Non-Toxic Stabilization for Mixed Reaction Gold

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ABSTRACT
In the field of printed circuit board (PCB) manufacturing, surface finishes play a crucial role, serving both as a protective layer and as a facilitator for various interconnecting techniques. Among the commonly used high-end processes Ni/Au, Ni/Pd/Au, and Pd/Au gold deposition is employed. Different types of gold electrolytes are available in the market, catering to varying target thicknesses. These electrolytes exhibit different plating mechanisms, ranging from fully immersion reaction types to mixed reaction types. Mixed reaction type gold electrolytes employ a combination of immersion and autocatalytic deposition behavior.

The latest generation of mixed reaction gold electrolytes, characterized by a heightened level of autocatalytic reaction, offer significant technical advantages by enabling the deposition of thick gold layers onto nickel and palladium surfaces without compromising the integrity of the nickel layer during plating. However, due to their increased autocatalytic properties, these electrolytes necessitate continuous dosing of stabilizer components, typically based on potassium cyanide, to maintain stability. Therefore, the plating mechanism of the gold electrolyte was thoroughly examined, elucidating the roles of cyanide and the reducing components. Given the associated health risks with handling potassium cyanide, alternative stabilizer components were explored and identified to effectively stabilize the gold in the plating electrolyte.

As a result, in this paper a novel gold electrolyte with autocatalytic properties is introduced. It is capable of depositing high layer thicknesses and defect-free ENIG (Electroless Nickel Immersion Gold) deposits. The stabilizer used in this electrolyte is non-toxic and does not contain free cyanide, ensuring an environmentally friendly approach. Extensive testing was conducted for Ni/Au, Ni/Pd/Au, and Pd/Au deposits, comparing the new electrolyte's performance results with the current industry-standard processes. The evaluation focused on solder joint reliability, nickel layer corrosion, thickness distribution, and characterization of the gold deposit. An easy, safe, and stable processing, with bath lifetimes up to 20 MTO at a gold concentration of 0.6 g/l could be proven with this new electrolyte.

Key words: Protective layer, Surface finish, Gold plating, ENIG, ENEPIG, EPAG, Mixed reaction type, Non-toxic, Cyanide-free, Environmentally-friendly, PCB, IC-substrates

INTRODUCTION
Gold plating in the PCB industry is used for various final finishes. Depending on the application and assembly technique, gold layers can be deposited on nickel or palladium. The gold electrolyte's plating mechanism can be a pure immersion reaction (IG) or a mixed reaction of immersion and autocatalytic portions (IG or AG). Ni/Au layers in this paper were referred to as ENIG and Ni/Pd/Au as ENEPIG. The naming is used as this naming is common in the industry. However, it must be kept in mind that the gold bath used in this paper is a mixed reaction bath where potentially also the naming ENAG and ENEPAG could be equally used.

This study therefore begins by exploring the differences between the various types of gold bath and how they evolved over time. Nowadays, three main types of gold electrolytes are used in the PCB industry, representing different stages of development [1]. The *first generation* represents fully immersion type electrolytes driven by nickel dissolution. The *second generation* includes additives with reductive properties to support the immersion reaction. That action results in reducing the nickel layer attack and therefore improving Nickel corrosion performance in ENIG layers. *Third generation* electrolytes use reducing agents for autocatalytic gold deposition, starting with an immersion reaction to form initial gold seedings on the surface:

$$Ni + \textit{complexing agent} \rightarrow 2Ni^{+}_{complexed} + 2e^{-}$$
$$2K\left[Au(CN)_2\right] + 2e^{-} \rightarrow 2Au\downarrow + 2K^{+} + 4CN^{-}$$

The reaction becomes autocatalytic as the gold seeds act as a catalytic surface for the reducing agent:

$$K\left[Au(CN)_2\right] + \textit{reducing agent} \xrightarrow{\textit{catalytic surface}}$$
$$Au\downarrow + \textit{reducing agent}^{+} + K^{+} + 2CN^{-}$$

The advantage of this reaction mechanism over the 1st and 2nd generation gold electrolytes is that it allows for the application of thicker layers and enables gold plating on nickel or palladium substrates without limitations on gold thickness. However, the autocatalytic properties of the electrolyte necessitate additional process control to prevent unwanted precipitation or plating out. To stabilize gold plating electrolytes with autocatalytic properties, the industry commonly uses a constant replenishment of KCN-containing solution to keep the gold complexed and prevent precipitation, as detailed in the mechanistic section below.

KCN is highly toxic and can be fatal if swallowed, inhaled, or in contact with skin [2]. To mitigate the high health and environmental risks associated with handling KCN solutions, the gold electrolyte presented in this study does not require additional KCN dosing during operation. Instead, stabilization is achieved using a non-toxic additive, compliant with GHS regulations. This eliminates the need for handling highly toxic substances during the plating process while still maintaining bath stability and longevity.

EXPERIMENTAL, TOOLS AND METHODS

Used Materials and Process Flow

All layers were deposited on designated test structures according to the process flow outlined in Table 1, using commercially available products.

Table 1. Process flow of ENIG/ENEPIG process

Process Step	T [°C]	t [min]
Acidic Cleaner	35	5
DI Rinse	RT	1
MicroEtch	35	1-2*
DI Rinse	RT	1
Pre-dip	RT	3
Pd Activation	35	1
DI Rinse	RT	1
E'less Nickel – mid-P	80	**
DI Rinse	RT	2x1
E'less Palladium	55	**
DI Rinse	RT	2x1
Mixed reaction gold	82	**
DI Rinse	RT	1
Hot Rinse	50	1
Dryer	60	10

*: 1-2 µm Etch depth

**: Dwell time according to desired thickness or specified time

Thickness Measurement

All deposit thicknesses were measured using X-ray fluorescence (XRF) with a universally applicable energy dispersive X-ray measuring instrument.

Electrochemical Investigations

Electrochemical measurements were conducted to study the reaction mechanisms and the role of reducing components in the plating electrolyte. Linear sweep voltammetry (LSV) was performed using a jacketed beaker with an electrolyte volume of 50 ml. An Au-RDE served as the working electrode. The counter electrode was a Pt rod, contained by an electrolyte bridge filled with the gold electrolyte without gold salt and the respective reducing agent components. The reference electrode was an Ag/AgCl electrode (3M KCl), also contained by an electrolyte bridge filled with the gold electrolyte without gold salt and reducing components.

The LSV measurements were carried out with a scan rate of 10 mV/s, starting at the OCP potential versus Hg/Hg2SO4 and ending at OCP + 1.4V versus Hg/Hg2SO4.

Crystal Structure

Scanning electron microscopy (SEM) is employed to visualize details of the sample surface in a nanometer-scale. In surface view, pads are stripped with an KCN based gold stripping solution. Cross-sections are polished after grinding. From the three and ten positions highlighted in Figure 1, Position 2 is exemplary used for both, pads and PTH's.

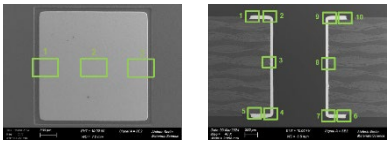


Figure 1. SEM. Investigated Spots. Left: Pad; Right: PTH

Surface Wetting

Solder dip and selective wave soldering tests were performed using SAC305 solder. For solder dip testing a flux for lead-free soldering was used. For selective wave soldering IF2005C flux was used. The reflow atmosphere was air for both tests at a reflow temperature of 280°C.

Solder Joint Reliability and Wire Bonding

The reliability of solder joints was evaluated using cold ball pull (CBP), ball shear (BS) test and high speed shear (HSS) testing. These tests were conducted with SAC305 solder balls, each having a diameter of 450 µm, on a test substrate with solder resist openings of 380 µm. A tacky flux (Kester TSF-6502JCR) was used, and the reflow profile was executed in a nitrogen atmosphere, reaching a peak temperature of 250°C. All reflow processes were carried out in a reflow oven.

For each condition, 30 solder balls were attached and either pulled or sheared. The ball shear test was performed with a shear speed of 210 µm/s and a shear height of 50 µm. Cold ball pull tests were conducted at a pull speed of 5 mm/s after a delay of 2 to 4 hours. High speed shearing was performed at 1,2 m/s at a height of 20 µm.
Failure modes for BS testing and HSS testing are displayed in Table 2.

Table 2. Fracture mode classification for BS and HSS testing

Mode 1	Pad pull-out
Mode 2	Intermetallic fracture < 5%
Mode 3	Intermetallic fracture < 25%
Mode 4	Intermetallic fracture < 95%
Mode 5	Intermetallic fracture > 95%

Failure modes for CBP testing are displayed in Table 3.

Table 3. Fracture mode classification for CBP testing

Mode 0	Mixture of Mode 1 and 4
Mode 1	Pad failure. Good bond.
Mode 2	Ball failure. Good bond.
Mode 3	Ball Extruded.
Mode 4	Bond failure.

Gold wires with a diameter of 23 µm were bond at 150°C. For pull testing a break load of 9,9 g was used. The pull test was conducted at a pull speed of 500 µm/s with 30 pulls per sample. The bond parameters are displayed in Table 4.

Table 4. Process parameter setting used for wire bond test

Parameter	First Bond (Ball)	Second Bond (Wedge)
US-Power [mAmps]	120	130
US-Time [ms]	25	20
Bond Force [g]	35	55

Fracture modes for wire bonding were evaluated as shown in Table 5 Figure 2.

Table 5. Fracture mode classification for Au wire bonding

Mode 1	Ball lift
Mode 2	Neck break
Mode 3	Wire break
Mode 4	Heel break
Mode 5	Wedge lift

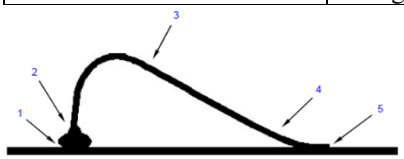


Figure 2. Fracture mode classification for Au wire bonding

Corrosion Rating

Different classes of corrosion depths are defined which are specified as 0 – 20%, 21 – 40%, 41 – 100%, >100% and surface corrosion (vgl. Table 6). Using this method allows a quantitative judgment of corrosion, which enables the engineer to compare different process conditions with statistical tools and relevance.

Table 6: exemplary table to rate corrosion in process development

		Number of identified corrosion events					
Sample ID	**Pad/ PTH ID**	**0 - 20%**	**21 – 40%**	**41 – 100 %**	**100 %**	**>100 %**	**Surface corrosion**
1	1	*3*	*5*	*1*	*0*	*0*	*0*
1	2	*2*	*3*	*4*	*0*	*0*	*0*
…	…						

The percentage values in the different columns allow a classification of the corrosion according to the penetration depth through the nickel layer.
Based on this evaluation a rating system was created internally to distinguish between critical and non-critical corrosion events.

For this typically 7 locations per PTH on 6 different areas per panel are evaluated, which include the sensitive through hole entrance regions but exclude the areas close to the soldermask. Their location is displayed in Figure 3.

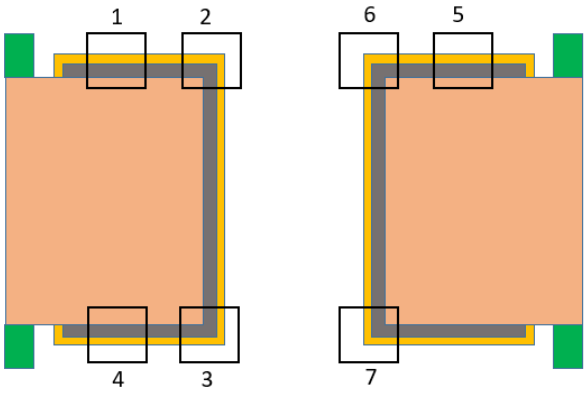


Figure 3: Definition of the location to be investigated per PTH

RESULTS

Understanding the Reaction Mechanism

The gold electrolyte, which operates through a combination of immersion and autocatalytic reactions, typically includes the following components: a) Potassium dicyanoaurate as the gold source b) Complexing agents c) Reducing agents d) Stabilizers e) Additives.
In this electrolyte, the reducing agents consist of two components that react to form the actual reducing agent. During the initial plating phase, the immersion reaction creates gold seedings that serve as a catalytic surface for the reaction of these two components. Once they react, the active reducing agent is formed, initiating the autocatalytic reaction. The interaction between all bath components is crucial for the reaction and stabilization of the electrolyte. To prevent spontaneous decomposition or gold precipitation, a KCN-containing solution is continuously dosed to support gold stabilization, as described below.
To evaluate the role of KCN and the two reducing components—referred to as part B and part C—stability measurements and electrochemical studies were conducted. During the stability measurements, the electrolyte was stored at operating temperature without additional stabilizer replenishment. When the solution's color changed, turbidity measurements were performed to quantify the decomposition rate.
Figure 4 illustrates the turbidity for three different samples with varying KCN content. The pale blue curve represents data for an electrolyte with no additional KCN, the yellow curve shows data for an electrolyte with a low KCN amount, and the dark blue dots indicate the behavior with a high KCN dosing.

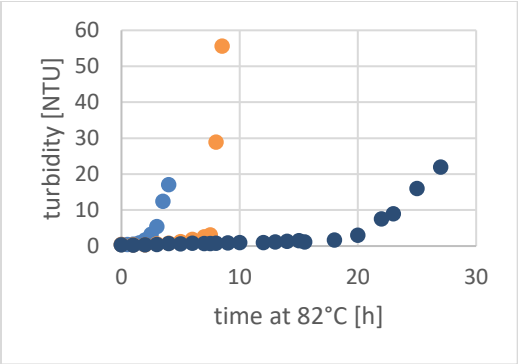


Figure 4. Turbidity data for a cyanide stabilized gold electrolyte with varying KCN addition

This result aligns with the effects of aurophilic interactions described in the literature. These interactions suggest the spontaneous aggregation of gold, forming dimers, trimers, and tetramers, which then transform into excimers and exciplexes. This process can potentially lead to the formation of unstable oligomers when the concentrations of complexing agents become too low. Figure 5 illustrates a schematic representation of gold stabilization by cyanide at high cyanide concentrations, the potential agglomeration of gold particles at lower cyanide concentrations, and the risk of precipitation when cyanide concentrations drop too low.

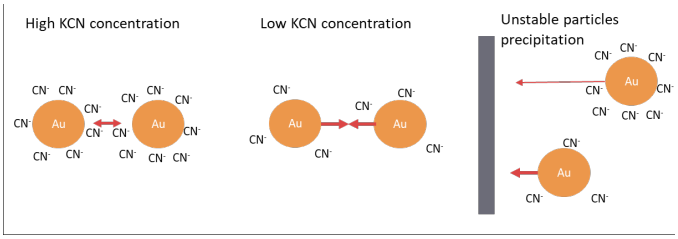


Figure 5. Schematic drawing of the stabilization mechanism of gold particles by cyanide in a cyanide stabilized gold electrolyte

Based on this assumption, various complexing agents were screened in combination with the remaining bath components to evaluate their effectiveness in stabilizing gold.

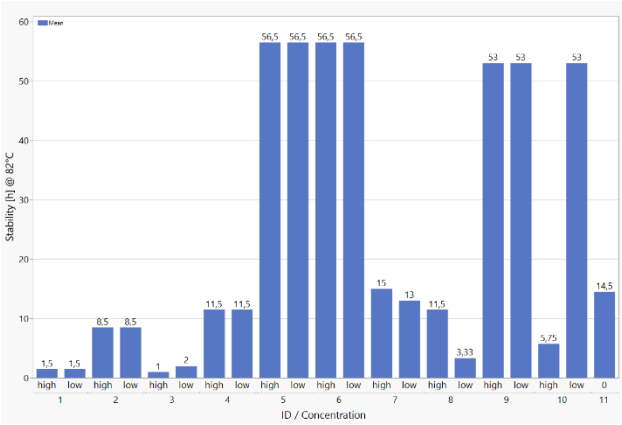


Figure 6. Stabilizer screening and impact on bath stability

Figure 6 presents exemplary results from stability tests conducted with various additives at different concentrations. This evaluation identified candidates 5 and 6 as significantly enhancing the stability of the plating electrolyte. Subsequent plating tests with these selected additives examined their effects on deposition rate, layer appearance, corrosive attack on the nickel layer, and assembly. This investigation successfully identified a non-toxic component capable of stabilizing gold in solution without interfering with the plating reaction.

In addition to evaluating the gold complex, further focus was placed on the reducing agent and the formation of the active component from parts B and C. Linear sweep voltammetry measurements were performed, varying the content and ratio of B and C, to assess their impact on the oxidation reaction.

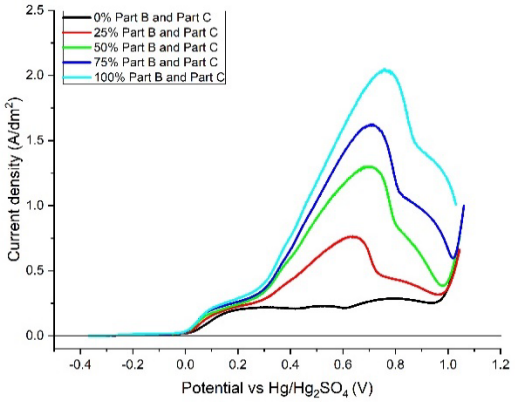
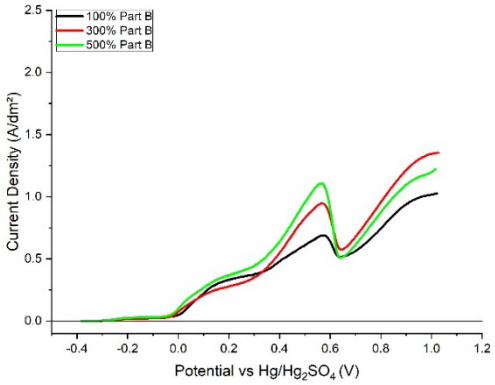


Figure 7. LSV measurement of the gold electrolyte with varying concentrations of Part B and C

When parts B and C are combined before being added to the gold electrolyte and introduced in various concentrations, an overall increase in the oxidation reaction is observed with rising concentrations of these components, as shown in Figure 7. When the individual ratios of parts B and C are altered, it becomes evident that each component has a distinct impact on the reaction. Figure 8 provides an overview of four different conditions that were tested.



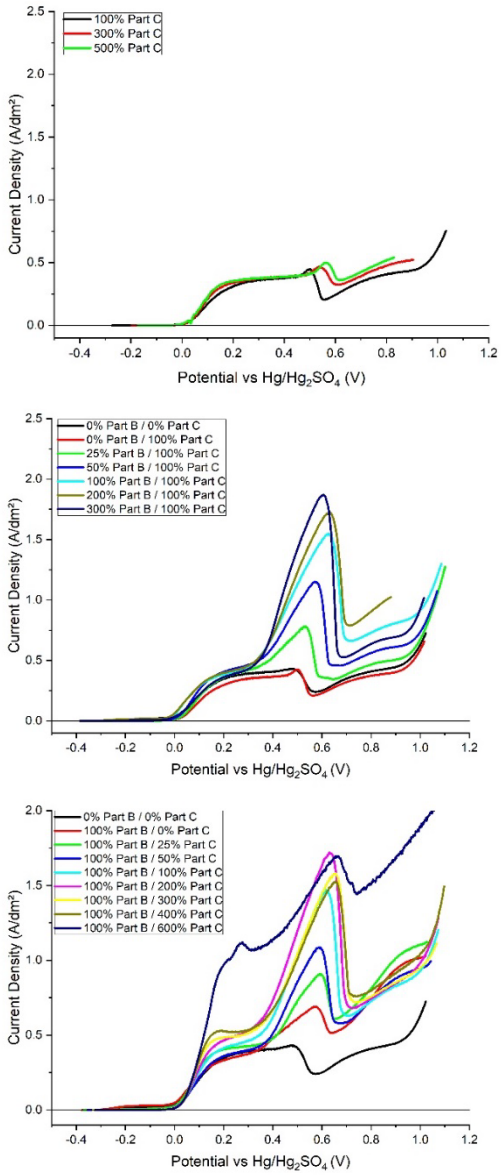


Figure 8. LSV measurements with different concentrations and ratios of Part B and C

The graph on the top shows that with a given concentration of part C, no reaction occurs without dosing part B. As the content of part B increases, the oxidation peak also rises. On the second graph, where the concentration of part B is kept constant and the concentration of part C is varied, a small oxidation peak is observed even without part C. This peak grows with increasing content of part C. These data suggest that both components are required in combination for a sufficient plating reaction, likely due to the formation of a reaction product that acts as the active reducing component. Comparison measurements with the individual components at different concentrations support these findings (see last two graphs). The first graph implies part B exhibits some reductive properties, but they are not strong enough to enable sufficient gold deposition on their own. When only part C is added, no oxidation reaction is detected. However, when parts B and C are combined and part C is dosed in very high ratios, a second oxidation peak appears as can be seen in the last graph. This supports the assumption that a reaction product is formed, which defines the activity of the reducing reaction.

Plating Characteristics

In conventional mixed-reaction gold electrolytes that use KCN-replenishment, a continuous dosing of KCN solution is required to maintain a constant CN concentration in the plating solution. This kind of replenishment was replaced by a new KCN free stabilizer component.

In the following this gold electrolyte with a non-toxic stabilizer was tested on a 110L scale and determined if it can perform comparably to KCN-stabilized mixed-reaction gold electrolytes.

It was operated with continuous plating for 220 hours up to 3 months before the test was stopped. During this time, the bath remained stable. No red dust could be observed in the tank or filter cartridge after finalizing the tests (see Figure 9).

Figure 9. Filter check after 3 months continuous operation

The bath was operated with a gold concentration of 0.6 g/L. In previous studies the bath loading was tested up to 20 MTO without compromises [1], which is more than three times the established process in the market.

The thickness distribution was evaluated on two different test boards on 16 copper pads with varying sizes from 0.25 mm² to 49.3 mm² with both, connected and isolated pads onto FR4 base material. The Pd thickness target was approx. 0,16 – 0,25 µm, the Ni thickness target approx. 5 µm and the gold thickness was varied according to the requirements.

The plating data over bath life range of 35 until 50 plating hours (blue) and 95-100 plating hours (red) are summarized in Figure 10:

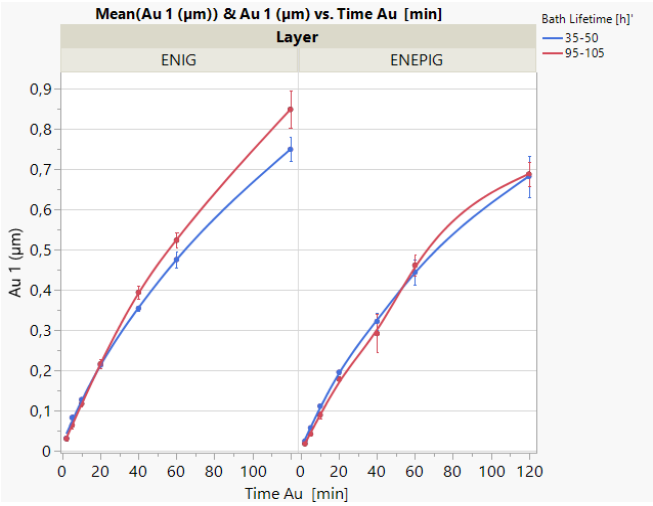


Figure 10. Gold thickness depending on exposition time and bath age

The graph is showing the achieved gold thickness (y-axis) over a certain exposition time (x-axis). From the graph it could be seen that the bath age has no (negative) impact onto the deposition rate. The deposition rate for both ENIG and ENEPIG samples were above target and very consistent over bath life. A high gold thickness of 120 nm was possible. As the test was stopped at 120 nm this does not reflect the process limit. The electrolyte was achieving consistent CoV (Coefficient of Variance) values below 5%. Therefore the gold CoV was in target. Throughout this aging test, the plating rate remained quite stable at approx. 8.5 nm/min for ENIG and 7.5 nm/min for ENEPIG.

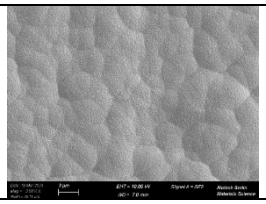
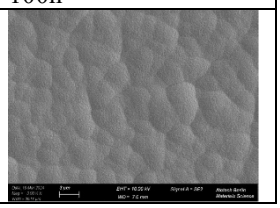
Layer Properties

In a study before it has been shown that mixed-reaction gold bath types could be used for various types of substrates [1]. In the following the properties of a ENIG and ENEPIG layer was checked on copper substrates only.

Crystal structure (SEM)

Both, ENIG and ENEPIG layers were checked on the surface and in the cross section of a PTH via SEM. Many positions are checked as according to Figure 1. There is only the exemplary result of position 2 displayed in Table 7 and Table 8. However, the other positions did not differ in their findings. For all three finishes dense and even gold deposits are formed with a defect free connection to the substrate metal. There is no indication for void formation or excessive nickel or copper corrosion.

Table 7. ENEPIG (120 nm Au)

	0h	100h
Pad		

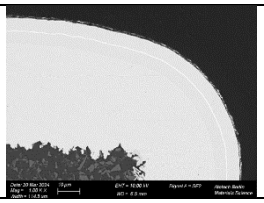
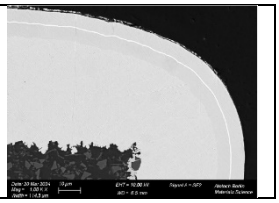
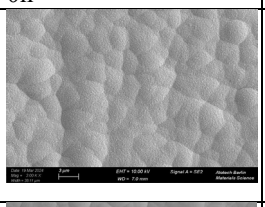
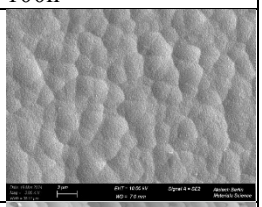
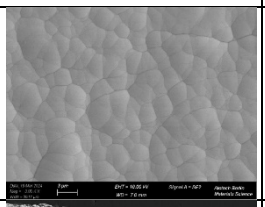
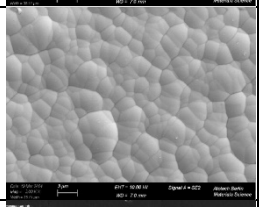
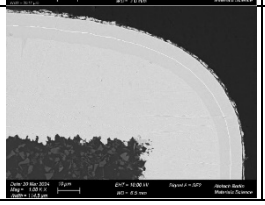
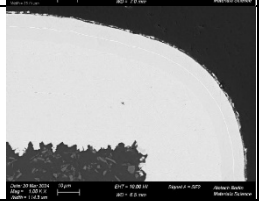
PTH		

Table 8. ENIG (140 nm Au)

	0h	100h
Pad		
Pad strippe d		
PTH		

For ENIG, Ni corrosion is of bigger consideration due to the absence of Pd with acts as a further barrier preventing nickel from corrosion. Therefore the pads of the ENIG layer were also stripped from the gold so that the Ni interface is exposed as visible in Table 8, middle row. No signs of corrosion or any other defects are visible for ENIG at the Ni interface, neither in cross-section view nor at the grain boundaries of the stripped surface.

ENIG Corrosion Investigation

A broader view in terms of Ni corrosion can be gained through microscopic corrosion investigation. Therefore ENIG layers are checked via cross-section.

The following classification was used:
0 – 20% of corrosion includes all corrosion events, which penetrate the nickel layer thickness up to 20% and less. Such corrosion events are usually assumed to be less critical because the impact on solderwetting and IMC formation is low. From 21 – 40% all those events are included, which penetrate the nickel between 21 – 40%. Even with this extend the corrosion is assumed to be less critical as long as the number of events is not too high because there is still enough nickel layer thickness left. More critical are corrosion events with a penetration depths of 41 to 100% as with that the corrosion event might penetrate the nickel down to the copper layer so that the barrier function of the nickel layer is affected and copper may migrate to the surface or to the solder joint.
Corrosion events penetrating the nickel layer more than 100% are so severe, that in such cases the copper underneath

is also attacked and dissolved bearing an even higher risk to lead to solder joint failures. Such events are very rare and usually a clear indication that the ENIG process is not operated in the specified range.

Also for "surface corrosion" the probes are screened, which typically included the surface attack to the nickel layer which results in the typical sponge-like nickel structure and does not penetrate the nickel in depth. Due to the sponge-like structure of the nickel, the increased light absorption leads to a darker appearance after the gold stripping which leads to the common term of "black pad". Black pad corrosion can usually observed over larger areas up to several µm in diameter at the nickel gold interface. When such a large area is affected the formation of the IMC during the soldering is inhibited which leads to the highest risk for soldering or bonding failures as described before.

For each location which was investigated a rating of corrosion depth and amount is performed according to Table 6 and Figure 3 and the corrosion is judged according the following criteria:

- Level 0: no corrosion events
- Level 1: less than 10 events with all events not deeper than 20% - or a single event with less than 40%
- Level 3: 10 or more events and more than 5 deeper than 40% - or surface corrosion with an extension of more than 30% of the image
- Level 2: every other observation

With this way of evaluation, it is possible to achieve a representative and quantified judgement of the corrosion on a certain location. To get an overall result for the PCB panel a rating is created based on the percentage of the occurrences identified in the level judgment. For this the following assumptions are applied:

- Corrosion rating 0: no corrosion
- Corrosion rating 1: more than 60% of the investigated locations have a level 0 or 1
- Corrosion rating 3: more than 40% of the locations show a level 3
- Corrosion rating 2: all other observations

This overall judgement allows to relativize the result and identify the corrosion which might be critical regarding the reliability of the finish. This evaluation is according to IPC-4552B [3] whereas 8 locations/PTH have been investigated instead of 7. Five samples per condition were checked leading to a total check of 40 locations per condition. Layer systems and approx. gold thicknesses applied can be seen in Table 9.

Table 9. Gold thicknesses for ENIG and ENEPIG

	Gold thicknesses [nm]		
ENIG	140	500	800
ENEPIG	120	450	700

For each condition cross sections were performed at zero hrs and 100 hrs of bath life. This leads to a total of 480 locations checked for corrosion.

The impressive result is that all of this 480 checked locations had a corrosion rating of 0. It could be therefore concluded that this mixed reaction bath with high autocatalytic reaction share enables the formation of a defect free ENIG layer.

This contrasts with the immersion gold baths commonly used in industry. In a previous study it was stated that those typically exhibit spikes or spreaders forming corrosive attacks. This should be especially true at through hole entrances where high solution flow is present [4].

Wetting, Soldering and Bonding

Wetting tests

Wetting tests are used in soldering to evaluate the quality of the solder joint as they help determine how well the solder adheres to the surfaces being joined. Good wetting indicates a strong bond, while poor wetting can lead to weak joints. Those tests can further reveal the presence of contaminants or oxidation on the surfaces, which can prevent proper soldering. The wetting tests published in this paper were applied for ENIG and ENEPIG with liquid solder: The solder dip and selective wave soldering tests.

For Solder Dip testing the evaluation criteria used is according to IPC/EIA J-STD-003C WAM1&2 [5]: A minimum of 95% of each of the surface being testes shall exhibit good wetting. There shall be no nonwetting or exposed base material within the evaluated area. The results are displayed in Figure 11.

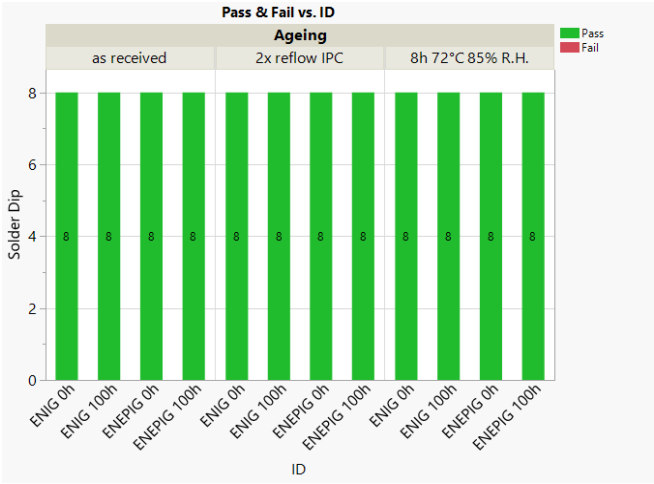


Figure 11. Solder dip test results.

For all conditions applied - as received (ASR), 2 times reflow according to IPC as well as 8 hrs at 72°C and 85% R.H. -all bath age conditions passed solder dip test for ENIG and ENEPIG. Therefore the surface exhibits a very good wetting.

The surface wetting on through holes could be examined via

selective wave soldering. For ENIG and ENEPIG at 0- and 100-hours bath age the same three aging conditions as in solder dip testing were applied (see Figure 12).

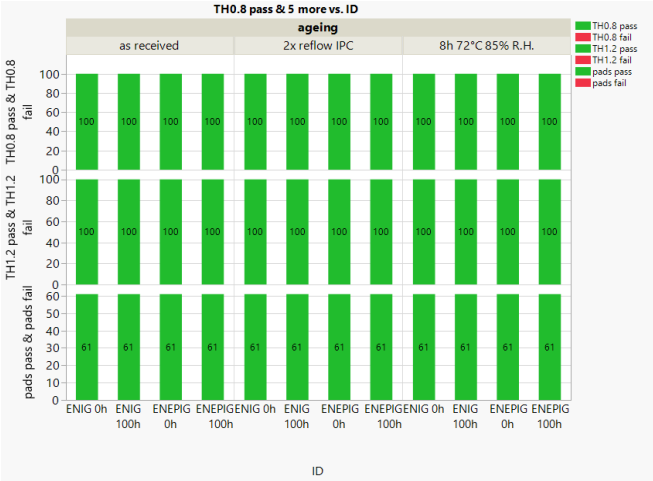


Figure 12. Selective wave soldering test results

All conditions passed selective wave soldering ensuring a good wettability in critical through holes.

Besides ensuring good wetting, a strong solder bond improves the reliability and longevity of the soldered connection, which is crucial in electronic components. For testing the solder bond ball shear, cold ball pull and high speed shear testing was performed.

Soldering tests

To assess the reliability of the final finish applied with the new gold electrolyte, ball shear cold ball pull and high speed shear tests were conducted using ENIG and ENEPIG deposits. As for wetting tests samples were plated from a fresh bath and an aged bath of 100h bath life at 82°C to examine the impact of bath age onto soldering performance. Figure 13 and Figure 14 presents the shear and pull forces of ball shear and cold ball pull testing alongside the observed fracture modes.

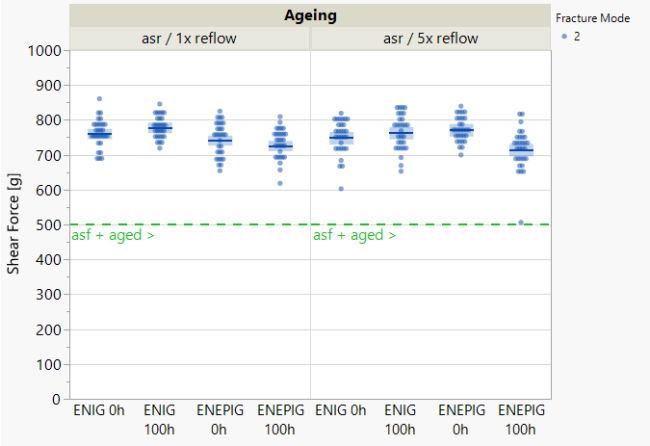


Figure 13. Ball shear (BS) test results – ENIG and ENEPIG

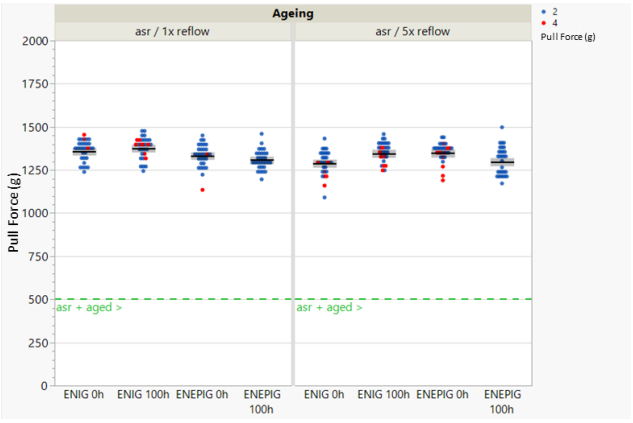


Figure 14. Cold ball pull (CBP) test results – ENIG and ENEPIG

Both, the ball shear test forces and the cold ball pull test forces all pass the minimum value of 500 g and are consistent for the as received condition as well as for the aged bath condition.

The fracture modes are also displayed in the graph with the only prevalent mode 2 in shear testing and mostly prevalent mode 2 and occasionally 4 in CBP testing. mode 4 signifies a bond failure (see Table 3 x), indicating the solder joint's brittleness. Conversely, Mode 2 denotes a ball failure, where the maximum force can be applied without impacting the intermetallic phase. Specifically, mode 2 shows an intermetallic fracture rate of less than 5%, while mode 4 indicates a brittle solder joint with fractures exceeding 95% of the intermetallic. In the ball shear test, the prevalent mode 2 could be interpreted as strong solder joint at all conditions, ASR and 5 times reflowed, fresh and aged bath condition for both ENIG and ENEPIG layers. There could be no significant difference in shear forces and fracture modes be observed amongst both finishes and all conditions indicating a robust soldering performance.

The same conclusion could be drawn from CBP test results, even though the fracture mode 4 prevalence is slightly higher. This can be explained with the general harsher impact of that test towards the solder bond. The fact that the ENEPIG samples of 100 hours bath age at one and five times reflow exhibit only ductile fracture modes 2 underlines the very good quality of the solder joint. In general, for this harsher test condition ENIG exhibits more fracture mode 4 than ENEPIG and therefore displays slightly more intermetallic fracture. This should be kept in mind as manufacturer or board designer when selecting an appropriate final finish for high reliability applications.

In the following, ENEPIG layers will be further evaluated. To assess the solder joint reliability of the ENEPIG finish under stronger conditions than BS and CPB testing, additional high-speed shear tests were performed (see Figure 15). These tests also serve as indicators of solder joint reliability, with the total energy (measured in millijoules) quantifying the strength and ductility of the solder joint. A

higher total energy value indicates a stronger and more ductile solder joint.

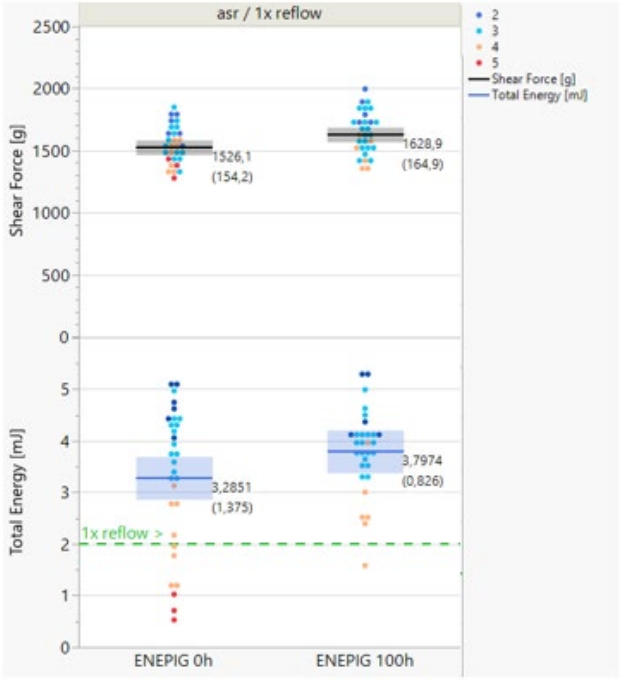


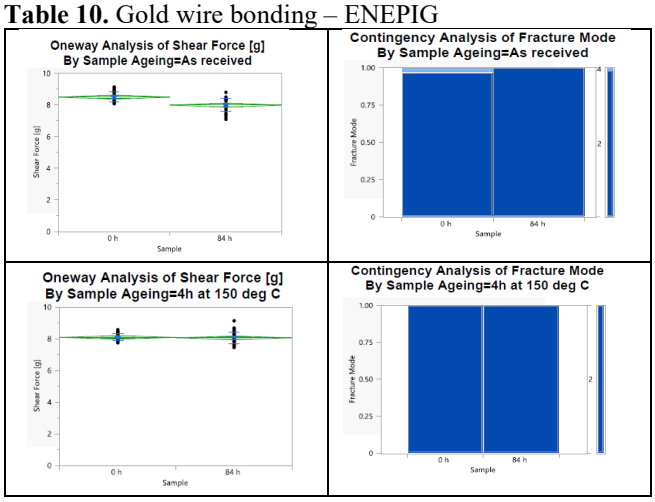
Figure 15. High speed shear (HSS) test –ENEPIG

All ENEPIG samples plated with the fresh bath make up as well as 100 hours of bath age passed the 1x reflow condition. Prevalent failure modes are mostly 2 and 3, indicating intermetallic fracture of less than 25% (see Table 2) and therefore a still sufficient, mostly ductile bond. This can be confirmed in previous tests [6].

Wire bonding test

In addition to examining solder wetting and solder joint reliability, the wire bonding capability of the three finishes was also evaluated. In Table 10 the results of Au-wire bonding for the ENEPIG finish are displayed. The tests were conducted both in their as-received condition and after thermal aging for 4 hours at 150°C.

Table 10. Gold wire bonding – ENEPIG



The acceptance criteria for pull tests, as outlined in DVS 2811 [7], specify that the mean force must exceed 50% of the wire's bond load (greater than 4.95 g). All Gold wire bonding tests passed with shear forces >8g on average which far exceeds the 4,95g threshold. A coefficient of variation (CoV) of less than 15% is acceptable for deviations. Also, this requirement could be met for ENEPIG at all conditions.
It can be further evaluated that ENEPIG demonstrates comparable pull forces in all conditions, fresh bath matrix and 84 hrs of bath age for ASR and aged condition 4h at 150°C. All conditions primarily exhibit fracture mode 2. There were no signs of peeling or lift-off, indicated by failure modes 1 or 5, detected. These results demonstrate that the gold layer on the surface finish is well bonded to the underlying nickel and palladium layers at all conditions.

SUMMARY/OUTLOOK

This paper introduces a novel gold electrolyte with KCN-free stabilization and mixed-reaction behavior. The differences in reaction mechanism between immersion and mixed reaction were explained and a hint to caution for the naming was given. Ni/Au layers in this paper were referred to as ENIG and Ni/Pd/Au as ENEPIG. It has to be kept in mind that for a mixed reaction bathes also the naming ENAG and ENEPAG could be potentially used. As the terms IG/AG in the process name do not necessarily reflect the exact properties of the plating bath, a clear guideline for naming in the industry could be a way in order to better clarify the differences in the reaction mechanisms on first sight.

The first chapter of the paper was dedicated to the process of elaborating a KCN-free alternative for mixed reaction gold bathes and deeper understanding of the reaction mechanism from an electrochemical point of view. A mixed-reaction gold bath of 0,6 g/l gold with nontoxic stabilization and therefore no cyanide handling for replenishment was invented. The so designed gold bath could be applied for various finishes: ENIG, ENEPIG and EPAG.

Next, this paper focused on checking the plating reliability of that new bath in terms of bath stability, ENIG corrosion performance and thickness distribution. A consistent behavior over bath life with thickness distribution of < 5% COV was found. In terms of ENIG Ni corrosion an outstanding result of corrosion rating of 0 at all 480 checked locations could be found.

In the last section reliability in terms of wetting, solder joint and bond performance was checked. Besides fresh bath make ups, also aged bath conditions were used. Further, the produced layers were tempered and/or (multiple) reflowed to examine the performance.
Wetting tests unveiled an excellent wetting result of the gold surface crated by the new bath electrolyte. On both, pads and more critical through holes an excellent solder adhesion to the surfaces being joined was found.

Ball shear testing revealed very good and consistent results over bath age and multiple, up to 5 times reflow for ENIG

and ENEPIG. Even in harsher cold ball pull testing ENEPIG samples of 100 hours bath age at one and five times reflow exhibited only ductile fracture modes 2. This indicates a very good quality of the solder joint and therefore high reliability. In this chapter, further implications for manufacturers and board designers were given in selecting an appropriate final finish for high reliability applications.

REFERENCES

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