CAN ALL LIQUID FLUXES WORK WELL ON A REFLOWED OSP PAD FINISH?

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ABSTRACT

Printed circuit board (PCB) assemblers are increasingly using Organic Solderability Preservative (OSP) as their preferred surface finish due to several advantages of this coating over metallic surface finishes. However, OSP coatings after exposure to one or more thermal excursions can become more challenging to solder especially during wave solder applications. For example, a thick multi-layered double-sided PCB coated with OSP that has been exposed to one or more SMT solder paste reflow cycles may experience reduced solder wetting or hole fill by the assembler when wave soldered.

PCB manufacturers and assemblers believe this reduction in solder wetting on pre-reflowed OSP is due to thermal degradation of OSP coating. Different mechanisms for this thermal degradation of OSP coating have been proposed by researchers. But until now no complete study has been reported detailing the chemical nature of the degradation and how to address the poor wetting issue on such degraded OSP coating.

In the current study, we have investigated the chemical changes OSP coating undergoes in thermal excursions. Elements of soldering flux that may neutralize the effect of such degradation were short-listed. Wetting property of Pb-free solder on thermally exposed OSP was studied in presence of these elements and fluxes containing them.

Key Words: OSP, Thermal Effects, Solder Wetting, Liquid Flux, Hole Fill

INTRODUCTION

Organic Solderability Preservative (OSP) is an ultra-thin organic final finish coating for copper pads on printed circuit boards (PCB), which provides protection from oxidation under a wide range of conditions. Being organic in nature this coating can be applied at a lower cost compared to any of the metallic coatings used for this purpose and is very easy to process. OSP coatings can also achieve excellent flatness or coplanarity among the pads which allows it to be fit for applications where miniaturized components are to be used. Solder joints formed on OSP surface finish do not contain any metallic impurity coming from the surface finishes thus forming stable Cu-Sn intermetallic and have negligible tendency for electromigration [1-3]. These advantages of OSP over the metalized final finishes made it attractive for the PCB fabricators and assemblers and this coating gained popularity in the industry for more than four decades. Recent surveys showed that OSP is used in PC fabrication today with over 60% of the market and it is expected to grow. Increased use of OSP is already being seen in high reliability markets like automotive which havetraditionally used metallized finishes like immersion tin orsilver.

OSP coatings having all the above benefits, however, suffer from a few drawbacks as well. Inadequate wetting of solder is one that is mostly talked about. The problem gets even more pronounced when PCBs with OSP coating undergo prior thermal excursions [1]. Especially for the wave soldering process of a double-sided PCB, which is always exposed to one or two prior reflow cycles, vertical solder wetting or barrel filling performance of plated through holes poses a huge challenge to all the assemblers. The situation gets even worse for Pb-free processes using SAC alloys with higher operating temperature.

Engineers and researchers, over past two decades, have come up with various solutions to mitigate poor wave soldering performance on pre-reflowed boards with OSP. But their approaches were more focused on modifying the PCB design, determining the correct hole to component pin ratio or optimizing soldering process parameters [1-2]. Some of them have also suggested to use more active fluxes, which may clean the solderable surfaces more efficiently leading to better wetting [2]. More active no-clean fluxes, however, will leave residues which are more corrosive in nature and may not be suitable for applications having stringent electrical demands. Keeping this in mind, in this work, we have tried to understand the chemical changes OSP coatings undergo during thermal excursions and identify elements of soldering flux which will work on such thermally exposed OSP to give a clean copper surface, which in turn will result into better wetting or hole-fill during soldering.

CHARACTERIZATION OF OSP COATING

As discussed earlier, OSP is an ultrathin coating on the copper pads on a PCB. This coating is achieved by dipping specially treated copper surface into a solution containing active OSP chemicals. A generalized diagram describing the steps involved in coating process of ENTEK PLUS HT has been shown in Figure 1 [4]. During this process OSP molecules attach themselves on the copper surface by forming co-ordination bonds with positively charged surface metal ions as well as by electrostatic attraction. As shown in Figure 1, the pre-coating step, just prior to final coating requires high pH environment. In this pH the top layer of the copper metal gets oxidized and forms a very thin oxide film on the base metal. Although a part of this film gets converted into copper ion in the final coating step and form co-ordination bond with the substituted benzimidazole molecules (OSP molecules), the rest of it remains at the interface of metal and organic layers of as coated OSP finish.
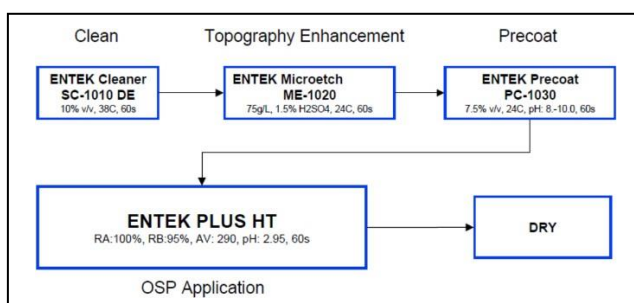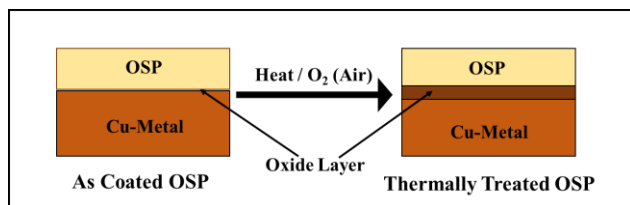

Figure 1. ENTEK PLUS HT OSP coating process

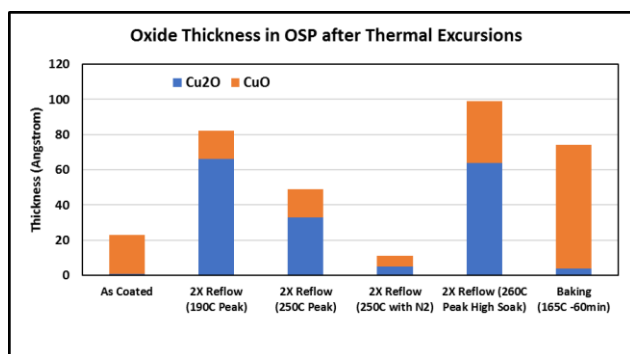**Figure 2.** Schematic diagram of oxide thickening at Cu – OSP interface

Figure 3. Oxide thickness in OSP coating after different thermal excursions

When a copper pads of a PCB coated with OSP undergoes thermal exposures (baking or reflow), the oxide layer at the interface gets thickened depending on the nature of the exposure (Figure 2). The oxide layer formed under different thermal conditions was quantified using Sequential Electrochemical Reduction Analysis (SERA) in a separate work [5].

The results showed that the oxide layer consists of both Cu_2O and CuO and it increases with the increase in exposure temperature or time (Figure 3). The same study also indicated that there may be a temperature range above which OSP coating softens and changes its morphology and during this transition phase OSP coating becomes less protective and allows external gas (oxygen) to penetrates through it which in turn increases the oxide layer thickness.

In the present work we have studied the morphology change of OSP coating after different thermal exposure by Atomic Force Microscopy (AFM). Three-dimensional AFM images (Figure 4) showed that as coated OSP surface consists of extensively large number of fine grained micro-peaks which largely disappear after Pb-free reflow with the appearance of larger grain like features. This morphology change is not noticed if the coupons are exposed to 165 C or less, independent of time of exposure. These observations reinforce the hypothesis of coating softening above 165 C determined in the earlier study.
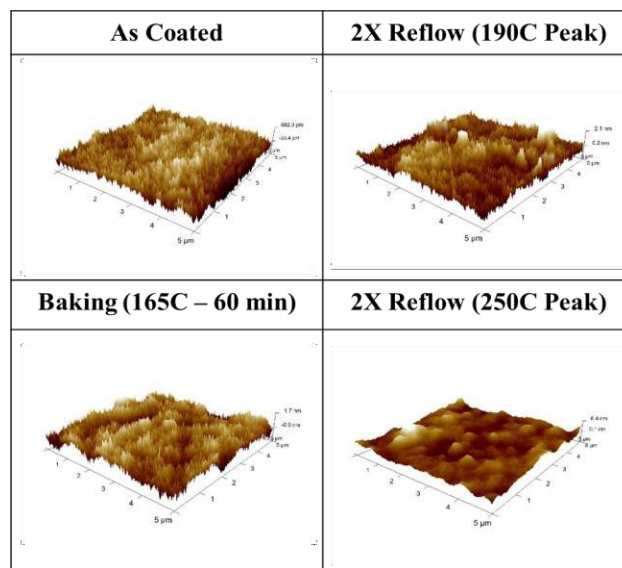

Figure 4. Three dimensional AFM images of as coated and thermally treated OSP coating

The obvious question here is "what type of changes in the organic layer result in larger grain morphology after OSP is exposed to high thermal conditions?". Images obtained from field emission scanning electron microscopy (FESEM) showed presence of small size random grains present on the surface of as coated OSP. These grains got converted into more ordered elongated fibre like structures when OSP coated coupons were subjected to standard Pb-free reflow in air or nitrogen environment (Figure 5). Appearance of such fibre like structures is possibly due to

the formation of supramolecular arrangements of substituted benzimidazole molecules via interactions of pi-electrons of its aromatic rings [6-7].
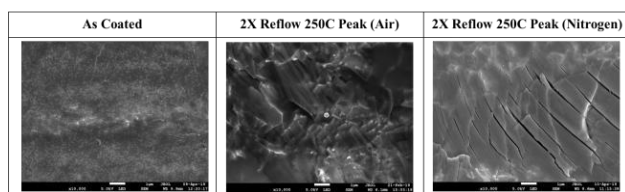

Figure 5. FESEM images of as coated and a thermally treated OSP coating

Results obtained from the above studies draw us to the conclusion that when OSP coated PCBs undergoes thermal excursions, two main changes take place – (1) oxide layer at the organic metal interface thickens and (2) active OSP molecules which form the organic layer get rearranged to form supramolecular fibre like structures. Oxide thickening requires both heat and air (or oxygen to be precise) while fibre formation is affected by the elevated temperature alone.

OSP FLUX INGREDIENT INTERACTION

Now with our understanding of the changes OSP undergoes after thermal excursion, we wanted to find what chemicals, often contained in liquid fluxes can overcome the effects of these changes and help the solder to wet on thermally exposed OSP. From our knowledge of chemistry, we understand organic solvents can dissolve the organic layer of the OSP coating. And we will need oxide removers (such as organic or inorganic acids, halides, halogens etc.) which will react with Cu_2O and CuO to open up the pristine metal surface for the solder to wet on it and form the joint.

In soldering flux industry, few organic solvents are loosely termed as 'OSP cutters' because of their ability to dissolve OSP coatings. We looked at their chemical structures closely and found more solvents of similar structures with comparable other physical properties. In an attempt to pick the best 'OSP cutter' among these solvents, their OSP dissolution efficiency was compared. As coated and 2x reflowed laminates of fixed dimension with ENTEK PLUS HT finish were dipped in fixed volume of each of these solvents (at 70 – 80 C) separately in beaker and it was shaken manually for three minutes. OSP coating dissolved in the solvents was quantified by measuring the UV absorption of the resultant solutions at 270 nm. Similar dissolution of OSP was done in 5% aqueous HCl at room temperature and absorption was measured. 5% HCl can fully dissolve as coated ENTEK PLUS HT [4] and absorption value corresponding to this can be taken as 100% OSP concentration in the resultant solution. Absorption value obtained from any other solution can now be converted into relative percentage of OSP dissolved in that solvent.

Figure 6 shows the relative amount of OSP dissolved in different solvents as well as in 5% HCl. From the plot it is

easily understood that most of the solvents taken for this experiment can easily dissolve the organic layer of as coated ENTEK PLUS HT finish. But once the coating undergoes two standard Pb-free reflow in air, solubility of OSP in the solvents decreases drastically, except in solvent SOL1 and 5% HCl, which can dissolve 40-50% of the coating under the experimental conditions. Solvent SOL1 is known to be one of the strongest organic solvent and thus it can break down the supramolecular arrangement of substituted benzimidazole molecules in thermally treated OSP coating and solubilize it. On the other hand, strong acid like HCl can react with benzimidazoles, which are basic in nature and the resultant salt with higher solubility helps it to get dissolved in this medium.
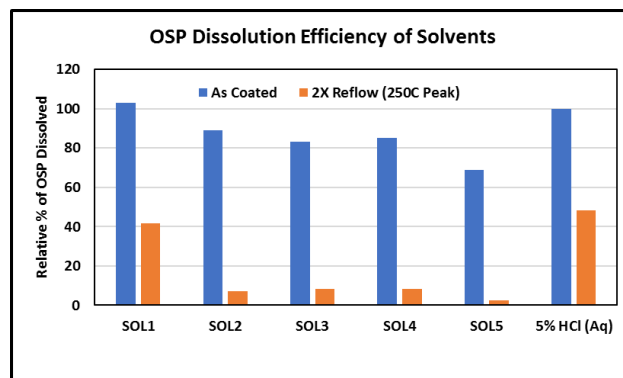

Figure 6. Relative percentage of as coated and reflowed OSP dissolved in different solvents

So, if inorganic acids can dissolve thermally treated OSP via salt formation will organic acids be able to do the job. To confirm this 1% solution of two organic acids, commonly used as activators in soldering fluxes, were prepared in SOL3 (this solvent cannot dissolve thermally treated OSP coating). OSP dissolution and absorbance measurement were carried out these two activator solutions as earlier. OSP coupons as coated, reflowed in air and reflowed in nitrogen were taken for this study. Results showed that both the solvent – activator solutions can dissolve ~ 80% of as coated OSP. But for the thermally treated OSP, while solvent can dissolve only 5-10% of it, activator solutions showed better efficiency, dissolving 20 – 30% of the OSP layer (Figure 7).
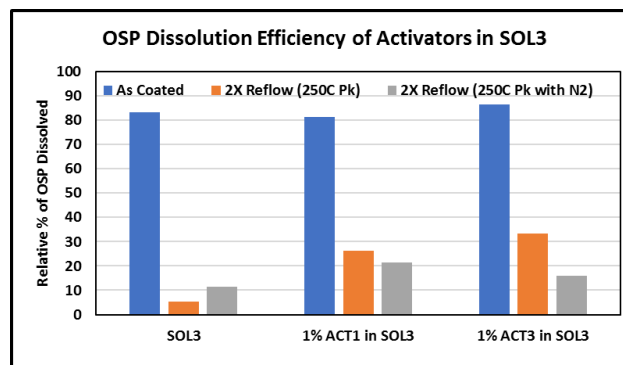

Figure 7. Relative percentage of as coated and reflowed OSP dissolved in solvent and activator solutions

Dissolving the organic layer, however, is only half of the job done. For solder to wet and forms a joint, the oxide film beneath the organic layer needs to be removed. Historically, organic or inorganic acids, halides, halogens etc. are used for this purpose and as a group are known as fluxing agents or activators. Here also, like the solvents, not all activators have same efficiency or activity to remove the oxide film from the metal surface. To understand how activators react with oxides, differential scanning calorimetry (DSC) was used. Since these reactions are acid – base type and they involve some amount of heat change, calorimetry is a very efficient tool to study such reactions. But limitation of the method is that we cannot put the thermally treated OSP coupons in DSC pan. In order to overcome this limitation, commercially available analytical grade cuprous and cupric oxides were used for this study. Mixture of oxide and activator (90:10 ratio) was prepared by dry mixing in a mortal pestle and was heated in DSC pan at 10 C/min ramp from room temperature to 300 C. A baseline DSC study of only activator was carried out to find if activator undergoes any heat change during this thermal ramp.

Representative DSC thermograms are shown in Figure 8 (a and b). DSC results reveal endothermic peaks for the only activator runs corresponding to the melting point of the activators. Additional exo- and endothermic peaks are observed for oxide-activator mixtures. These additional peaks we believe are resulting from the reaction between activators and copper oxides.
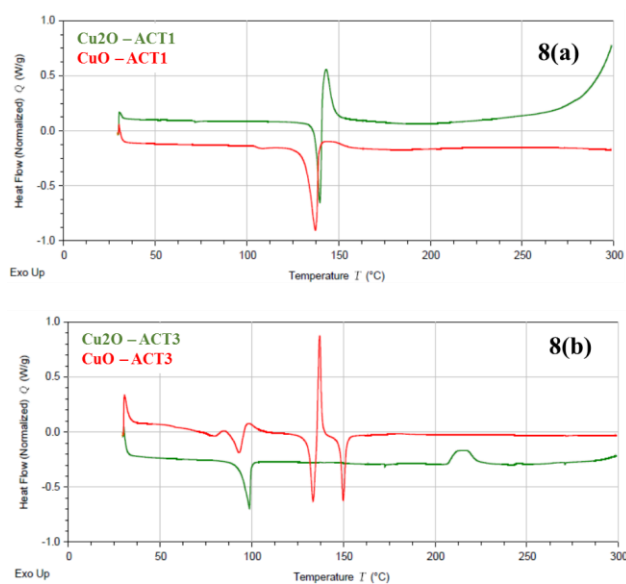

Figure 8. Representative DSC thermogram of activator copper oxide mixtures

A closer look at the thermogram also reveals one of the activators, ACT1 reacts with cupric oxide just after it melts around 140 C, while the other, ACT3 reacts with cuprous oxide at similar temperature after melting at 100 C. ACT3 also showed a smaller reaction exotherm around 220 C with cupric oxide. The results indicate that different activators

have affinity towards different oxides of copper and different activators react with a particular oxide at different temperature range. Thus, to efficiently remove the copper oxides from a thermally treated OSP coating, a mixture of activators is necessary, where different components will react with different oxides at different temperature zones resulting into a clean metallic surface which in turn will facilitate good solder wetting and subsequent joint formation.

WETTING OF SOLDER ON OSP

Now with the knowledge on the flux ingredients require to remove thermally treated OSP, we wanted to evaluate their efficiency to wet solder. Few activators and solvents selected from above studies were shortlisted. A few combinations of these solvents and activators were prepared as shown in Table 1. Solder wetting evaluation were carried out on ENTEK PLUS HT coated copper coupons, also known as OC-3 coupons (Figure 9a). Malcomtech SWB-S2 wetting balance tester (Figure 9b) with SAC305 solder bath at 260C was used for all the measurements. Wetting property data were collected on both as coated and 2X Pb-free reflowed coupons. Solder score (S) for each measurement was calculated using the equation, $S = [3.5 - T_0] + [4 - T_{2/3} - T_0] + [F_{max} \times 10]$, where, F_{max}, T_0 and $T_{2/3}$ stand for maximum force, time to zero wetting and time to reach two third of maximum force respectively [8]. T_0, $T_{2/3}$ and F_{max} values were obtained from the instrument and solder scores (S) for each run were calculated using that data.

Table 1. Details of solvent activator combinations for wetting balance study

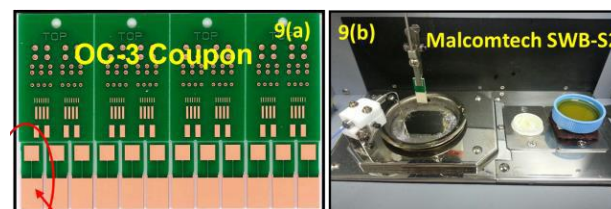| Ingredients | Combination No | | | | | | | | | |
	1	2	3	4	5	6	7	8	9	1
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	W	
ACT1	2.0				2.0	2.0	2.0			
ACT2		2.0								
ACT3			2.0							
ACT4				2.0						
ACT5										
ACT6										
SOL1										
SOL3										
IPA										

Figure 9. OC-3 coupons and Malcomtech SWB-S2 wetting balance tester

As solder score plot (Figure 10) shows that all solvent – activator combinations except 7 have excellent wetting properties on as coated OSP. All these combinations have solder score above 5.93, which represents a passing solder

score, calculated from Set A requirements of IPC J-STD-003C. However, when tested on 2X Pb-free reflow OSP coupons, solder scores for only a few combinations were found to be greater than 5.93. Which means only these solvent – activator combinations were able to remove the thermally treated OSP coating effectively and thus aiding the spread of solder on clean copper surface. Use of such solvent – activator combinations in fluxes impart superior wetting performance to those products. Solder score data obtained from such simple wetting experiment helps flux formulators to shortlist ingredients to develop new products with best in class wetting on pre-reflowed OSP.
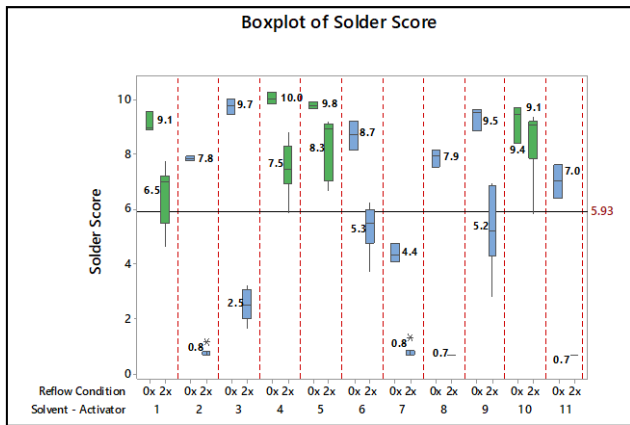

Figure 10. Solder score plot for solvent – activator combinations

Another interesting observation from this experiment is that whenever a secondary solvent is used – solder scores of those combinations have declined. Combinations 7 and 8 contain the same activator as combination 1 with addition of two different secondary solvents and combination 11 have same activator as 10 with same secondary solvent used in combination 7. We have seen in the earlier section that these solvents can remove thermally treated OSP. Authors assume this anomaly or results between two set of experiments is due to the partial drying of the coupons during wetting balance experiments. The wetting balance instrument does not have an efficient preheat system to dry all the volatiles like secondary solvents. Whenever a partially dry coupon is dipped in the solder bath, the volatiles present in coupons dilutes the activator system, which in turns results into poor activity. These volatiles also spatter when coupons are immersed into the bath, disturbing and delaying the wetting process. Wetting balance is an excellent tool to screen the efficiency of activator systems for fluxes, but it may not be the most reliable method to compare flux performance. Especially many of the modern fluxes, used in Pb-free processes as they contain secondary solvents to preserve their activity at higher temperatures. For these fluxes we need to use more complex evaluation processes like wave or selective soldering to compare the activity and other properties.

Table 2. Details of activators and solvents present in commercial fluxes taken for wave soldering performance

Flux	Solvent - Activator Combination Used
A	Combo 3
B	Combo 5
C	Combo 5
D	Combo 6
E	Combo 5 + SOL3
F	Combo 11

To verify this, we selected few commercially available liquid fluxes containing some of these activator – solvent combinations. Details of the solvents and activators present in the fluxes are described in Table 2. Wave soldering performance of these fluxes were benchmarked on a 2.4 mm thick 6-layer PCB having ENTEK HT PLUS pad finish. PCBs were subjected to air reflow twice prior to wave process. Wave soldering were carried out on ERSA Power Wave machine using SAC305 bath at 265C. Flux loading for all the fluxes were controlled in such way that activator amounts on the board remain constant. Wetting performance of the fluxes were evaluated by comparing the x-ray images of the PCI connector barrel filling (Figure 11).
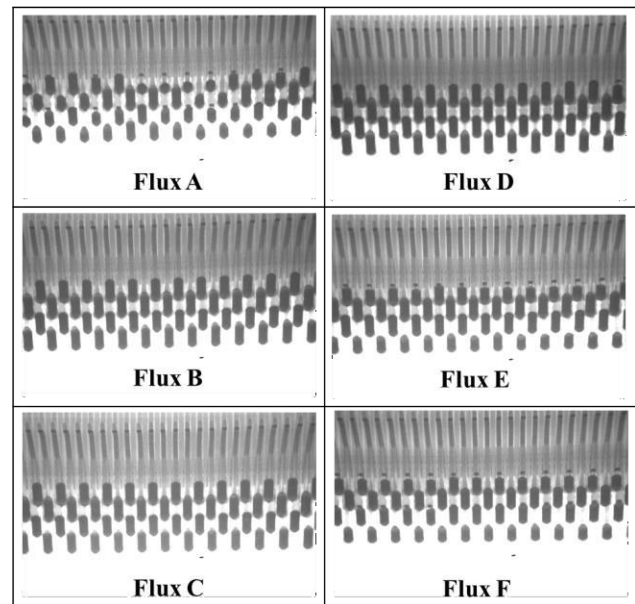

Figure 11. X-Ray images of PCI connectors showing the barrel filling for different fluxes

From the barrel fill images, it is very clear that Flux A containing solvent – activator combination 3 has the worst performance among the fluxes. Flux B and C with solvent – activator combination 5 and Flux D with combination 6 showed excellent barrel filling. Wave soldering performance of these fluxes corroborates the results obtained in wetting balance experiments. But with addition to these, Flux E having solvent SOL3 and activator combination 5 and Flux F with combination 11, also demonstrate soldering performance equivalent to flux B, C and D. For fluxes E and F, secondary solvent is helping the

flux to remove the thermally treated OSP, thus assisting in solder wetting process. Most of these solvents evaporate in high preheat of Pb-free process thus does not show any adverse effect in solder wetting in wave soldering application. As discussed earlier in many Pb-free capable fluxes, these solvents prevent the activators from decomposing or evaporating in the preheat stage, thus preserve the flux activity for the soldering zone.

CONCLUSION
OSP coupons as coated and after thermal excursions were characterized using electro-analytical, spectral, thermal and chemical analysis. Results indicate that when OSP coating undergoes thermal excursions, two major changes take place. Copper oxide film at organic metal interface thickens as Cu_2O and CuO formation takes place in presence of heat and oxygen. In-addition, substituted benzimidazole molecules in the OSP rearrange themselves to form elongated fibre like structures via intermolecular attraction and become more compact an dense.

Some of the solvents traditionally used in soldering fluxes can dissolve the organic layer of thermally exposed OSP at elevated temperatures. The organic layer also can be stripped off by using organic acids solutions in combination with these solvents. Flux activators can react with the oxides and remove them at elevated temperatures. Different activators found to react with oxides at different temperature, they also showed selectivity towards only one of the oxides. This indicates that a multi activator package in a soldering flux is more efficient to remove all the oxides from OSP coated PCBs, compared to single activator system.

To compare the efficiency of flux activators to remove thermally exposed OSP, wetting balance can be used. Activator packages for new fluxes can be selected by analysing the solder score data obtained from wetting balance experiments. However, for fluxes containing solvents with very high boiling points, wetting balance data may lead to erroneous interpretation about their wetting properties. For these products, performance benchmarking with wave for selective soldering will be a better way to compare their efficiency. Results obtained from both wetting balance and wave soldering experiments, however, confirm the effectiveness of fluxes with multi activator package to achieve superior wetting on thermally treated OSP.

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