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PWB Final Surface Treatment Process and Film Characteristics that Satisfy Lead-free Solder Mounting

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Abstract
Because of environmental concerns, elimination of lead from electronic components has been recently encouraged, and as a result, lead-free solders are frequently adopted for solder mounting. The OSP and HASL treatments have been primarily used for the majority of final surface treatments for PWB's used for electronic components, while conventional electroless Ni/Au plating process has been used for the remainder. Lead-free solder mounting can lead to poor solderability in the case of some OSP-treated PWBs. The problems associated with HASL for the latest generation PWBs and packages is already well documented.

Under the present conditions in which manufacturers are switching from conventional solders to lead-free solders and are beginning mass-production, this problem is being highlighted. Consequently, it is urgently required to establish a treatment method that can replace OSP treatment.

This paper compares the solderability of immersion Ag, immersion Sn, and immersion Au plating that is treated directly on copper, and electroless Ni-P/Au plating, all of which are now attracting industry wide attentions as alternative surface treatments for PWB's. The paper makes recommendations regarding the treatment method that supports future lead-free solder mounting.

Introduction
Because of environmental concerns, the industry is going "lead-free", that is to pursue the lead elimination from joining of base materials and parts that comprise electronic assemblies. As a result, for solders used for mounting, lead-free solders such as Sn-Cu-Ag, etc. have been adopted. In addition, reduction in size and weight is demanded in electronic instruments. The solder joining area is growing smaller and smaller, and cases in which incomplete solder joining occurs during mounting have markedly increased because lead-free solders tend to provide poorer spreading characteristics than conventional eutectic solders for the required higher mounting temperatures.

In particular, in the HASL or OSP treatment that accounts for the majority of the PWB final treatment methods, the technological limit seems to have been reached with respect tousing lead-free for solders. It is urgently necessary to choose the PWB final surface treatment method that can replace HASL and OSP treatment.

Under such circumstances, for alternatives, immersion Ag, immersion Sn and immersion Au plating processes which are treated directly on copper and which we propose as alternatives, have been attracting a great deal of attention.

Furthermore, a new type of electroless Ni/Au plating process in which the solderability has been recently greatly improved is added to the candidate alternatives. To date, in the course of developing the electroless Ni/Au plating process, we have studied the method for determining whether the solder mounting required after packaging is satisfied or not and the method for analyzing the results obtained. Making the best of the know-how we have accumulated, this paper proposes alternative methods for the PWB final surface treatment process that satisfies the requirements for going lead-free.

Outline of the Experiment
Investigation of Various Types of Final Surface
Treatment Plating
Comparisons were made on immersion Ag, Sn (both our own commercially available baths and other manufacturers are used for comparison). Data is also presented regarding a commercially available heat resistant OSP, immersion gold direct over copper, and two electroless nickel / immersion gold systems. One electroless nickel / immersion gold system is an improved process in which the gold is deposited both by an immersion reaction and an autocatalytic reduction process.

Specimen Preparation Method
The test coupon for testing solder joint reliability is

made by copper electroplating on copper clad laminate, and forming BGA pads of 0.5mm diameter with the solder mask. Copper electroplated copper clad laminate was used for the solder spread test coupons. The above test pieces were plated with the processes shown below. The plating method is described as follows. Ag, Sn, and direct Au plating were carried out directly on the copper substrate that was pretreated by acid cleaner, soft etching (treatment solution of sodium persulfate + sulfuric acid) and acid cleaning (sulfuric acid solution).

Table 1 shows our electroless Ag, Sn, Au plating processes and Table 2 show the new electroless Ni/Au plating process.

The electroless Ag plating film was made under condition at 50°C and 2 minutes with our new type bath for 0.2µm thickness, and for comparison, was made under condition at 50°C and 1 minute with other manufacturer's commercially available bath for 0.3µm thickness. The electroless Sn plating film was made under condition at 60°C and 10 minutes with our new type bath for 0.7µm thick, and for comparison, was made under condition at 50°C and 9 minutes using other manufacturer's commercially available bath for 1µm thickness. For direct copper immersion Au plating, which is our original process, the plating film was made under conditions at 85°C and 10 minutes for 0.04µm thickness. For electroless Ni-P/Au plating, the plating film was made under conditions of our standard process; the new immersion/electroless Au plating bath in which our new type of plating reactions comprises replacement and part reduction. For comparison, the Ni plating film of 5µm thickness and Au plating film 0.07µm thickness was applied.

For the comparison evaluation reference of the current PWB final surface treatment method, a commercially available OSP treatment chemical (water-rinsing type) with improved heat resistance was used.

Table 1 – Immersion Sn, Ag, Au Processes

Cleaner		
Rinse		
Soft Etching / H2SO4+SPS		
Rinse		
Acid Dipping / 5% H2SO4		
Rinse		
Pre-dipping	Immersion Ag	Direct Immersion Au
Immersion Sn	Rinse	Rinse
Rinse / hot water	Acid Dipping	
Rinse	Rinse	
(Neutralizer)		
(Rinse)		
Note) We recommend DI water rinsing after etching, especially EL-Ag process.		

Table 2 – Standard Process for New Electroless Ni / Immersion Au

Cleaner
Rinse
Soft Etching / H2SO4+SPS
Rinse
Pre Dipping
Activator
Rinse
Electroless Ni
Rinse
New Immersion Au
Rinse

Evaluation Method

Solder Joint Reliability Evaluation (Shear Test and Pull Test)

The solder ball shear test and pull test are assumed effective means for judging the solder joint reliability of electroless Ni-P/Au plating in our company. Based on these results, the correlation of solder bond strength on the mounted PWB is actually verified and a large number of the data that supports the correlation have been accumulated. In this paper, ball shear tests and pull tests were carried out for solder joint reliability evaluation.

The test pieces, which were treated by the immersion Ag, Sn, Au, and electroless Ni-P/Au as well as conventional OSP treatment, respectively, were compared for solder joint reliability using eutectic Sn/Pb solder balls and Pb-free solder balls. Using a reflow simulator (Malcom Reflow Simulator RS-1), reflow was done with the following profiles as shown in Figure 1.

For the heat resistance test, two types of 0.65 mmϕ solder balls (63Sn - 37Pb eutectic solder and 95.75Sn-3.50Ag - 0.75Cu lead-free solder) were reflowed on the BGA pads of each of test boards which were as plated. Each sample was then treated after one time and second times with each reflow in the same method by the use of the reflow simulator using an RMA type flux (529D-1 available from Senju Metal Industry). Each sample was evaluated by the shear test and the pull test. Figures 2 and 3 show the shear and the pull test methods. Using the solder bond strength measurer, Dage's #4000, the shear and the pull tests were conducted with measuring tools set at 170µm/sec tool speed and 50µm tool height.

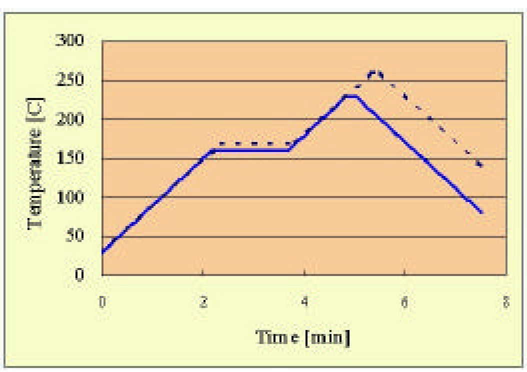


Figure 1 – Temperature Profile of Reflow Simulator for Sn-Pb and Pb-Free Solder

Solder Spreading Test

After applying RMA type flux (529D-1 available from Senju Metal Industry) to each of the solder spreading test samples, two types of 0.65 mmϕ solder balls used for solder bonding strength measurements were placed on the copper plated coupons. Using the same reflow simulator as that used in the preceding section, solder reflowed out in accordance with each of the solder reflow profiles. The solder wet spreading was measured as shown in Figure 4.

The solder spreading ratio was calculated as follows: Spreading ratio $\{mm^{-1}\}$ = solder spreading area $\{mm^{-2}\}$÷solder ball volume $\{mm^{-3}\}$

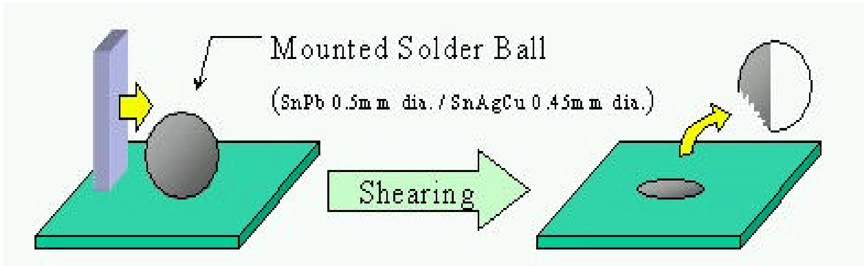
Evaluation Results

Solder Ball Shear Test and Solder Ball Pull Test Results

Figures 5, 6, 7, and 8 show the shear strength and the failure modes of the solder ball fractured surface as shear test results of eutectic solders and lead-free solders in accord with surface treatment methods. In the same manner, Figures 9, 10, 11, 12 show the pull strength and the failure modes as shear test results of eutectic solders and lead-free solders in accord with surface treatment methods.

The solder balls were mounted in order to compare the relationship after heat treatment. The solder balls were reflowed on the test boards, which were treated after one time and a second time with each reflow profile (used in the reflow simulator). The shear and the pull test results are also shown on the each of the cases.

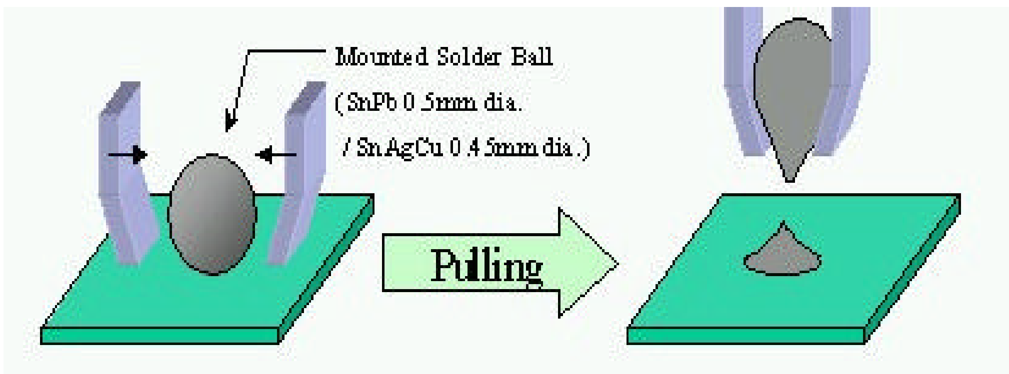
The shear test and the pull test results in the case of eutectic solder and lead-free solder in electroless Ni-P/Au plating differ from those obtained by the other surface treatment methods. The diffusion layer formed by reflow of electroless Ni-P/Au plating with Sn in the solders is not the Cu-Sn diffusion seen with immersion Ag, Sn, and Au, but is the Ni-Sn layer. Therefore, their failure mode results are shown separately in Figures 13, 14, 15, and 16.



Ball shear strength and failure mode are evaluated
Especially, micro soldering technology will focus in solder joint less than 0.5 mm diameter.
Equipment: Dage #4000 / Tool Rate : 170µm/sec
Flux: RMA –type/Senjukinzoku 529D-1
Reflow condition: Hot Air Reflow/Malcom RS-1

63Sn 37Pb	Pre-heating/160°C – 90 sec	Top/230 °C – 10 sec
95.75Sn-3.50Ag-0.75Cu	Pre-heating/170°C – 90 sec	Top/260 °C – 10 sec

Figure 2 – Solder Ball Shear Test Method



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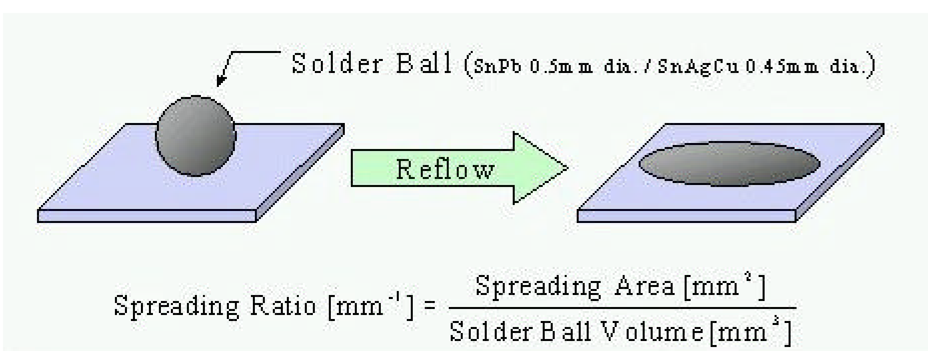
63Sn 37Pb	Pre-heating/160°C – 90 sec	Top/230 °C – 10 sec
95.75Sn-3.50Ag-0.75Cu	Pre-heating/170°C – 90 sec	Top/260 °C – 10 sec

Figure 3 – Ball Pull Test Method



Flux: RMA-type/Senjukinzoku 529D-1
Reflow Condition: Hot Air Reflow/Malcom RS-1
(Sn-Pb, Sn-ag-Cu) Pre-heating/160°C, 170°C - 90 sec
Top Temp/230°C, 260°C - 10 sec

Figure 4 – Solder Spreading Test Method

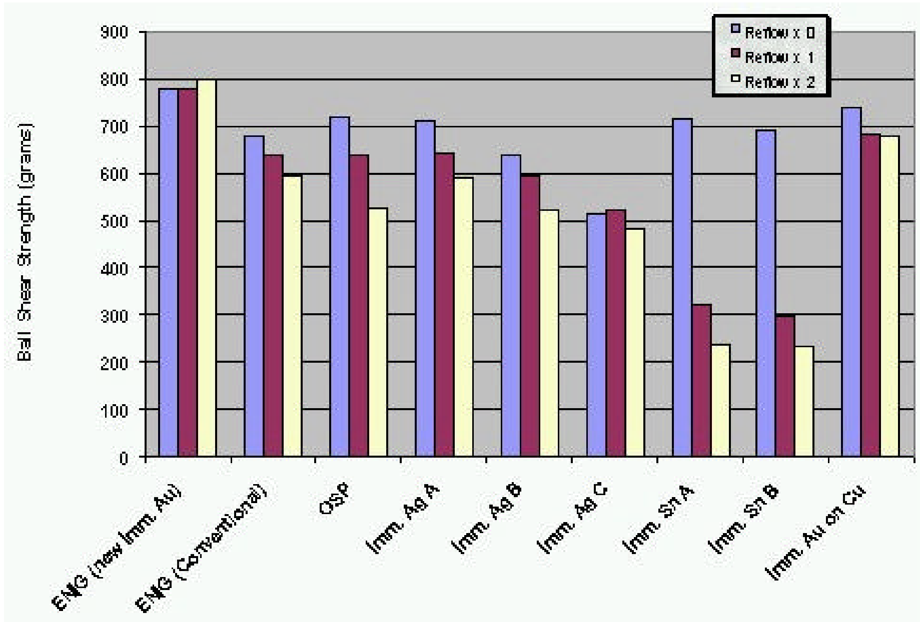


Figure 5 – Ball Shear Strength for Sn-Pb Solder

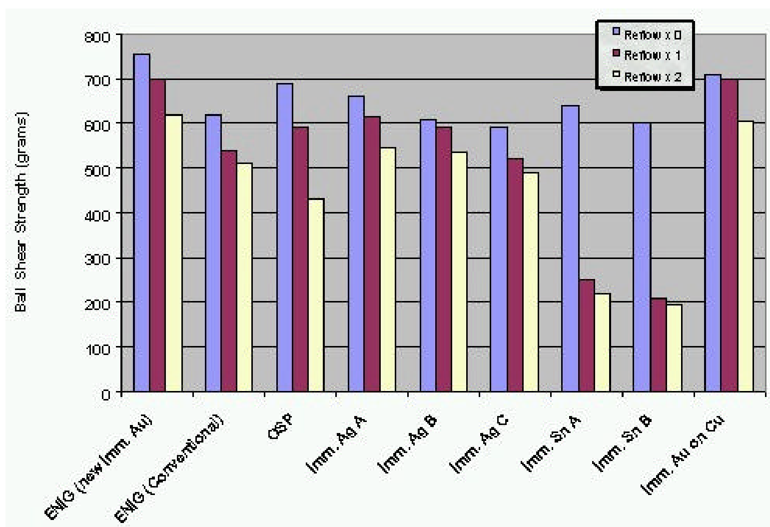


Figure 6 – Ball Shear Strength with Pb-Free Solder

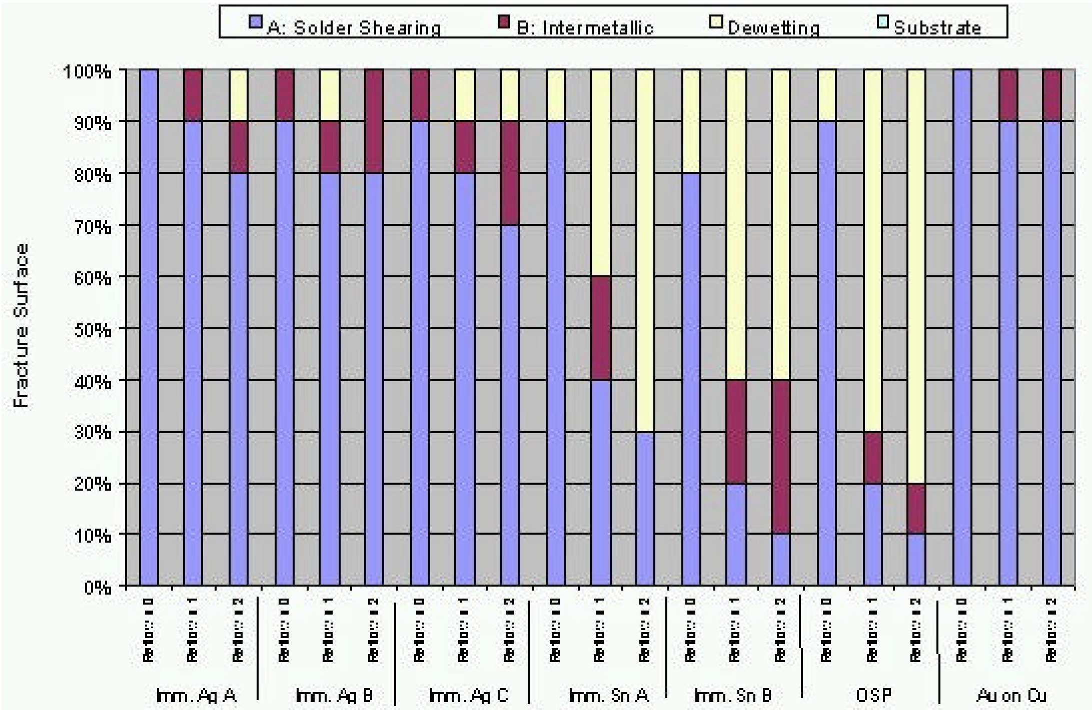


Figure 7 – Ball Shear Mode for Sn-Pb Solder with Reflow Cycles

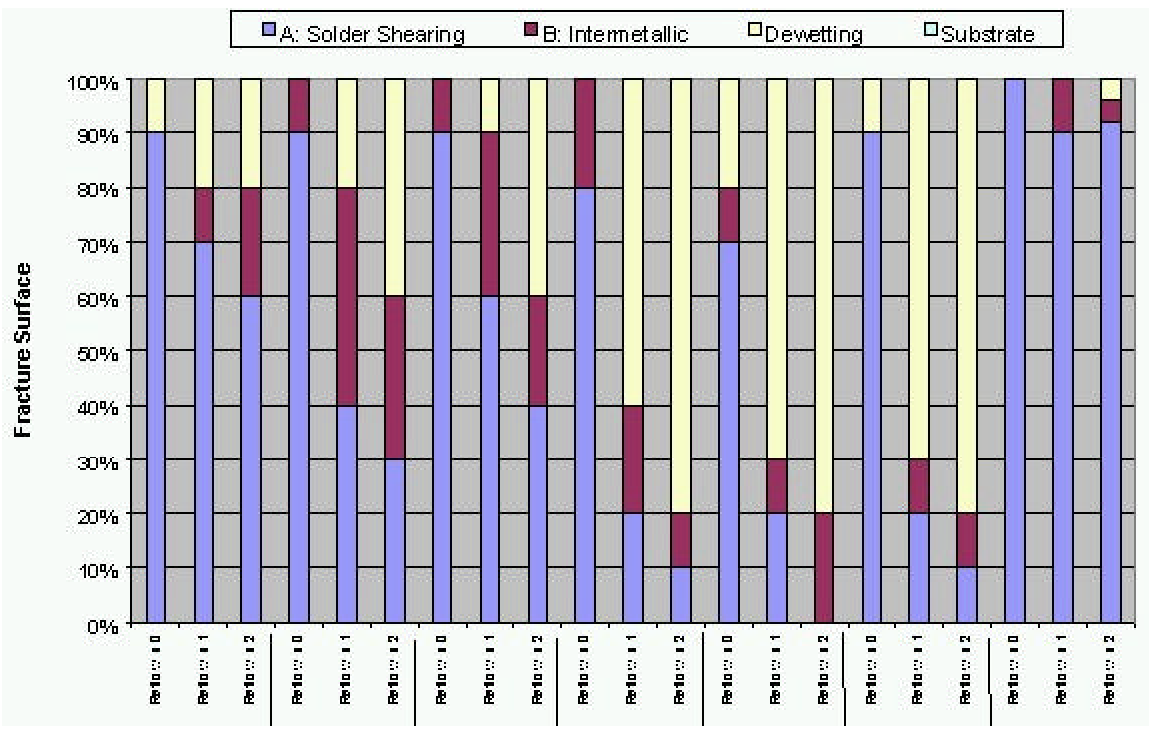


Figure 8 – Ball Shear Fracture Mode, Pb-Free Solder, with Reflow Cycles

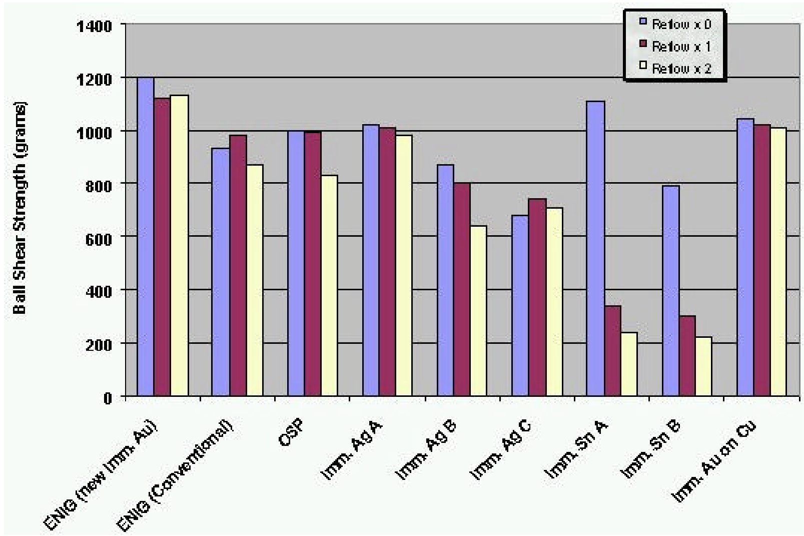


Figure 9 – Ball Pull Strength, Sn-Pb Solder, with Reflows

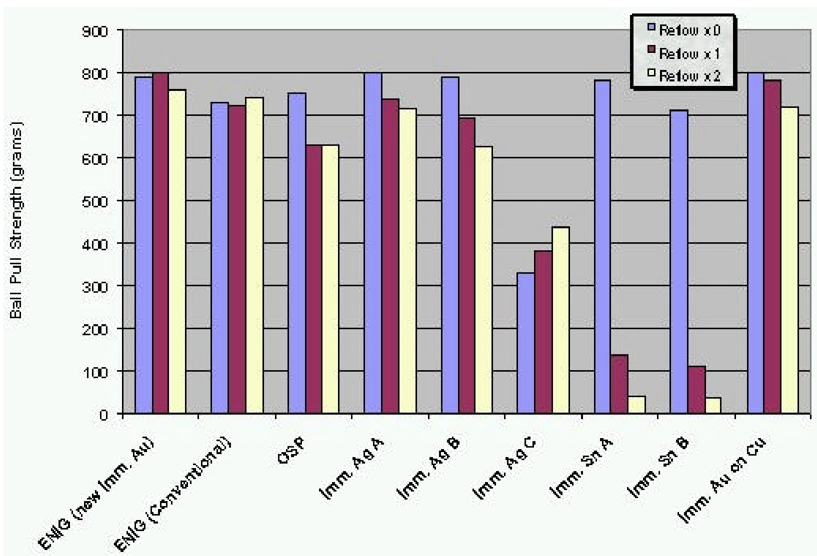


Figure 10 – Ball Pull Strength, Pb-Free Solder, with Reflows

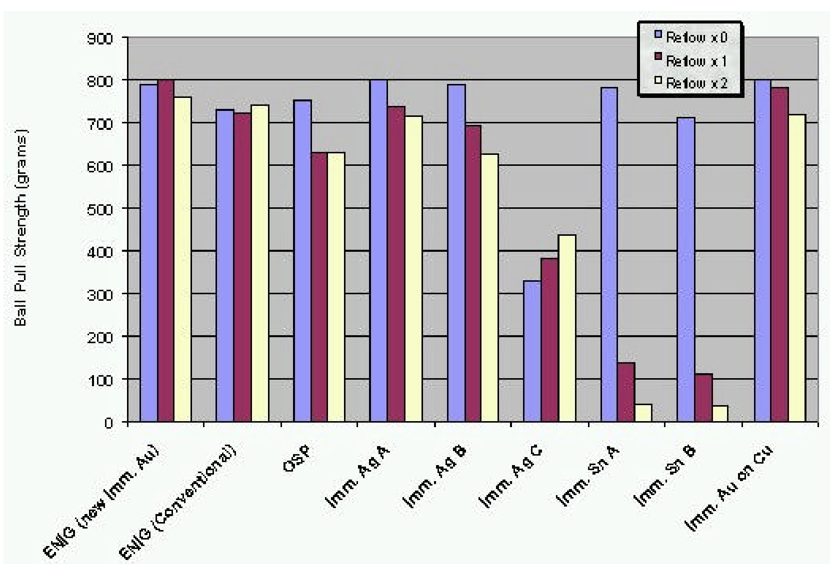


Figure 11 – Ball Pull Mode, Sn-Pb Solder, with Reflows

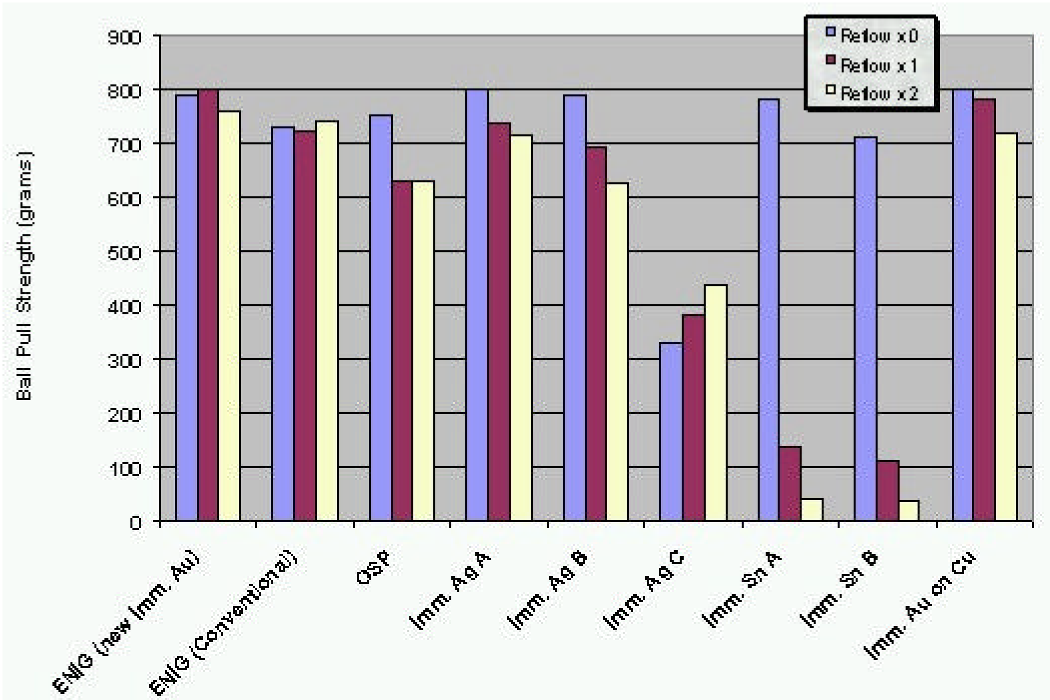


Figure 12 – Ball Pull Mode, Pb-Free Solder, w/Reflows

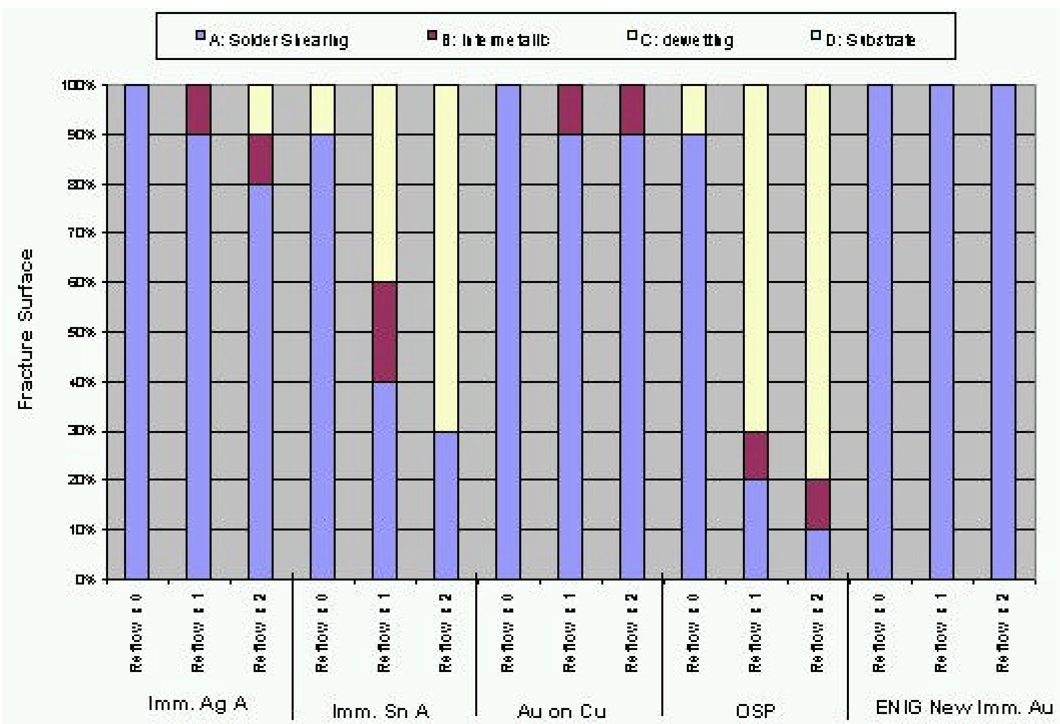


Figure 13 – Ball Shear Mode, Sn-Pb Solder with Reflows, Comparing with ENIG

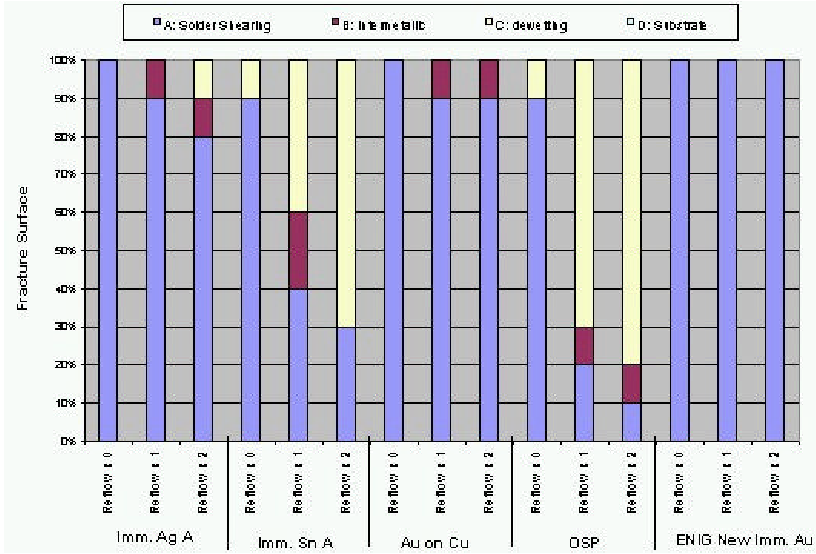


Figure 14 – Ball Shear Mode, Pb-Free Solder, w/Reflows, Comparing with ENIG

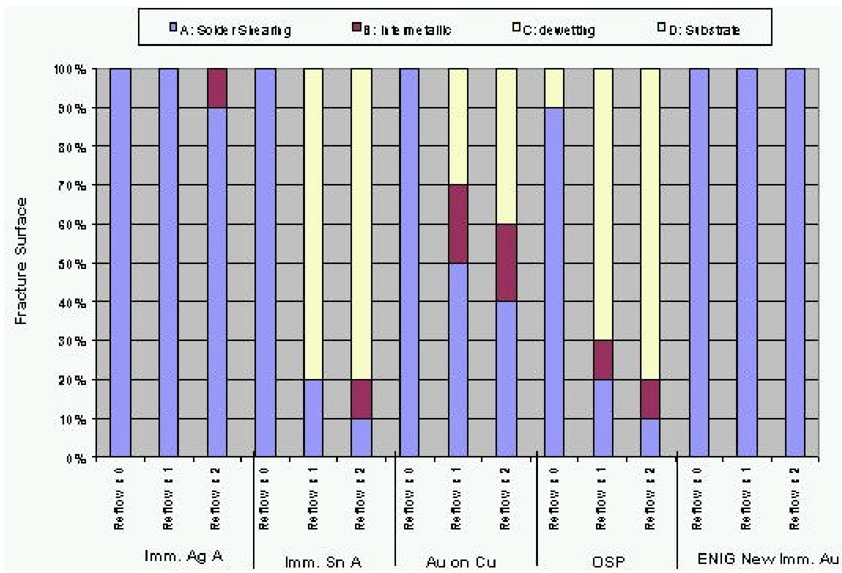


Figure 15 – Ball Pull Mode, Sn-Pb Solder, w/Reflows, Comparing with ENIG

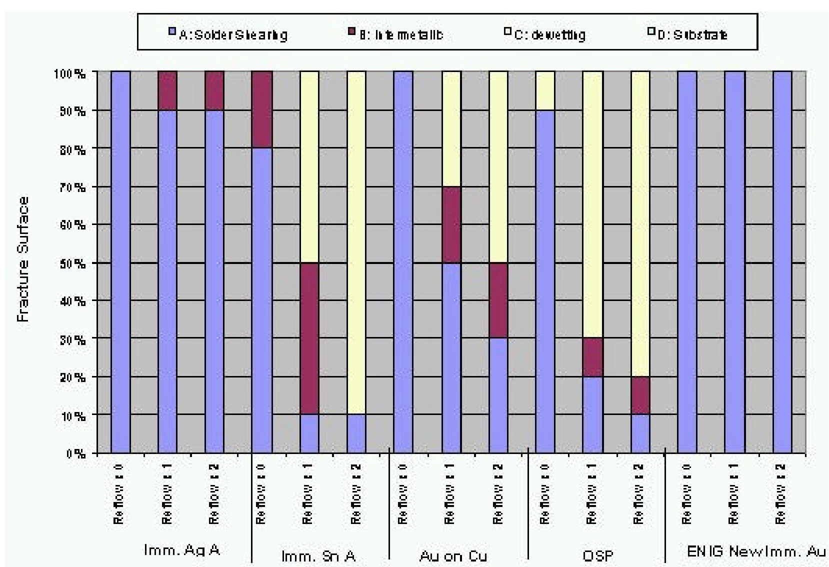


Figure 16 – Ball Pull Mode, Pb-Free Solder, w/Reflows, Comparing with ENIG

First of all, what can be confirmed from the results of the shear and the pull strength results can be summarized as follows:

- When the treatment methods are compared, irrespective of eutectic solders and lead-free solder, electroless Ni/Au achieves same shear strength and pull strength. It is followed by direct Au on copper plating, immersion Ag plating, OSP, and immersion Sn plating, which achieve nearly the same level of strength.
- Similarly, with respect to shear strength and pull strength by heat treatment, results indicate marked lower values for immersion Sn and OSP treatment of the conventional method. However, for other surface treatments, the ratio of decrease is smaller.

Next, discussion will be made of the shear and pull failure modes. First of all, the comparison results of immersion Ag , immersion Sn and immersion Au plating on copper indicate the same results as the conventional OSP method, and are summarized as follows:

- When the treatment method is compared, for both eutectic solders and lead-free solders, immersion Au plating achieves the extremely stable shear and pull failure modes. It is followed by immersion Ag, which is slightly inferior to the direct Au but indicates comparatively satisfactory mode. Comparatively, immersion Sn and OSP indicates lower shear and pull failure modes than those of direct Au and immersion Ag. Regarding immersion Ag plating, some differences were seen depending on the type of bath.
- With respect to heat treatment, no deterioration in strength was observed with immersion Au on Cu and immersion Ag plating, though the strength slightly decreased in accord with the number of reflows. As compared to those, considerable deterioration was observed in terms of the number of reflows for immersion Sn and OSP. In addition, considerable differences were confirmed for immersion Ag and Sn in accord with the type of bath. This indicates that immersion Ag plating bath design would be the point as is the case of immersion Sn.

Figures 13, 14, 15, and 16 show the cases in which electroless Ni-P/Au plating is compared with immersion Ag plating, immersion Sn plating, and immersion Au plating on Cu as the PWB final surface treatment method with respect to the shear and the pull fracture modes. What can be confirmed from these are shown as follows:

- In either eutectic solders or lead-free solders, the new type of electroless Ni-P/Au plating provides the best characteristics as compared to other treatment methods.

However, conventional electroless Ni-P/Au plating processes are difficult to keep the P content in the Ni-P film constant and stable. Because of excessive elution reactions to the Ni-plating film are seen by the immersion Au reaction, corrosion of the Ni film layer and grain boundaries occurs and oxides are formed at the Ni film surface. This lowers the solderability. When the substrate is subject to heat after solder mounting, diffusion of the Ni-P film and Sn in the solder takes place; the P-rich layer is formed at the interface between the Ni-Sn diffusion surface and the solder, and voids are also generated at the interface between the diffusion layer and the Ni-P layer, causing problems. Figure 17 shows the P content of electroless Ni-P and the conditions of eutectic solder joined interface. Consequently, this problem is avoided by OSP treatment where the solder-joined surface is copper.

For example, the partial electroless Ni-P/Au plating process is performed on several types of cellular phone substrate (Figure 18). The places used for button key contacts are electroless Ni-P/Au-plated and the places where small-diameter solder ball packaging such as CSP, etc. is OSP-treated.

Figure 19 shows the partial electroless Ni-P/Au plating process.

The substrates are produced through this kind of extremely complicated process. Consequently, the gold surface may be contaminated and the original gold plating film characteristics may possibly be degraded.

The objectives of carrying out thistype of complicated process is to secure a certain level of the stable bond strength, which is the Cu/Snsolder joint on BGA pads. However, this method cannot be said a reliable method that can provide stable bond strength, as indicated by the present results if the lead-free solders are used.

It was desired to hold the P (wt.%) content of the electroless Ni-P deposit stable to 5.5-8% and suppress the corrosion caused by the immersion Au platingonto the Ni-P layer to solve the problem of uncertainty of solderability. We have developed an electroless Ni-P/Au plating of a new type that can achieve stably 6 - 8% P content in the electroless Ni-P plating film and that comprises replacement reactions and partial reduction Au deposition reactions. This has widened the range in which electroless Ni-P/Au plating can be applied.

We have released the information on the relationship between the P content of electroless Ni-P plating and replacement Au plating. As an example, Figures 20 and 21 show the cross sectional SEM of invasion into the Ni-P layer and Figure 22 was shown the solder ball shear mode for P content of electroless Ni-P plating and types of Au deposition.

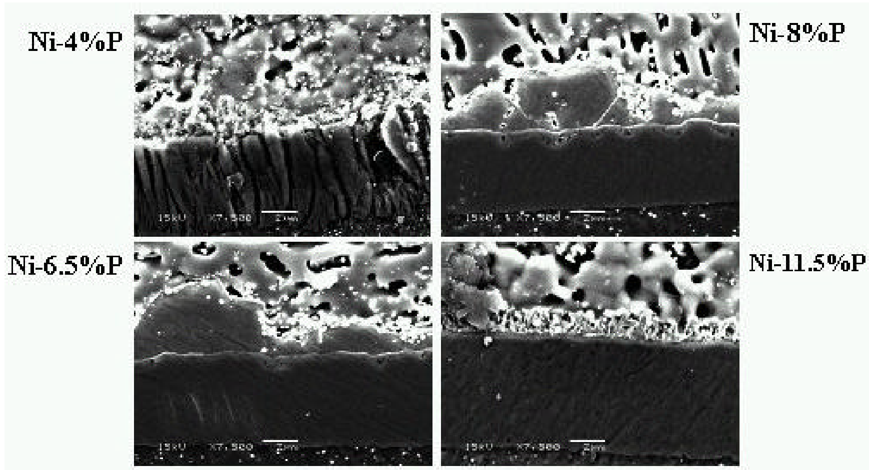


Figure 17 – Cross Section of Solder Ball Joint Area, 230^0 C, 30 minute Reflow

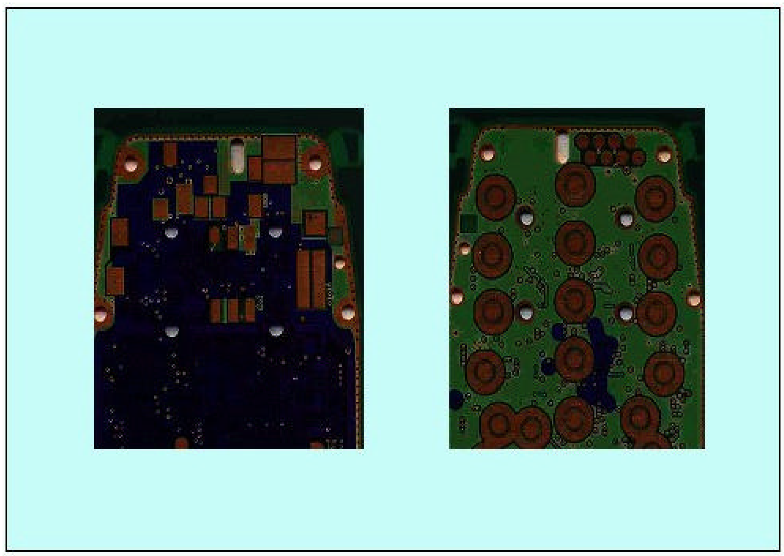


Figure 18 – Mobile Phone PWB (Selective Plating Type)

Figure 19 – Process of Selective ENIG for Mobile Phone PWB

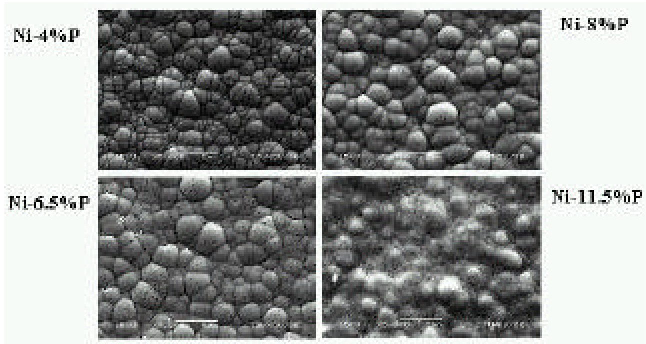


Figure 20 – Ni-P Surface After Gold Stripping (Conventional ENIG)

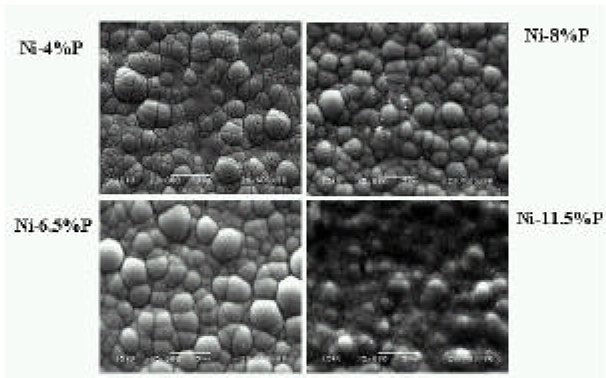


Figure 21 – Ni-P Surface After Gold Stripping (New Imm. Au for ENIG)

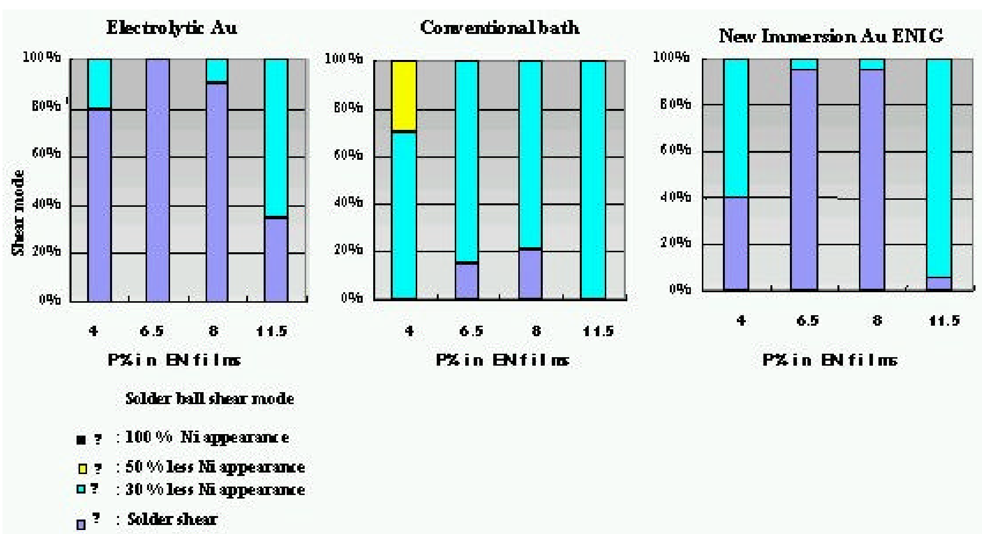


Figure 22 – Ball Shear Mode Result for Different %P in EN Film

Solder Spreadability

Figure 23 was shown the solder spread results when the reflow heating is applied in each of the final surface treatment methods in the case of eutectic solders and Figure 24 shows the same results for lead-free solders.

Based on the results of solder spread results, the treatment methods are compared as follows:

- Irrespective of eutectic solders or lead-free solders, electroless Ni-P/Au plating provides superior characteristics, which is followed by immersion Ag plating, direct Au plating on Cu, and immersion Sn plating.

However, OSP treatment exhibits poorer solder spread in the case of lead-free solders.

- When the relationship with heat treatment is compared, electroless Ni-P/Au plating, direct Au plating on Cu, and immersion Ag plating indicate some decrease with reflow cycle, but conspicuous lowering of solder spread is observed in OSP treatment and immersion Sn plating.

This data indicates the problems now seen in the mounting technology in which switching to lead-free solders is underway.

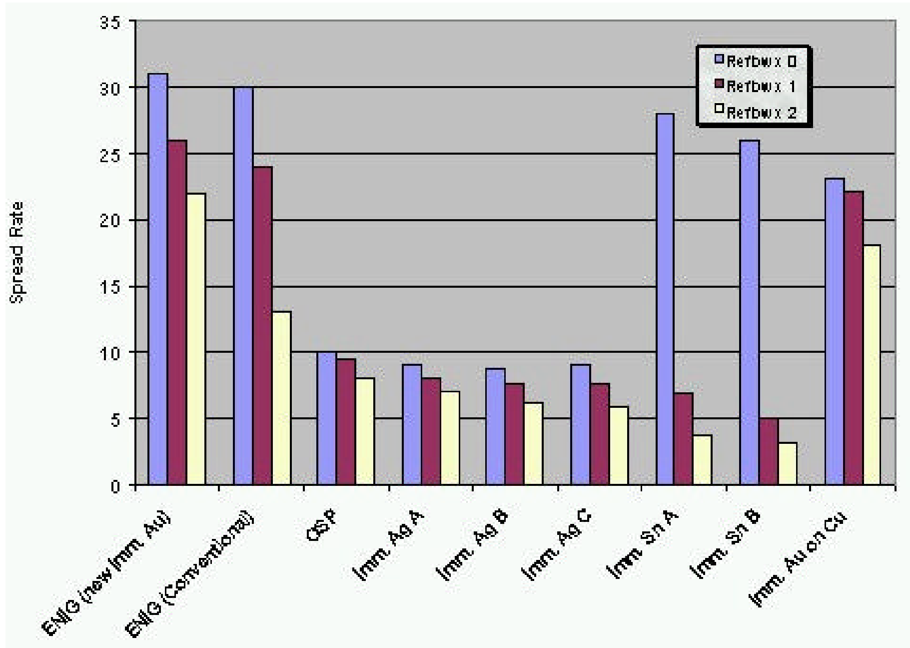


Figure 23 – Solder Spreading Comparison, Sn-Pb Solder, w/Reflows

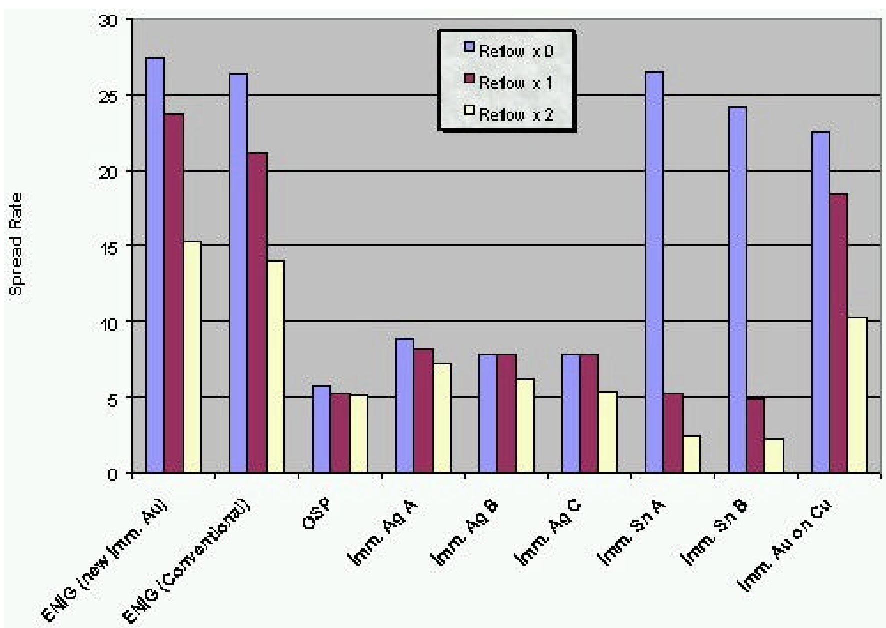


Figure 24 – Solder Spreading Comparison, Pb-Free, w/Reflows

Summary

Presently, the majority of PWBs are produced by the conventional OSP and HASL treatment for the final surface treatment. As indicated also by the results of the present report, when lead-free solders are used for mounting in the future, it is predicted that soldering failures are likely to occur. Presently, the industry attention is suddenly focused on the immersion Ag plating and immersion Sn plating as alternative techniques for OSP treatments. However, one needs to carefully consider the choice of immersion Ag plating or immersion Sn plating as a direct replacement for OSP treatment especially in the light of the use of lead-free solders. In the present report, electroless Ni-P/Au plating and direct Au plating on Cu was added for comparison. This is because test results indicate that the new electroless Ni-P/Au plating method that solves problems of conventional electroless Ni-P/Au plating is a viable alternative that can successfully withstand the higher reflow temperatures seen with lead-free solders.

We hope that all the treatment methods can find niches for themselves, respectively, in accordance with their suitable applications taking into account the results presented in this paper.