High-speed NiP Process for Connector Applications

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Thin gold coatings applied over electrolytic NiP have been proposed to be an alternative for conventional nickel/gold systems for connector applications. In addition to its functional benefits, the reduction of applied gold thickness enables a reduction in overall cost. It is important that the phosphorous content in the deposit be maintained at a minimum of 11-12% in order to achieve the desired corrosion resistance. Current systems are able to meet this requirement only at lower current densities. A new electrolytic NiP process has been developed that allows operation at current densities of up to 35 ASD with a cathode efficiency of 60%. The deposit was shown to have a high phosphorous content of > 11% over a wide CD range.

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Introduction

Due to its wear and corrosion resistance NiP layers are widely employed in different applications. Electroless processes have the distinct advantage of producing deposits of uniform thickness particularly on components with complex shapes. Depending on the bath composition and operational data it is possible to deposit NiP layers with a P-content of > 11 %. However, the plating rate of these baths is quite low which makes electrolytic processes very interesting. Recent developments show that electrolytical NiP baths enable the deposition of layers with a high P-content at a high plating speed. As a result of this advantage a new contact system is possible based on NiP/gold flash. For certain applications the standard contact systems (Ni 1-3 µm, Au-alloy 0.8-2 µm) can be replaced by this cost saving alternative.

Bath Compositions of Electrolytic NiP Processes

In order to gain an idea of the substances which are generally used in electrolytic NiP processes the following table shows some typical bath compositions

Table 1: Typical bath compositions of electrolytic NiP processes

	US 6099624	EP 0266020
Nickel sulfate		
Nickel chloride		X
Nickel alkane sulfonate	X	
Nickel carbonate	X	X
H3PO4 (phosphoric acid)	X	X
H3PO3 (phosphorous acid)	X	X
H3PO2 (hypophosphorous acid)	X	
Buffer (H3BO3)	X	
Surfactant (sodium lauryl sulfate)	X	
Stress reducing agent	X	
Nickel chelating agents	X	

In US 6099624 [1] the benefit of nickel alkane sulfonate (instead of nickel sulfate or nickel chloride) is emphasized. One reason is that since energy costs are an important consideration in the electroplating industry it would be advantageous to use an electrolyte which had higher conductivity than the baths of the prior art, thereby requiring less voltage for the same current density. Beside a nickel salt, a phosphorous source is the other major component with phosphorous acid (H_3PO_3) as the principle source. However, additions of phosphoric- and/or hypophosphorous acid are possible which may help to improve the deposit and the operational data.

Other additives include:
a) a buffer such as boric acid
b) a surfactant (e.g. sodium lauryl sulfate) to reduce surface tension
c) a stress reducing additive to impart compressive stress to the deposited coating. Examples: aromatic sulfonic acids, such as aminobenzene sulfonic acid, benzene disulphonic acid and other compounds including cysteine hydrochloride, saccharin or thiourea.
d) nickel chelating agents.

In the European Patent Application 0266020 [2] the use of nickel chloride is preferred rather than nickel sulfate since the deposits are alleged to have higher inherent brightness less tensile stress and less graininess than deposits obtained from sulfate baths.

Operational and Deposit data

The properties of a NiP layer are largely determined by the P-content of the deposit. Depending on the application it has to be maintained within specified limits. To provide good wear and corrosion resistance it should be > 11-12 %. The P-content is being influenced by several parameters, such as
1) CD
2) agitation
3) temp
4) pH
5) additive content
Therefore, these factors and their influence on the P-content have to be checked very carefully in order to determine the optimum operational parameters.
The results of our investigations are explained in the following:
The tests in the lab were mainly carried out with the jet lab as this method simulates the conditions of a jet plating line. Furthermore, experiments with the rotating cylinder are presented as well as results from a reel to reel line.

ad 1) Influence of CD on P-content and plating speed

Figure 1 shows the benefit of a new high speed NiP bath over a conventional process. In this trial (jet lab) the P-content goes down below 11 % at a current density > 10 ASD which makes this process unsuitable for high speed applications. With the new process a P-content of 8% is obtained at 40 ASD but it has to be kept in mind that it can be easily increased by changing pH and or/ temperature.

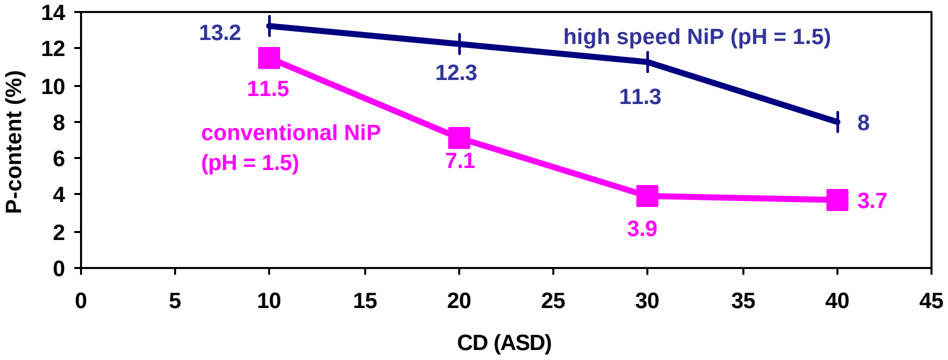


Fig.1 P-content depending on current density (CD)
Jet lab (T = 70°C, flow rate = 580 dm^3/h = 2.5 m/s impinging velocity)

Even though the P-content of the conventional system is very low at high CD's (> 25 ASD) the plating speed is lower compared to the new system.

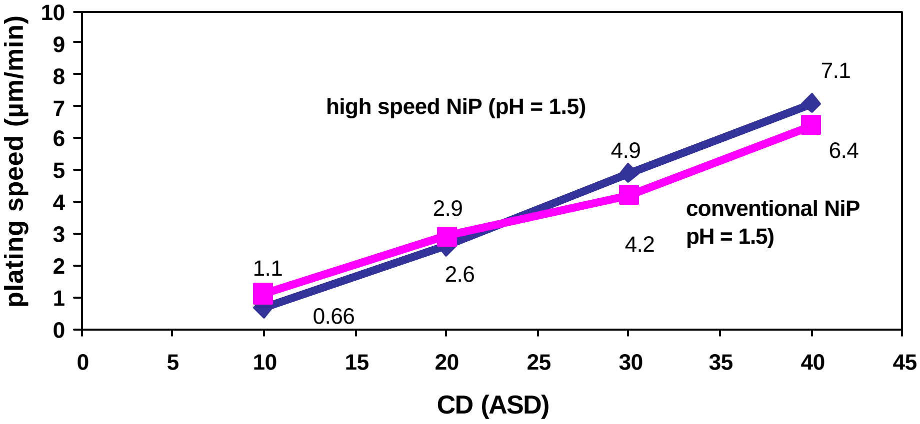


Fig.2 Plating speed depending on current density (CD)
Jet lab (T = 70°C, flow rate = 580 dm^3/h = 2.5 m/s impinging velocity)

Although obtained under different plating conditions, the results of the rotating cylinder tests show the same trends. As CD increases, the plating speed increases and the P-content decreases gradually.

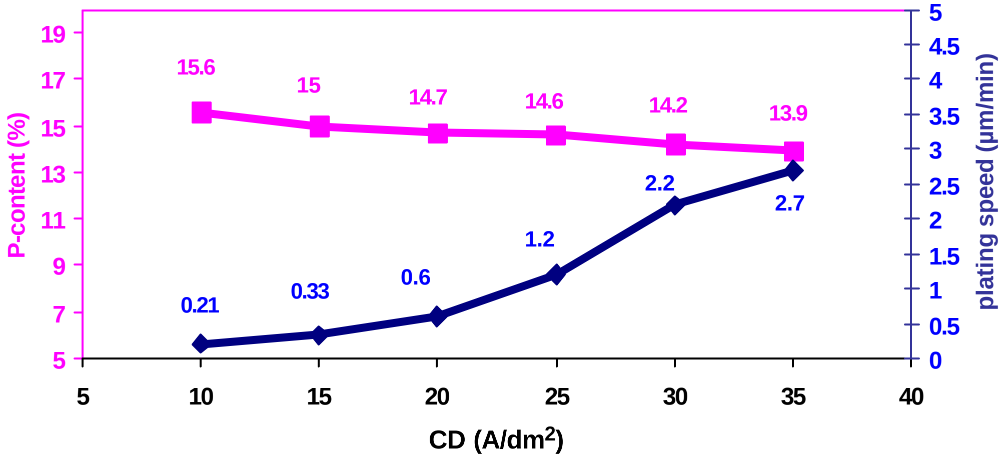


Fig.3 P-content and plating speed depending on current density (CD)
Rotating cylinder (T = 75°C, pH = 1.2, 1000 rpm)

ad 2) Influence of agitation on P-content

Agitation is a parameter which always depends on the individual plating line. Different geometries and flow techniques influence the deposit characteristics, applicable current density, etc. Therefore, the optimum parameters always have to be established in each plating line but the general effect of different flow rates can be seen from figure 4 and 5 (below).

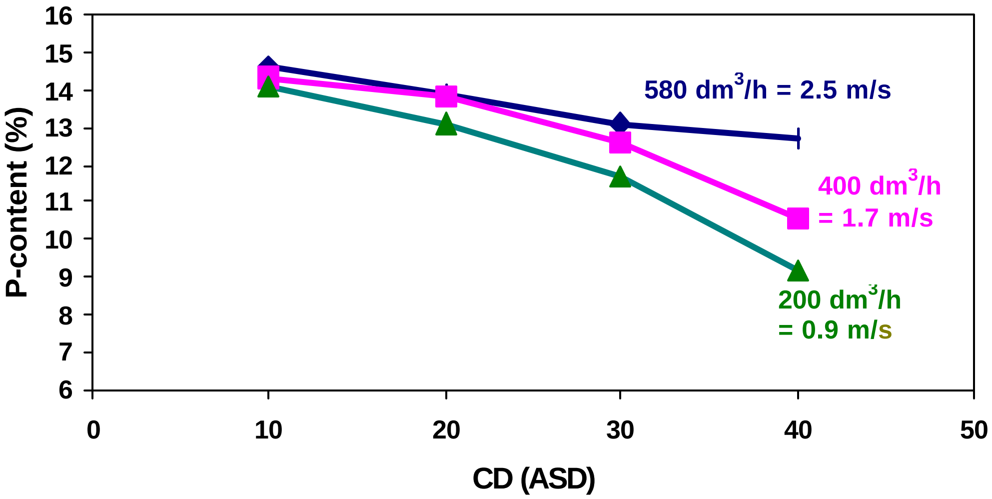


Fig.4 P-content depending on flow rate and current density (CD)
Jet lab (T = 70°C, pH = 1.3)

The circulation of the pump, measured in dm^3/h, was recalculated into velocity of the impinging jet (m/s) which gives you a good idea about the conditions under which the samples have been plated. It is observed that increasing the flow rate always results in an increased P-content at the individual current densities. This trend could be confirmed using the rotating cylinder with different speed of rotations ranging from 500 – 2000 revolutions per minute.

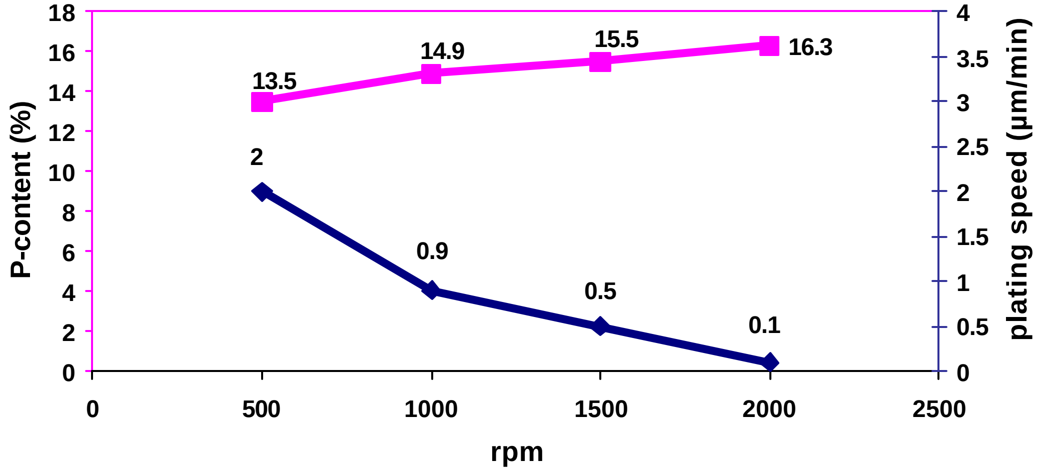


Fig.5 P-content and plating speed depending on speedf of rotation
Rotating cylinder (T = 75°C, pH = 1.2, CD = 25 ASD)

ad 3) Influence of temperature on P-content and plating speed

It is not surprising that deposit properties are influenced by the temperature of the working solution. The findings of several tests show that in contrast to electroless nickel baths the P-content increases upon increasing the temperature.

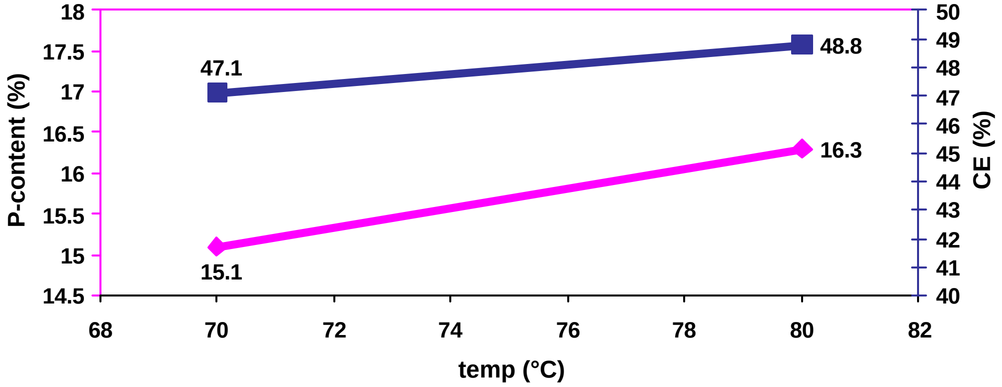


Fig.6 P-content and current efficiencydepending on temperature
Beaker test with high speed mixer (pH = 1.1, CD = 15 ASD)

ad 4) Influence of pH on P-content and plating speed

A careful control of the pH of a plating bath is crucial for obtaining constant results during operation. As can be seen from figure 7, pH is a good means to adjust the P-content to the desired level. Furthermore, it could be shown in this experiment that only at 40 ASD at pH = 1.5 the P-content dropped below 11 %. Therefore, the high speed NiP process can be operated over a broad CD range with good corrosion resistance of the deposit.

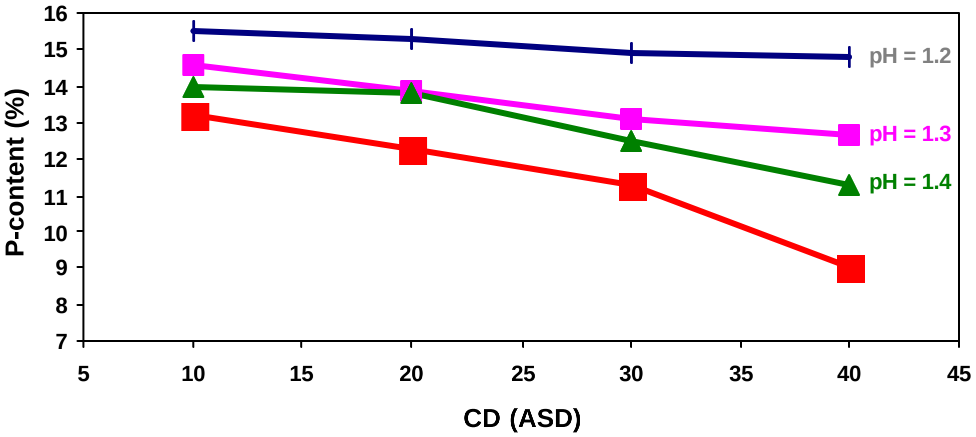


Fig.7 P-content depending on pH and current density (CD)
Jet lab (T = 70°C, flow rate = 580 dm^3/h = 2.5 m/s)

Table 2 summarizes the outcome of the experiments shown above which gives a good overview about how the P-content in the deposit can be controlled and adjusted.

Table 2 Parameters influencing P-content in the deposit

	high speed NiP	electroless NiP
pH ↑	P (%) ↓	P (%) ↓
T ↑	P (%) ↑	P (%) ↓
CD ↑	P (%) ↓	
Agitation ↑	P (%) ↑	
c (additive) ↑	P (%) ↑	

Production tests

Not only lab experiments but also tests in production lines (e.g. in a reel to reel line) prove that the required P-content of > 11 % can be easily achieved if the operation parameters are well controlled. The following figure shows that the required P-content of minimum 11 % is achieved not only in the middle of the substrate but also in the high CD area of the edges.

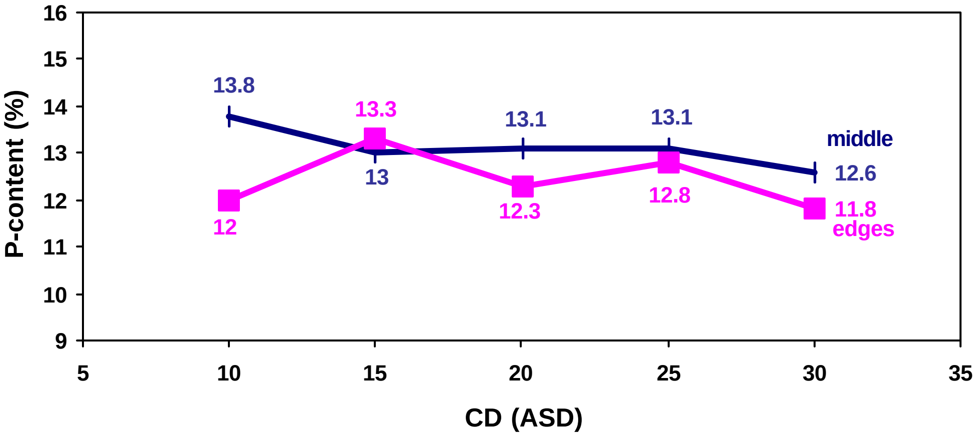


Fig.8 P-content depending on CD (Substrate plated in a reel to reel line)
(T = 73-75°C, pH = 1.13-1.17)

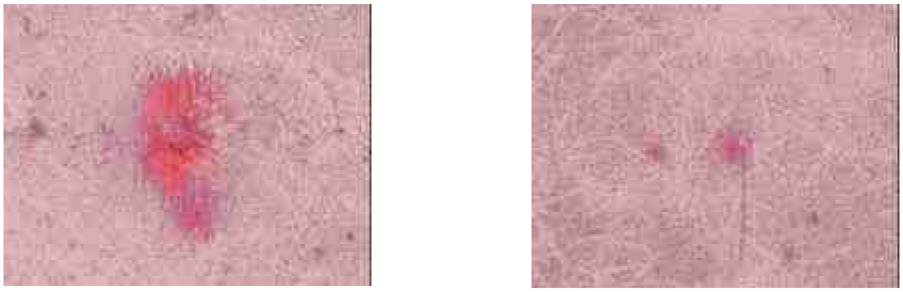
Characterization of the NiP- layer

1) Porosity test

With regard to corrosion resistance not only the P-content of the alloy but also the porosity plays an important role. It has to be ensured that the protective layer prevents contact with a corrosive media with a corrodible substrate (or underlayer). For this reason the minimum NiP layer thickness has to be determined to ensure effective corrosion protection.

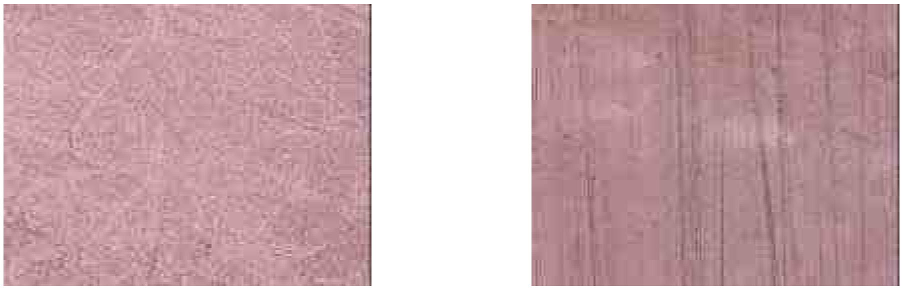
In the following test series a substrate was coated with semi bright nickel followed by a NiP layer of different thicknesses. Anodic treatment of the specimen in dimethylglyoxime (DMG) indicates possible pores by the appearance of red spots.

As can be seen from figure 9 several pores were identified with a 0.3 µm and a 0.6 µm NiP layer.



2 µm Ni, 0.3 µm NiP

2 µm Ni, 0.6 µm NiP



2 µm Ni, 0.9 µm NiP

brass, 0.6 µm NiP

Fig.9 Dimethylglyoxime test with different NiP layer thicknesses

No red inner complex salt could be identified with layer thicknesses ≥ 0.9 µm which means that no pores were present. Additionally a NiP layer directly on brass was subjected to this test.

2) Corrosion test

Corrosion resistance is one of the major reasons why NiP is considered to be an alternative for conventional Ni/Au systems. As indicated earlier, the P-content has to be maintained at > 11 %. The following test clearly shows the benefit of the high speed NiP process over the conventional system. The corrosion test was carried out by exposing different coating systems to HCl and HNO_3 vapour, respectively, for 60 min. It does not come as surprise that in the first test series the specimen corrodes heavily since a thin Au layer of 0.15 µm cannot prevent the attack of the corrosive vapour on the underlying nickel.

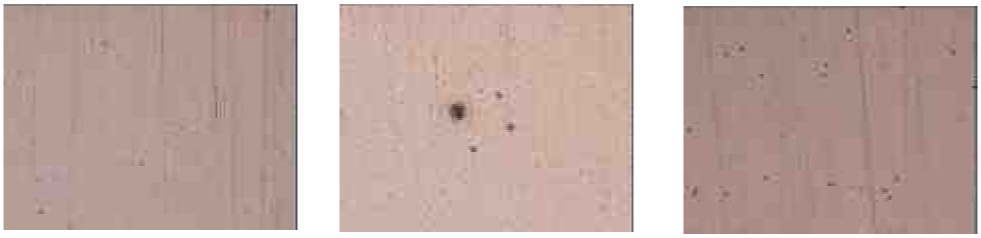
2 µm matt Ni, 1 µm semi-bright Ni 0.15 µm Au

As is After HCl test After HNO3 test

Fig.10

The following test shows that the P-content of a deposit obtained from a conventional NiP process at 20 ASD is too low to guarantee full corrosion resistance

2 µm matt Ni, 1 µm conventional NiP (T = 70°C, 20 ASD) 0.15 µm Au



As is After HCl test After HNO3 test

Fig.11

Only test samples plated with 1 µm high speed NiP pass the HCl as well as the HNO_3 test

2 µm matt Ni, 1 µm high speed NiP (T = 70°C, 20 ASD) 0.15 µm Au

As is | After HCl test | After HNO test

Fig.12

3) Contact resistance

In order to simulate the strain, to which connectors are generally exposed in practical applications, various test methods have been established. An important parameter here is the contact resistance which can be measured after a sequential combined conditioning. The criteria here is that the contact resistance, after the tests, may not change more than 5 mOhm compared to the initial condition. A typical test sequence to check the reliability of connectors is shown in figure 13.

2 µm Ni/ 2 µm NiP/ 0.2 µm AuCo

125 mating cycles → 4 gas test → 125 mating cycles
(SO_2, H_2S, NO_2, Cl_2)
passed passed failed

2 µm Ni/ 0.5 µm NiP/ 0.2 µm AuCo

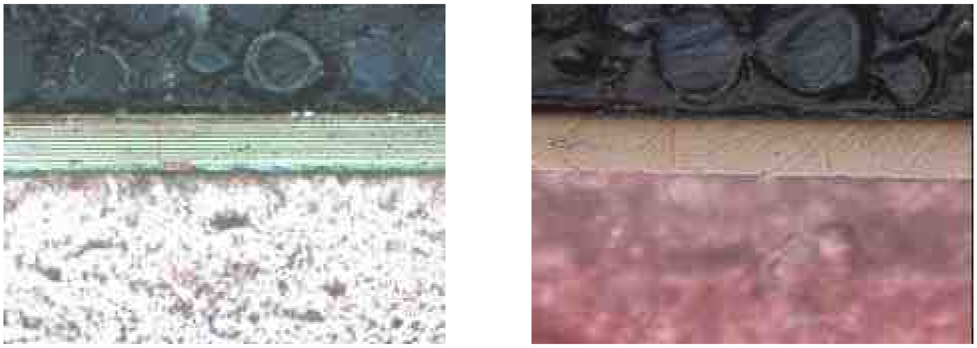
125 mating cycles → 4 gas test → 125 mating cycles
(SO_2, H_2S, NO_2, Cl_2)
passed passed passed

Fig. 13 Contact resistance after sequential combined conditioning (Bellcore GR-1217-Core)

Interestingly, the sample plated with only 0.5 µm NiP shows the better result. This coating system is less hard which results in a larger contact area and therefore lower contact resistance.

4) Cross section

A comparison between a NiP layer from a conventional and a high speed system shows the differences between these two processes.



Conventional NiP (10 ASD)

High speed NiP (10 ASD)

Fig. 14 Cross section of different NiP layers

After etching with HNO_3: CH_3COOH 1:1 the conventional NiP clearly shows a laminar structure which resembles electrolytic bright nickel. By contrast, the layer obtained from the high speed process doesn’t show any structure at all.

5) XRD-spectra

A totally amorphous layer does not diffract X-rays, since there is no lattice plane where diffraction can take place. So an amorphous layer does not show any peaks at all in a XRD spectra. On the other hand, a perfect regular structure is characterized by distinct sharp peaks. Widened peaks indicate that the material has areas with a regular structure as well as amorphous fractions. Increasing the amorphous moiety results in a further broadening and flattening of the peak until it disappears completely when a regular structure is no longer present. The following XRD-spectra coincide with the observations from the cross-sections. Apart from the distinct peaks (which come from the Cu-base material) the spectra of the high speed NiP process shows only a sign of a broad peak which indicates that the deposit consists almost exclusively of amorphous material. By contrast, the peak in the spectra from the conventional NiP system is much more distinct which means that there are more areas with a regular structure.

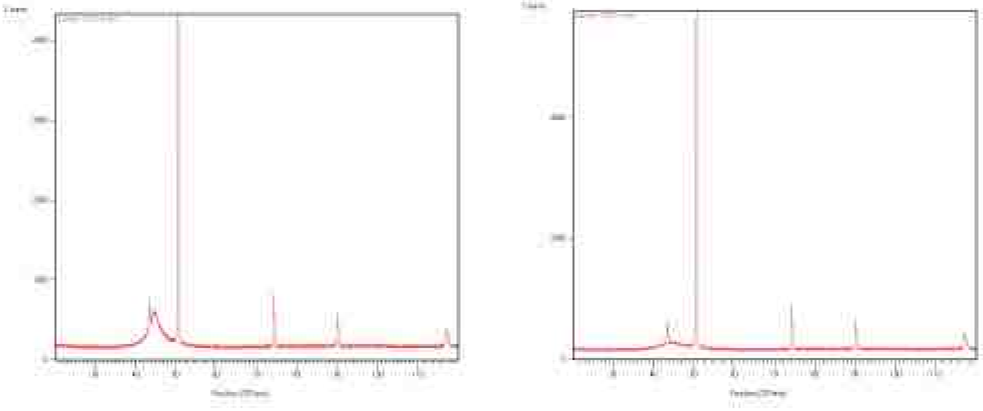

Conventional NiP (10 ASD) High speed NiP (10 ASD)

Fig.15 XRD spectra

Summary/ Conclusion

Results from extensive test series showed that electrolytical NiP layers can be deposited economically under high speed conditions. The deposits were shown to have a P-content of > 11 % over a wide CD range. This P-content provides good corrosion resistance as the HCl and the HNO_3 test showed. No pores could be identified with deposits ≥ 0.9 µm. In standard contact systems the thickness of the applied gold layer is up to 2 µm. However, not only the deposited gold is a considerable cost factor. In order to achieve these layer thicknesses the plating cells need to have an appropriate length. The result is the necessity of a high bath volume which at an Au content of 15 g/l is a sizeable capital investment. Therefore, depending on the application, considerable savings can be achieved by using the alternative system NiP/gold flash. Field tests show that it is well suitable for applications with lower mating cycles. Where higher mating cycles are required (particularly in a corrosive environment) either the gold thickness has to be increased or a pore blocker can be applied.

References

1 Nicholas M. Martyak U.S. Patent 6,099,624

2 Rodger L. Gamblin European Patent Application 0266020