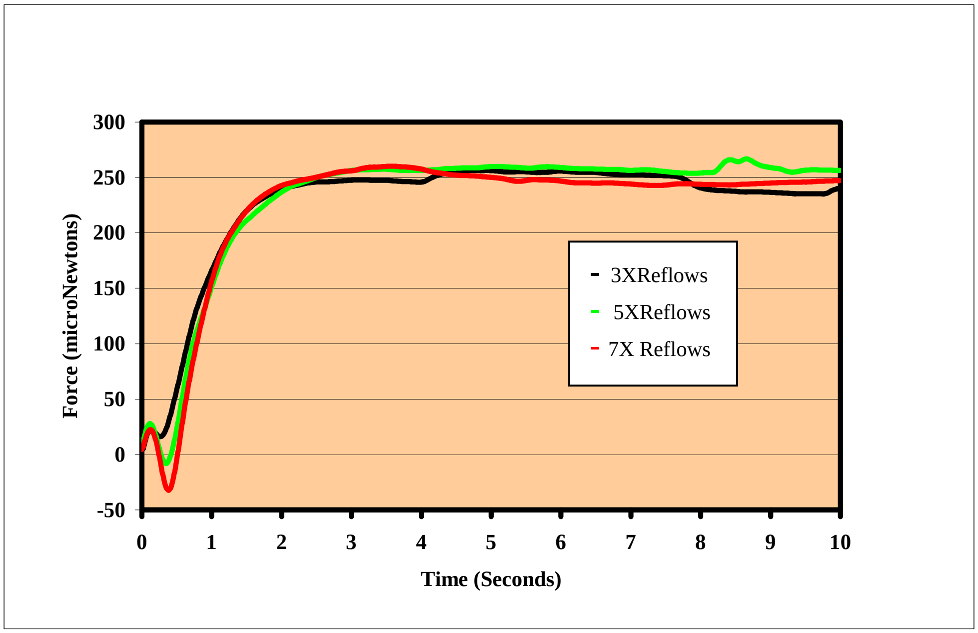

Figure 17: Wetting balance tests with multiple lead-free reflow cycles
(EF-8000 flux, SAC 305 solder)

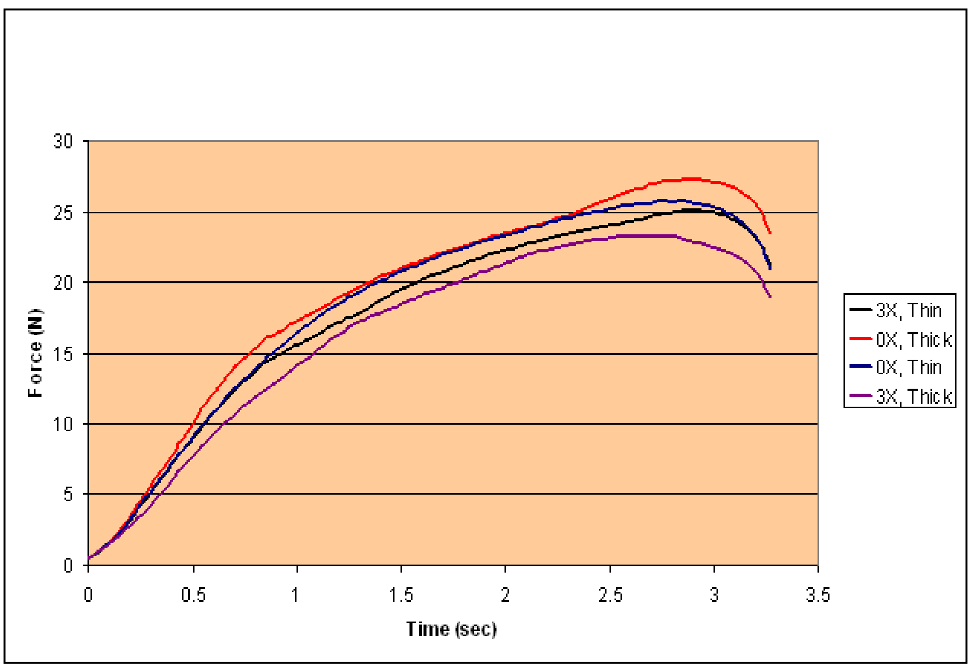

Figure 18: Shear curves of SAC305 alloy on HT OSP without proceeding reflow and after proceding three lead-free reflow cycles

4. Solderability Tests

Figure16 shows that the through-hole solderability of the HT OSP is superior to that of existing industry standard after multiple lead-free reflows. The excellent solderability of HT OSP is consistent with the excellent thermal resistance. From the wetting balance tests, in general, as the number of reflows increases, time to zero (T_o) gradually increases and the maximum wetting force slightly decreases. However, it is shown that excellent solderability is maintained by the HT OSP through seven lead-free lead-free reflow cycles (see Figure 17). As shown in Figure 18, the shear force increases gradually and reaches the maximum at 25N. Since the shear strength depends on the cross sectional area at which the shear takes place, the results would vary with the geometrical shape of the solder ball and the clearance between the shear and pad. The shear force is independent of OSP thickness as long as the copper surface has enough protection from oxidation.

The latest generation HT OSP is more temperature resistant due to higher thermal stability of poly (benzimidazole-zinc) chemistry. It has been developed and released to withstand higher temperatures and make no clean flux penetration easier, thus resulting in improved solderability. HT OSP can meet the stringent demands of today's most complex PWB lead-free assembly processes. Compared to the existing industry standard OSP, the HT OSP has the ability to withstand more than three lead-free reflow cycles without significant solderability degradation. This has been confirmed with through-hole and wetting balance solderability testing, shear strength tests, as well as production experience.

Conclusions

1. Alkyl benzimidazole-HT used in HT OSP has the lowest volatility, compared to alkyl benzimidazole-STD used in the industry standard OSP and aryl phenyl imidazole used in other OSP coatings in the market.

2. HT OSP has the highest decomposition temperature, compared to the industry standard OSP and the other OSP.

3. After five lead-free reflow cycles, HT OSP has only 1% of increase of oxygen content and much less than industry standard OSP, which has 7.5% of increase of oxygen content. Also HT OSP has almost no discoloration after five lead-free reflow cycles.

4. HT OSP offers excellent solder reliability in terms of through-hole tests, wetting balance tests after far more than three lead-free reflow cycles because of its unusual thermal resistance.

5. HT OSP provides high reliability solder joints as evidenced by shear strength tests.

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