Palladium as diffusion barrier - a way to a multifunctional printed circuit board finish

以鈀作擴散阻擋層—一種多功能線路板表面處理方法

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1. Introduction

Due to the continuing miniaturization in the electronics industry, several different interconnect techniques such as adhesive bonding, soldering and wire bonding are used to an increasing extent for the joining and contacting of electronic components on printed circuit boards.

For this purpose, the assembly pads of the printed circuit boards are protected with an organic solderability preservative (OSP) or with suitable metal deposits, preferably of precious metals, as final surface finishes. If this final finish can be used for different interconnect techniques, it is called a multifunctional finish. For this, it must at least meet the requirements listed below:

- planar surface
- processable with all common interconnect techniques such as
  - conductive adhesive technology
  - multiple wave and reflow soldering
  - ultrasonic and thermosonic wire bonding

The coating must be able to withstand the higher solder temperatures required for lead-free solders without oxidation. The higher surface tension of the lead-free solders as opposed to the eutectic tin-lead solders used up to now must be compensated for with a good wettability of the surface finish.

A multifunctional final finish on printed circuit boards should be easy to apply, with short process times and without thick and cost-intensive precious metal layers.

Figure 1 gives a brief overview of the most common processes final finishes on PCB's.
In the following, the coatings which are not bondable such as OSP, immersion tin and immersion silver will not be discussed in detail, since these coatings are not multifunctional.

1. 引言

因著電子工業不斷的小型化，數種不同互聯技術如黏合劑鍵接(adhesive bonding)、焊接(soldering)及打線鍵接 (wire bonding) 等於線路板上電子零件連接及(電)接點被應用範疇不斷增加。

基於此用途，線路板組裝墊位(Assembly pads)需被一層有機可焊防氧膜(OSP)或適當金屬沈積膜(尤其貴金屬)作為最後表面處理之保護，如這最後表面處理層可用於不同互聯技術(interconnect technigques)，可被稱為多功能表面層 (Multi-functional finish)。因此，作為多功能表面層，最少必須符合以下要求：

- 平整的表面
- 能應用於所有常用之互聯技術如：
  - 導電黏合技術
  - 多次波峰及回流焊接
  - 超音波(ultrasonic)及熱超音波(thermosonic)打線鍵接

層膜必須能夠抵受無鉛焊接之更高焊錫溫度而不被氧化。而相對於共晶鉛錫焊料，更高表面張力之無鉛焊料必須有一良好濕潤性表面層作此補償。

於線路板上表面層膜應該為應用容易、流程時間短、及沒有濃而高成本之貴金屬層。

圖1為線路板最常用最後表面處理層膜簡單概觀。

以下，由於某些不能鍵接層膜如 OSP、浸錫、浸銀等，因不是多功能層膜，不會在此詳細討論。

	OSP 有機可 焊保護	immersion tin ISn 浸錫	immersion silver IAg 浸銀	ENIG 沉鎳浸金	e'less Ni/ e'less Pd/ immersion Au ENEPIG 沉鎳沉鈀浸金	e'less Ni/ e'less Au ENIGEG 沉鎳浸金沉金	e'less Ni/ immersion Pd/ /immersion Au ENIPIG 沉鎳浸鈀浸金
conductive adhesive 導電黏合	-	(+)	+	+	+	+	+
multiple leadfree soldering 多次無鉛焊接	(+)	+/-	+	+	+	(+)	+
US bonding 超聲波鍵接	-	-	-	+	+	(+)	+
TS bonding 熱超聲波鍵接	-	-	-	-	+	+	+
electrical contacts 電子接點	-	-	(+)	+	+	+	+
universal final finish 表面層膜通用性	-	-	-	-	+	(+)	+
process handling 流程操作控制	++	+	+	(+)	-	-	+
costs 成本	+++	++	++	+	+/-	-	+

Figure 1: Overview of the most common final finishes on PCB's
圖 1: 線路板常用表面處理概觀

2. Advantages and drawbacks of the surface finishes and introduction of the new gold wire bondable final finish (ENIPIG)

2.1 Electroless nickel/ immersion gold (ENIG)

ENIG shows a very good wettability with soldering, even with multiple soldering cycles. Under the right storage conditions ENIG finish can be stored for up to a year without losses of processability ENIG is also suitable for keypads.

Unfortunately, the layer cannot be thermosonically bonded without special pretreatment. Since the immersion gold layer is very thin, nickel may diffuse to the surface through the pores in the gold coating if stored for a longer period. By contact with oxygen, nickel oxides are formed which worsen the solderability and ultrasonic bondability. Depending of the electroless nickel with the immersion gold process, there is the possibility of hypercorrosion of the nickel layer if the concentrations of metallic stabilizers and organic sulphur compounds in the

2. 表面層膜優點和缺點 及 嶄新可打金線鍵接表面層膜 (ENIPIG) 之介紹

2.1 沉鎳浸金 (ENIG)

沉鎳浸金於焊接及即使多次循環焊接都仍具有良好濕潤性。在合適儲存條件下，沉鎳浸金表面處理其存放期可長達一年而不失其功能性。它也適用於按鍵應用。不幸的是，在沒有特別前處理下，層膜不能應用於熱超音波鍵接，因著浸金層很薄，若存放期太長，底層鎳會經過薄金層孔隙擴散至金層表面，接觸空氣後，會形成氧化鎳，從而使其焊接性及超音波鍵接性變差. 而某些沉鎳浸金流程，如在沉鎳溶液其金屬穩定劑及有機硫化物含量過高，或會形成沉鎳層有過腐蝕現象。這現象被稱為“黑盤”(black pad)，因嚴重被腐蝕的鎳層為深黑色。

2.2 沉鎳沉鈀浸金 (ENEPIG)

鈀是一個良好的鎳擴散阻擋層，因著這原故，此層

Ni-electrolyte are high. This hypercorrosion of the Nickel is called "black pad" because of the then dark colour of the extremely corroded nickel layer.

2.2 Electroless nickel/electroless palladium/immersion gold (ENEPIG)

Palladium is a good diffusion barrier to nickel. This is the reason why this layer system resists even harsh ageing conditions as regards solderability and bondability. Two big advantages are the good thermosonic bondability with gold wire as well as the excellent solderability with lead-free solders. Unfortunately it is said that the electroless palladium baths are not very stable and their operating windows may possibly be too small. As with some of the electroless nickel baths, quite significant variations in Pd layer thickness may occur on the printed circuit boards with sophisticated circuit patterns which are caused by potential differences between the assembly pad areas. The costs of this layer system are essentially determined by the palladium and gold layer thicknesses applied and the excessive process control effort.

2.3 Electroless nickel/immersion gold/electroless gold

If a thermosonically bondable surface is demanded, this final finish has been frequently used up to now. The gold layer thickness is mostly more than 0.5 µm. The long dwell time of the printed circuit boards in the electroless gold bath involves a risk which should not be underestimated: the leaching of the solder resists and substrates as well as the accompanying contamination of the sensitive electroless gold bath.

With ultra fine line and spaces of clearly less than 100 µm in particular, the system may come up against the limits of selectivity. Insufficient edge definition or even random deposits on the solder resist often result in short circuits between the pads areas on the printed circuit boards.

The high metal costs for the thick gold layers already stand in the way of a widespread use of this

膜能抵受如焊接及鍵接之嚴酷老化測試條件。其兩大優點為具有良好熱超音波鍵接性及於無鉛焊料之非常優良焊接性。不幸地，據説沉鈀浴不太穩定並且其可操作參數範圍或許很窄小。而配合某些沉鎳浴而言，沉鈀在一些複雜線路圖形的線路板上因著組裝盤位(assembly pad)之電位差或會引致鈀層濃度有相當明顯差異。此層膜體系的成本主要決定於鈀和金層濃度及其嚴格流程控制要求代價。

2.3沉鎳浸金沉金(ENIGEG)

如要求具有熱超音波鍵接性處理表面，此層膜被經常應用及至現下。 其金層濃度一般高於0.5微米。 而對於線路板於沉金缸的冗長浸泡時間所涉及風險不應被低估：例如於敏感的沉金缸內，阻焊保護層和底材釋出物質及其它伴隨污染。

值得注意在少於100微米精密線寬及線距，此體系或會超出其選擇性界限，滲鍍或甚至過鍍在阻焊保護層上，從而經常於線路板上組裝墊位之間導致短路。

厚金層高昂金屬成本已使此體系停滯於廣泛應用路上，而冗長流程時間導致低生產效率也是其中原因。

2.4 電鎳/電純金

多年來，此鍍層體系已有很廣泛實際應用經驗。不幸地，除了黃金高金屬成本外，在其所有組裝墊位需要導電引線連接及因著電鍍鎳層不良濃度分佈從而局限其在市場成果。而當電鎳電純金系統被應用為蝕刻保護層時，線路邊緣卻未能覆蓋。

2.5 一種嶄新概念，可熱超音波鍵接，結合了 沉鎳/浸鈀/浸金 層膜 (ENIPIG)

用作打金線鍵接(gold wire bonding)，不一定需要使用相對較濃貴金屬層膜。多年來，這已可獲得証實

final finish, the altogether long process time in all baths worsens productivity, too.

2.4 Electrolytic nickel/electrolytic fine gold

For many years, there has been extensive practical experience with this layer system. Unfortunately, the always required power connection of all assembly pads as well as the poor thickness distribution primarily occurring in the electrolytic nickel bath are responsible for the limited market success, besides the high metal costs of the gold. When the electrolytic nickel/electrolytic fine gold system is used as an etch resist, the edges of the lines are not covered.

2.5 Concept of a new, thermosonically bondable layer combination of electroless nickel/immersion palladium/immersion gold (ENIPIG)

For gold wire bonding, not necessarily relatively thick precious metal layers have to be applied. For many years, this has been proved by the electrolytic plating of so-called pre-plated lead frames, where the Ni-layer is only very thinly electroplated with palladium and gold afterwards. This basic idea was used to develop a similar though electroless process using these three metals. The overview in Figure 2 clearly shows the common features of both systems.

According to the process sequence shown in Figure 3, an electroless nickel layer is deposited on a copper substrate activated with palladium, followed by an immersion palladium layer and afterwards an immersion gold layer:

The essential advantages of such a layer sequence are:

- prevention of Ni diffusion to the surface by a thin Pd layer
- the stable immersion palladium bath,
- the short dwell time in the palladium bath (≤2 min),
- therefore minimized attack on the electroless nickel layer,
- the low costs because of the very thin palladium and gold coatings.

於一種電鍍流程稱為預鍍導線架(pre-plated lead frames)，其鎳層上為很薄電鍍鈀和金層。此基本概念，被引申發展為相類似以此三種金屬無電流程。圖二之概觀清楚説明此兩種系統共同特點。

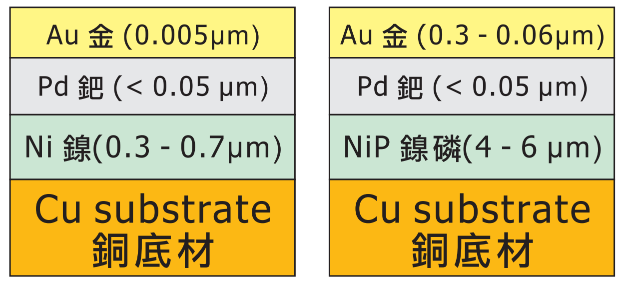

Figure 2: Layer sequence for electrolytically plated pre-plated lead frames (on the left) and for printed circuit boards using the electroless ENIPIG Process (on the right)
圖 2: 層膜次序，於電鍍預鍍導線架 (左)及於線路板應用無電沉鎳浸鈀浸金流程 (右)

按照圖三所示流程次序，沉鎳層通過活化鈀沈積於銅底材後，再沈積浸鈀層及最後為浸金層：

Figure 3: Process sequence of the electroless nickel/immersion palladium/immersion gold process (ENIPIG)
圖 3: 流程次序，沉鎳/浸鈀/浸金 流程 (ENIPIG)

此次序流程其主要優點為:

- 以一薄鈀層作為防止鎳擴散滲移至層膜表面
- 穩定的浸鈀鍍浴
- 浸鈀鍍浴浸泡時間短暫 (少於 2 分鐘)，

As can be easily seen from Figure 4, the palladium layer thicknesses can be measured even through the immersion gold deposition. Despite the low thickness, the measuring values for the immersion palladium layer without or with immersion gold coating are almost identical. For measurement, the x-ray fluorescence measuring instruments FISCHER XDAL and SEIKO S II 9455 were used. At the short dwell times of maximally two minutes in the immersion palladium bath, the increase in palladium layer thickness is linear in first approximation, see Figure 4.

That the thin palladium layer actually acts as a diffusion barrier to nickel is confirmed by comparative photoelectron spectroscopic analyses (XPS/EDS) after different ageing periods at 150°C (see Figure 5). The measuring method provides information about the concentration of elements at the deposited surface from only a few nanometres depth. In this way the atomic ratio between nickel and gold can be determined there, it is a measure for the diffusion of nickel to the surface. The nickel oxides forming at the surface after contact with oxygen seem to be the main reason for the poorer solderability and bondability of the printed circuit board final finishes after long ageing periods.

For the aged electroless nickel/immersion gold layer (ENIG) with a gold thickness of 0.08 μm, the nickel concentration is highest, when the thin immersion gold layer is increased to about 0.4 μm thickness with an immersion thick gold bath, diffusion of the Nickel will take longer to reach the surface. At a gold layer thickness of approximately 0.7 μm, the aged layer system electroless nickel/immersion gold/electroless gold (ENIGEG) shows an even lower nickel concentration at the surface. The two aged layer systems with intermediate palladium layer come off best. On the aged electroless nickel/electroless palladium/immersion gold (ENEPIG) as well as on the aged electroless nickel/immersion palladium/immersion gold (ENIPIG) with a thin Pd-layer, hardly any nickel diffused to the surface can be detected, both curves are almost identical.

- 因而減少對沉鎳層的攻擊
- 非常薄鈀及薄金層使降低成本

從圖表4可容易看出，這鈀層濃度即使經過浸金層也可被測量出來。儘管其濃度很薄，浸鈀層的測量數值在有或沒有浸金層下也大致一樣。此測量，所用之儀器為X-射線螢光測量儀 FISCHER XDAL 及 SEIKO S II 9455。在浸鈀缸最多兩分鐘短暫浸泡時間，在第一接近值其鈀層濃度增加為線性，見圖4。

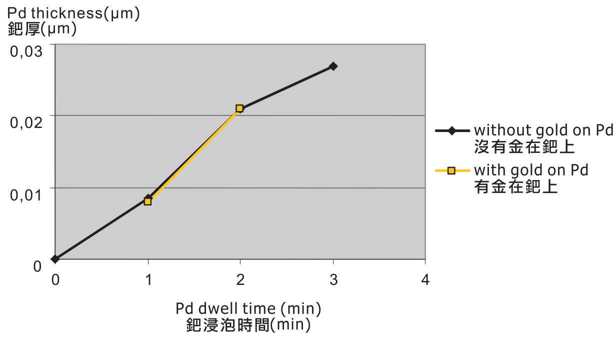

Figure 4: Palladium layer thicknesses vs. dwell time; without and with immersion gold coating
圖 4: 浸鈀層濃度 vs. 浸泡時間；有及沒有浸金層

此薄鈀層，可在不同老化測試週期於150°C處理後以光電子分光鏡分析(XPS/EDS)進行比較法去確認其實際作用為擔任鎳之擴散阻擋層(看圖 5)。 此測量方法提供幾個納米深度層膜表面之元素濃度資料。以此方法來測定鎳和金之間原子比率，作為鎳擴散至層膜表面一種測量。而於表面接觸空氣形成的氧化鎳，看來像是線路板最後層膜在冗長老化週期後引致不良焊接性及鍵接性之主要原因。

以0.08微米金濃沉鎳浸金層(ENIG)老化後,其表面擴散鎳濃度為最高，當浸金層濃度以浸濃金流程增加至0.4微米，鎳的擴散須較長的時間到達表面。在沉鎳/浸金/沉金(ENIGEG)層膜體系金層濃度約0.7微米時，經老化後層膜表面顯示更低鎳濃度。而另兩種中間加入鈀層層膜體系經老化測試後其表現最好，經老化處理後之沉鎳/沉鈀/浸金(ENEPIG)或沉鎳/浸鈀/浸金(ENIPIG) 層膜，因著中間加入的薄鈀層，測試

The topography of the ENIPIG final finish on PCB's is essentially determined by the structure of the electroless nickel layer. Two scanning electron micrographs with magnifications of 1,000 and 5,000 are shown in Figure 6.

The thermosonic bondability of the new ENIPIG layer system was determined on printed circuit boards which had been aged for four hours at 150°C before bonding. The dwell times in the immersion palladium and in the immersion gold baths were modified. As shown in Figure 4, after two minutes in the palladium bath a little more than 0.02 µm of palladium was deposited. The dwell times in the immersion gold bath of three, eight and 13 minutes are equivalent to layer thicknesses of about 0.03µm, 0.06 µm and 0.08 µm of Au. The average wire pull force of the 33 µm gold wire is independent of the layer combination more than 15.9 cN, the coefficient of variation in all tests is never higher than 8.6 %.

顯示很難發生有任何鎳擴散至表面而可被檢測出來，且兩條曲線幾乎一樣。

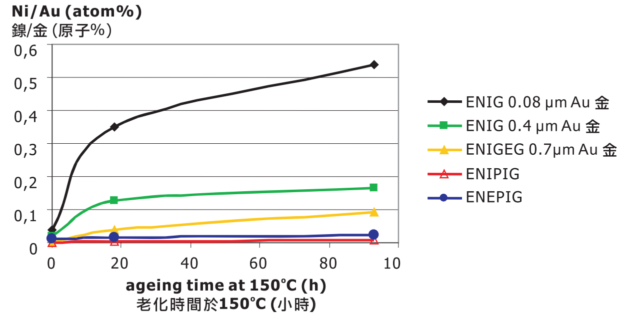

Figure 5: Atomic ratio nickel/gold vs. aging time of different surface finishes
圖 5: 原子比率鎳/金vs.不同表面處理老化時間

沉鎳/浸鈀/浸金ENIPIG的結晶表形實質上被決定於沉鎳層的架構. 兩幅掃描電子顯微照片的放大倍率為1000和5000 顯示於圖6。

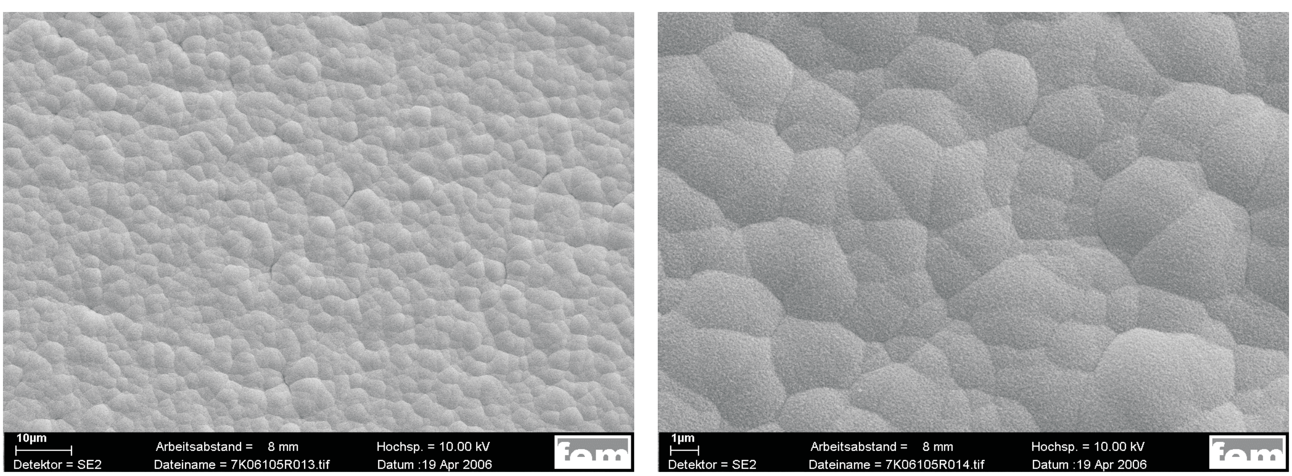

Figure 6: SE micrographs of ENIPIG surface; on the left at 1,000 x magnification, on the right at 5,000 x magnification
圖 6: 沉鎳/浸鈀/浸金掃描電子顯微照片; 左為 1,000 x 放大倍率, 右為 5,000 x 放大倍率

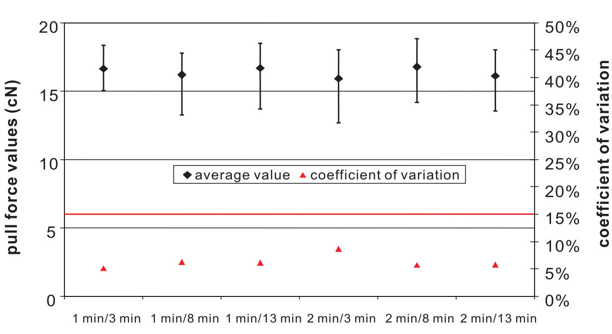

Figure 7: Thermosonic bondability with 33 µm gold wire on aged samples (4 h/150 °C)
圖 7: 熱超音波鍵接性(Thermosonic Bondability)，33 微米金線在經老化測試後樣板 (4 小時/150°C)

此新沉鎳浸鈀浸金層膜系統，可在線路板鍵接前於150 °C老化4小時，以測定其熱超音波鍵接性。而浸鈀及浸金鍍浴的泡浸時間可作出不同更改。如圖4所示，於浸鈀鍍浴浸泡2分鐘後，沉積鈀厚略為多於0.02微米。於浸金鍍浴泡浸時間分別為3、8 及13分鐘相當於金層厚度約為0.03微米、0.06微米及0.08微米。以33微米金線測試於不同的層膜組合其線拉力平均值大於15.9 cN，在所有測試其差異系數均不大於8.6 %。

A PCB manufacturer in Switzerland has carried out extensive reliability tests in the course of qualification and validation of the ENIPIG for the medical and automotive industries. For this purpose Swiss PCB-manufacturer has to meet the quality management standards EN ISO 13485 and ISO/TS 16949 among others:

- thermosonic bond tests with 102 samples were evaluated: $\bar{x}$=15,23g, σ = 1,26 g.
- 159 samples were submitted to a thermal cycle test: All samples passed 305 cycles with a range between -40 and +115 °C (hold time 30 minutes, ramp time > 10 seconds).
- 159 samples as well were successfully tested for 504 h under humidity conditions at 40 °C and 93 % relative humidity.
- The luminous flux of bonded LED's was unchanged after ageing.

For determining the process capability as regards thermosonic bondability, the process capability index Cpk was used for the alternative layer system electrolytic nickel/electrolytic fine gold.

The electrolytic fine gold layer had an excellent Cpk value of 2.93 for gold wire bondability (Figure 8).

The gold wire bondability of the electroless nickel/immersion palladium/immersion gold layer system is similarly good as that of the electrolytic fine gold layer. With comparable pull forces and a very good Cpk value of about 2.18, only a fraction of the precious metal necessary for the electrolytic fine gold layer is required, however.

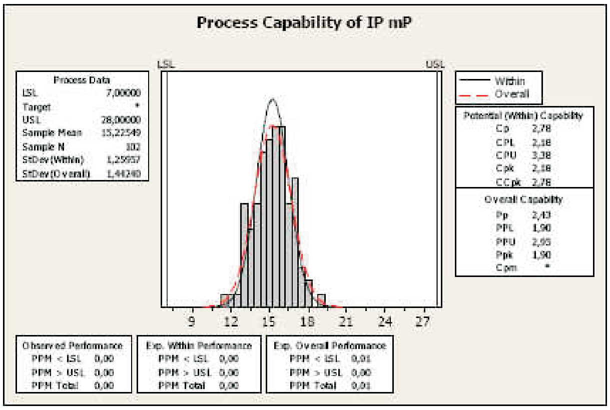

Figure 9: Process capability of the electroless nickel/immersion palladium/immersion gold coating (ENIPIG process)
圖 9: 沉鎳浸鈀浸金層流程能力(ENIPIG 流程)

瑞士一家線路板製造商在沉鎳浸鈀浸金層膜實行了大量的可靠性測試以透過在醫學及汽車工業資格認受性。因此瑞士線路板製造商需達到品性管理標準規格EN ISO 13485 及 ISO/TS 16949：

- 熱超聲波鍵接測試於102個樣板作評估：$\bar{x}$=15,23g，σ = 1,26 g。
- 159個樣板提交作溫度循環測試：所有樣板通過305個循環於溫度在 -40 及 +115 °C 之間 (恒定時間 30 分鐘，轉移時間 > 10 秒)。
- 159 個樣板也成功通過504小時測試於濕度條件40 °C 及93 % 相對濕度。
- 發光助焊劑其鍵接發光二極體LED's 經老化後沒有變化。

相對於熱超音波鍵接性的測定流程能力，Cpk 能力指數被用於另一層膜系統電鎳/電純金。電鍍純金層於打金線鍵接性有非常良好2.93的Cpk 值。(圖 8)。

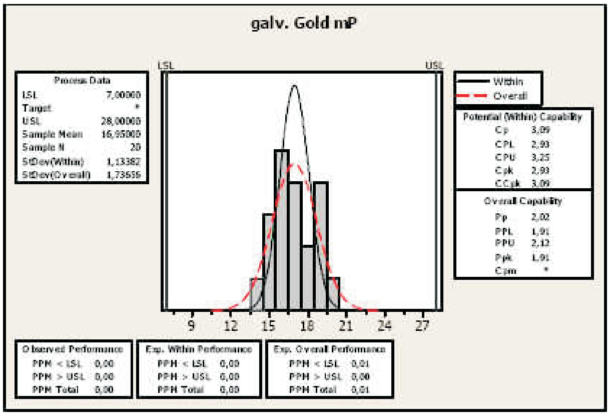

Figure 8: Process capability of the electrolytic fine gold coating
圖 8: 電鍍純金層流程能力

沉鎳浸鈀浸金層膜系統的打金線鍵接性有近似電鍍純金層般良好，有著同等拉力值及非常良好Cpk 值約2.18，然而，其所需貴金屬相對於電鍍純金層只需要很小一部分。

3. Summary

The common surface finishes on PCB's for soldering and gold wire bonding are discussed with their advantages and drawbacks. It has been known for years from the experience with pre-plated lead frames that even very thin precious metal layers of palladium and gold ensure reliable gold wire bondability. From this knowledge, an electroless nickel/immersion palladium/immersion gold layer system (ENIPIG) has been developed. This new final finish ENIPIG is used in the production of PCB-manufacturer in Switzerland and subcontracting service in Germany for several years now. However, all three metallization baths must be adapted to each other to achieve the desired multifunctional finish on the printed circuit boards. Due to the low thickness of the precious metal coatings, considerable costs can be saved compared to other final finishes, as shown in the final overview in Figure 10 (prices on 15 July 2008).

3. 總結

上文已討論了有關常用表面處理於線路板焊接(soldering)及金線鍵接(gold wire bonding)的一些優點及缺點。從預鍍導線架過往多年經驗已知即使很薄貴金屬鈀層及金層已可有保證可靠的金線鍵接性。從這一知識，沉鎳浸鈀浸金層膜系統 (ENIPIG)被研發出來。此嶄新表面處理ENIPIG現多年來被瑞士線路板製造商及德國加工廠所採用。然而，此三種金屬鍍液需互相配合才能於線路板工藝上達成理想多功能層膜。因著其薄貴金屬層膜，相對於其他表面處理，可節省頗大的成本，可見於圖10之最後概觀。(為2008年7月15日價格)。

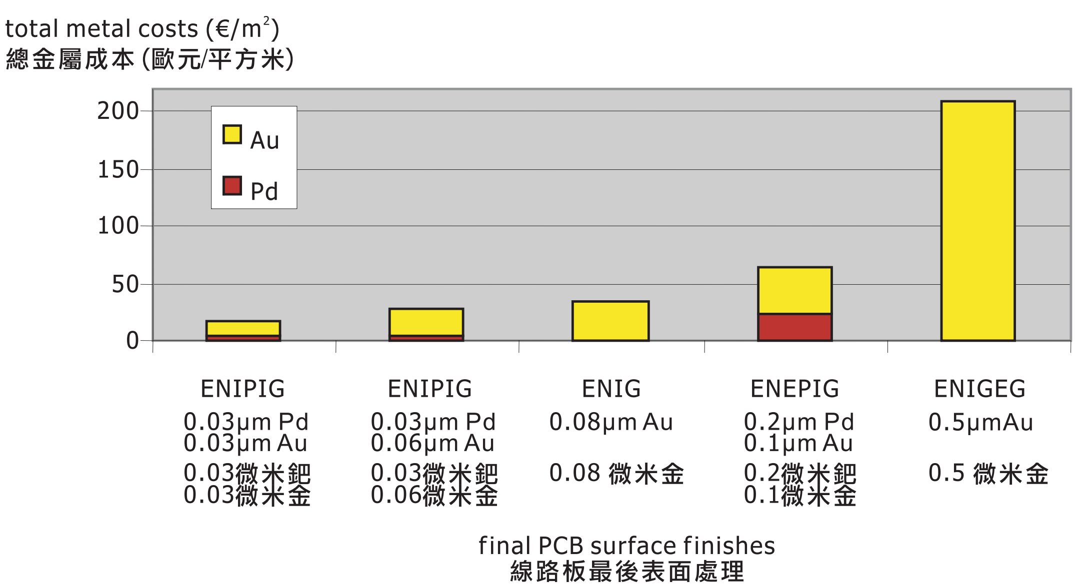

Figure 10: Precious metal costs per square metre of coated surface
圖 10: 每平方米層膜表面貴金屬成本