High Phosphorus ENIG – highest resistance against corrosive environment

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Abstract: Over the past years there has been consistent growth in the use of electroless nickel / immersion gold (ENIG) as a final finish. The finish is now frequently being used for PBGA, CSP, QFP and COB and more recently gathered considerable interest as a low cost under-bump metallization for flip chip bumping application.

One of the largest users for this finish has been the telecommunication industry, were millions of square meters of PCBs with ENIG have been successfully used.

The nickel layer offers advantages such as multiple soldering cycles and hand reworks without copper dissolution being a factor. The nickel also acts as a reinforcement to improve through-hole and blind micro via thermal integrity. In addition the nickel layer offers advantages such as co-planarity, Al-wire bondability and the use as contact surface for keypads or contact switching. Especially those pads, which are not covered by solder need a protective coating in corrosive environment – such as high humidity or pollutant gas.

This paper describes the influence of co-deposited Phosphorus within the Nickel layer, regarding the influence to the ENIG process itself (especially the corrosive attack of the immersion gold reaction) and the survivability of PCBs in corrosive atmosphere.
Within this paper, different test methods are described and discussed to check the protective performance of a high Phosphorus ENIG layer.

Introduction: Over several years the assembly industry has experienced a defect known as "Black pad" with electroless nickel immersion gold finished (ENIG) printed wiring boards (PWBs), which resulted in a defect solder joint.
Several chemical vendors / PWB fabricators / Contract manufactures / OEM's have investigated the defect, to gain an understanding of the mechanism. The common theory on black pad is the hyperactivity of the immersion gold bath resulting in severe corrosion of the nickel / phosphorous layer. This prevents the normal growth of tin / nickel intermetallic during soldering, leads to a brittle joint. Or in other words - controlling the immersion gold reaction – controls corrosion of the e'less nickel - controls “Black Pad”.

Secondly another phenomena is reported from industry, which is based on the same mechanism – corrosion of e'less nickel.
Not soldered ENIG areas on a PWB show in high humidity environment a corrosive attack introduced by humidity and pollutant gas. Corrosive products created on these pads show the risk of shorts. Also the function of these pads is affected, due to change in contact resistance, either if those pads where designed to be keypads or service / control interfaces for electrical maintenance they can fail.
The task of the investigation was to generate on the one hand a corrosive resistant nickel layer, which withstands the hyper corrosive attack of the immersion gold bath resulting in “Black Pad” and on the other hand a highly resistant nickel / gold finish, which withstands corrosive environments.

For evaluation testing three methods were chosen:

1) Kesternich Test, EN ISO 6988. This test is specified and used in industry to control performance of corrosion protective coatings. According to EN ISO 6988, this test performs @ 40°C / 100% humidity with SO_2 pollutant gas for 24 h. The pass / fail criteria is an optical inspection (50x) of the more or less, by this corrosive environment, attacked specimen. It is ranked into a classification (Atotech Standard) of three values of corrosion resistance.

Classification

Class 1

Class 2

Class 3

According to the amount of attack, class 1 samples show the highest resistance towards the harsh environment of the Kesternich test, followed by class 2 and worst by class 3 classification.

2) HCl Dip Test. Standard test coupons are immersed using HCl @ 20% V/V for 8 h at ambient temperature. Further on the HCl dip is analyzed by AA to quantify the nickel concentration. Typical nickel concentrations for the shown test coupon size are maximum 3ppm.

Test coupon: 20 x 60mm

During this test the HCl solution will solve nickel areas, which are not protected by gold. The more pores within the gold layer and the less protective the nickel layer, the more nickel is being attacked and solved into solution. By having the same ENIG area on each coupon, the resulting nickel concentration in the HCl dip gives a direct correlation to the porosity of the gold layer. The pass / fail criteria, by AA detected nickel concentration, depends strongly on the size of the specimen.

3) HNO_3 Dip Test. A simplified dip test, using only nickel plated (no gold) specimen, dipping into a 50% V/V HNO_3 @ 25°C for 30 sec.

Nickel / Phosphorous alloys with a low P-content will show an insufficient resistance towards the corrosive attack of the Nitric acid. Within the immersion time of the HNO_3 Dip Test these layers will be attacked and turn dark / black. Pass / Fail criteria is the resistance towards the Nitric acid solution, either withstanding this harsh environment or turning dark.

Why choosing the P-content in the nickel layer as main variable to increase corrosive resistance?

As substantial part of the ENIG process, electroless Nickel is followed by immersion Gold. Due to the nature of the immersion reaction, nickel is displaced by gold:

$$\mathbf{Ni^{0} + 2Au^{+} \rightarrow Ni^{2+} + 2Au^{0}}$$

The following plating variables influence the plated gold thickness, for the gold bath: time, temperature, pH and concentration of ingredients.

Automation of equipment and process control should allow a narrow range with reproducible gold thickness. Time, temperature and pH are set and controlled by the plating equipment, for the concentration of ingredients enough

production data is available to run within a narrow range.
This should allow constant gold thickness, but this is not always seen. Gold thickness does vary, with a very strong dependence of the chemical vendor of the ENIG process.

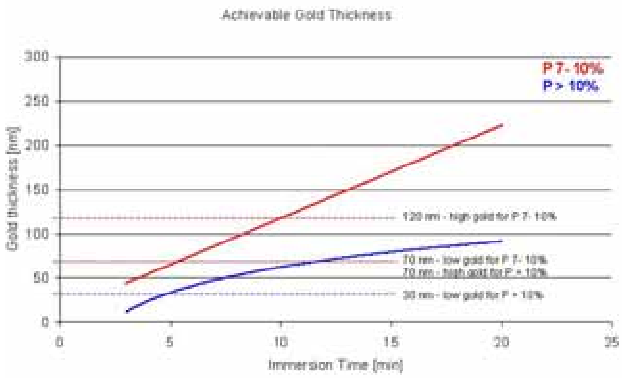
The question to be asked is why does the plated gold thickness vary, even if there is auto-control and analytical process control, which ensures constant bath parameters?
The key to these variations are to be found a process step before – the electroless nickel bath.
As shown, the immersion gold reaction takes place by dissolving the nickel. One major function, which influences the gold thickness in the same way as time and temperature, is the resistance of the e'less nickel layer to "withstand" the immersion gold reaction.
If the resistance of the nickel layer is low, the attack is easy, resulting in a high gold thickness. Vice versa, the more resistance the nickel layer is, the lower the gold thickness will be.
This resistance, for the nickel layer is described in the amount of Phosphorous (P-content). Where a low P-content (< 7%) shows a minor resistance to an immersion attack and a high P-content (> 10%) shows a high resistance towards attack.
Therefore the P-content in the nickel layer needs to be added to the variables, which influence the gold thickness.

Poor understanding of this basic function, between the nickel layer and the gold reaction, will end up in an insufficient process installation – with an up and down in the P-content resulting in the described gold thickness phenomena.
What happens?
Example: due to nickel bath parameters (e.g. replenishment of chemistry), which are not set correctly, the P-content changes – resulting in a variation in the gold thickness.
By checking the gold thickness, a low gold thickness is detected.
To achieve the specified gold thickness for further production, gold bath parameters such as temperature or time are being adjusted.
Meanwhile the nickel bath plates faster e.g. due to pH adjustment, resulting in a lower P-content. Panels plated with these "new" nickel bath conditions will show a decrease of the P-content.
Usually, the resulting gold thickness would be within the standard variation of the process (0.07 – 0.12 µm). Based on the fact that the gold plating parameters are adjusted, now the immersion gold reaction is more aggressive. The gold thickness increases abnormal (>> 0.12µm) due to heavy immersion gold attack and heavy corrosion. The plated gold thickness will be at the higher end of specification.

In extreme, this up and down in P-content results in an aggressive immersion gold attack, known as hyper corrosion or "Black Pad".

An in-depth knowledge of the influence of the P-content allows a process set-up, which ensures constant plating parameters for e'less nickel with constant thickness results for immersion gold.

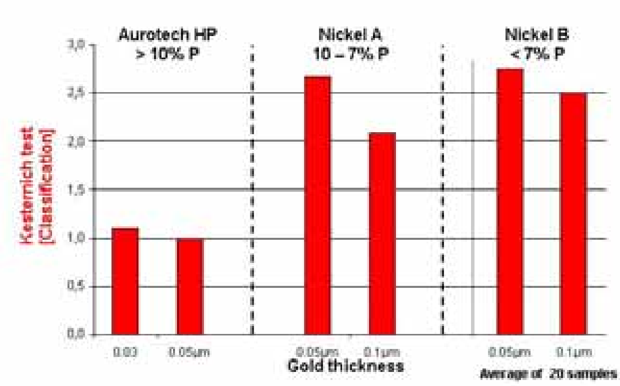
Generally, a higher P-content widens the plating window for the gold bath parameters, especially for plating time, temperature and pH.
In fact, nickel layers with a P-content > 10% are showing a lower achievable gold thickness. The gold thickness is nearly self-limiting, based on a denser gold layer plated by a slower immersion gold reaction.



By increasing the P-content > 10% in the nickel layer the risk of heavy immersion attack or hyper corrosion – "Black Pad" – is totally banned. Extreme corrosion and heavy immersion attack cannot take place, seen in the resulting lower gold thickness.

Results

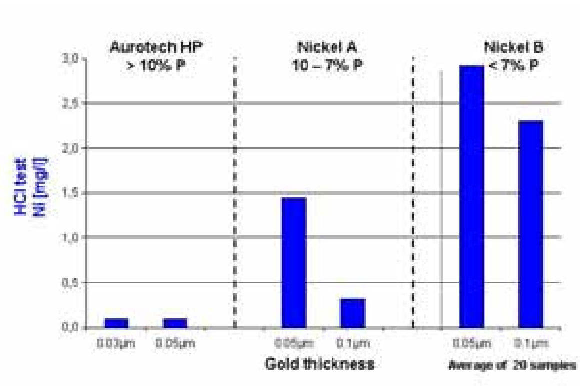
Kesternich Test



Shown in the above graph, nickel layers with a high P-content > 10% perform mostly within class 1, regardless of the plated gold thickness – 0.03 or 0.05µm. Medium range nickel layers with a P-content between 7-10% show in general a rating of class 2- 2.5, with a strong influence of the plated gold thickness. For the medium range nickel a 0.1µm gold thickness results in a class 2 rating, where as 0.05 µm gold results in summary in class 2.5. Low P nickel < 7% results regardless of the gold thickness (0.05- 0.1µm) in class 2.5. Here is no beneficial influence of a higher gold thickness seen.

Based on the classification of 1- 3, high P nickel layers (> 10%) perform best with lowest attack during the Kesternich test. High P nickel layers show the highest resistance towards the Kesternich - SO_2 test at 100% humidity / 40°C for 24h.

HCL Test



As seen in the graph above, nickel concentration in the HCl dip is lowest with a P-content at 10%.

For high P its regardless if the gold thickness is at the lower end 0.03µm of specification or in the center of specification 0.05µm.

A typical mid range e'less nickel / phosphorus alloy, shows a lower nickel concentration in the HCl dip with an optimum gold thickness 0.1µm, than with a gold thickness of 0.05µm. This shows clearly that the optimum gold thickness results in less pores and denser gold layer, which is beneficial for protecting the nickel in corrosive environment.

For the low P nickel layer it is regardless if the gold thickness increases or not. The nickel concentrations after the HCl dip test are much higher than the concentrations for a medium P nickel and dramatically higher than for high P nickel.

This concludes into following, a P-content > 10% is less attacked in the corrosive environment of this HCl test.

HNO_3 Test

Aurotech HP > 10% P Nickel A 10 – 7% P

For this test only the high P > 10% and the medium range P 7- 10% nickel layer were tested. As seen, the three samples coated with a high P-content > 10%, show no evidence of attack or corrosion after 30 sec in Nitric acid. Their appearance stays unchanged comparable to untreated samples. The medium range P 7- 10% shows a clear discoloration turning into black after 30 sec in Nitric acid.

This is again a clear indication, that a high P nickel layer is not attacked where as the medium P nickel layer shows already a strong discoloration. This simple test with a clear "black or white" result is ideal for monitoring if the P-content during production is higher or lower 10%.

Conclusions

From the achievable gold thickness, the results from the Kesternich test, the HCl Dip test and the HNO_3 dip test on the various P-contents in the nickel layer, the following observations were made as conclusions to this investigation:

All tests focusing on corrosion show a clear dependence on the resistance of the nickel layer. Based on its resistance, typical values for each finish were observed, which allows a clear rating.

The correlation between the achievable gold thickness and the corrosion tests show a strong dependence on the P-content. The higher the P-content, the lower the gold thickness and the less the corrosive attack.

Nickel layers with a P-content > 10% show superior results for Kesternich and HCl test.

Generally nickel layers with a P-content < 10% fail in the Nitric acid test, due to strong discoloration. This HNO_3 test could be used in PCB production to control / monitor if the P-content is higher 10%. Due to its short testing time of less than 5 min until result including sample preparation, this is an ideal quality control test directly at the ENIG line.

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