PALLADIUM-NICKEL AS AN ALTERNATIVE TO GOLD IN CONNECTOR APPLICATIONS

by

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BACKGROUND

For many years, efforts have been made to find an economical substitute for gold in electronic connector applications. Although lower precious metal cost has always been a major incentive, gold substitute programs gained considerable momentum when gold prices reached recor high levels at the end of 1979. It was at this time that Berg Electronics intensified its program to find a substitute for gold which was not only lower in cost but also demonstrated performance equivalent to that achieved with gold.

Berg's program has evolved through a series of four phases. First, a laboratory progra was set up to find the best gold substitute. This study concluded that the best candidate was proprietary palladium-nickel alloy. Second, this process was scaled up so that pin connector could be manufactured under actual plant conditions and subsequently evaluated. Following th successful completion of this stage, the process was commercialized for customer use. Th fourth phase in which we are currently engaged is the optimization of the process for specifi connector applications. This paper will review the current status of this program.

LABORATORY EVALUATION

Many candidates are available for use as a gold substitute on electronic connectors. T efficiently determine which, if any, of these substitutes were viable, a two-step laborator program was completed.

First, processes ranging from gold alloys to platinum group metal chemistries were scrutinized and tested in the laboratory. From this extensive evaluation, the eight best candidate were selected. All of these processes produced either pure palladium or palladium alloy deposits. These eight processes were evaluated and compared using the two basic criteria whic are the most important for the majority of connectors. These criteria were:

- Properties
    - Contact resistance
    - Porosity
    - Solderability
    - Bend ductility
    - Internal stress
- Process stability

Berg's palladium-nickel process proved to be superior to every other candidate in terms o porosity, bend ductility, low internal stress, and process stability. In addition, it was discovered that superior solderability could be achieved by the application of a thin soft gol flash over Berg's alloy. The only area where any of the candidates were equivalent to thi unique process was contact resistance.[1] For these reasons, the Berg palladium-nickel allo process was selected for the manufacture of pin contacts on a plant scale.

COMMERCIAL PRODUCT TESTING

Introduction

Laboratory testing under a controlled environment is important to discern differences between processes and the properties of their resultant coatings. However, to determine the performance of the coating in its end use, the importance of testing actual product cannot be overemphasized. For our purposes, the products selected for initial testing with the palladium-nickel alloy were Berg's 0.025 inch square pin products, which include BergStik™, BergPost™ BergPin™, and Press-Fit Pins. Because of the potential advantages of a soft gold overcoat[2,3,4,5,6], alloy-coated pins both with and without the gold flash were tested.

Whereas the laboratory phase of our study was concerned with the performance of the allo relative to other gold substitutes, this phase of the program was set up to evaluate the performance of production-quality connectors with the Pd-Ni alloy coatings as compared to standar gold connectors. In addition, confirmation of the laboratory data was desired.

The properties selected for detailed connector testing included the following:

- Contact resistance
- Porosity
- Solderability
- Bend ductility
- Wire-wrap performance
- Wear resistance
- Environmental resistance

In each case, the pin connectors tested were plated with 1.25 um (50 uin.) of nicke followed by the precious metal(s).

Contact Resistance

Low contact resistance is perhaps the most basic requirement for most high reliabilit contact materials. Our tests measured contact resistance of 0.75 um (30 uin.) palladium-nicke pins with and without a gold overflash, as well as 0.75 um (30 uin.) gold pins. Contac resistance measurements were made per MIL-STD-1344, Method 302, with the following details:

Female connector:	0.75 um (30 uin.) gold Berg PV™ terminal, 0.0035 inch spring
Test current:	2.5 milliamperes dc
Open circuit voltage:	20 mV dc maximum

After testing 240 connector couples of each type, it was concluded that all coatings ha equivalent performance. The average contact resistance for the palladium-nickel pins was 3.0 m . The gold overflashed palladium-nickel values averaged 2.96 m , and the gold pins yielde an average of 2.90 m . The standard deviation for each coating type was less than 0.20 m No significant difference in contact resistance performance is apparent.

Porosity

Porosity tests have been used in the electronics industry to serve as an indicator of con tact performance. Any pores indicated by the test are potential sites for contact corrosion an subsequent failure while the connector is in use.

Electrographic techniques have been used to demonstrate the superiority of Berg's palladium-nickel coatings over both pure palladium and hard gold deposits.[7] Additional testing ha been conducted using other porosity measurement techniques to assure agreement.

Alkaline polysulfide testing has been conducted on all of Berg's palladium-nickel wire products manufactured to date. This test dictates immersion of the products into an alkaline polysulfide solution heated to a temperature of 74°C for 60 seconds. The treated samples are the examined for dark blossoms under 10X magnification, which would indicate the presence of an pores to copper. This large body of data has shown that in no case were any contact areas foun to contain pores to copper as defined by the test. Three levels of coating thickness, whic ranged from 0.375 um (15 uin.) to 1.25 um (50 uin.) palladium-nickel were tested. These result confirm the earlier electrographic tests showing the extremely low porosity associated wit Berg's alloy coating.

Exposure to nitric acid fumes is a common test utilized by the connector industry to indicate the porosity of a coating. Testing was conducted to determine the performance of 0.75 u (30 uin.) palladium-nickel with a gold flash compared to the performance of various thicknesse of gold on pin connectors. Table 1 summarizes the number of pores found for each coating afte exposures of 30 and 60 minutes for the pins tested. A minimum of forty contacts were examine for each condition. At 30 minutes exposure, the gold-overflashed palladium-nickel shows n porosity whatsoever. However, at each level of gold thickness, some pores are apparent. Afte 60 minutes exposure, the 1.25 um (50 uin.) gold coating appears to be somewhat better than th palladium-nickel/gold combination, although it should be noted that the performance of the allo is certainly acceptable according to normal pass/fail criteria. The two lower thicknesses o gold indicate two to three times higher porosity than the overflashed palladium-nickel coatings This again verifies the superior porosity performance of palladium-nickel over gold, thickness-for-thickness.

Gold plated over a nickel undercoat often demonstrates a tendency to blister after exposur to nitric acid fumes. This behavior is expected and is explained by Antler as preferenti lateral attack of the nickel at a pore site.[8] An interesting observation concerning blister was made in the course of this investigation. Blister counts for each coating are shown i Table 2. No blistering whatsoever was found on the gold-overflashed palladium-nickel coate pins. The hard gold pins showed an expected increase in blisters with decreasing thickness particularly after 60 minutes exposure time. In terms of performance through the test, th alloy system is superior to all gold coating thicknesses tested.

Solderability

Solderability is an important performance criterion for many of Berg's 0.025 inch squar wire products because many of these products are soldered to circuit boards in their end use As defined by MIL-STD-202, Method 208, acceptable solderability is greater than 95% solde coverage of the surface after the application of flux and a 5-second solder dip. Hard gold-plated product generally passes this test, but is subject to variability. After soldering th gold-overflashed palladium-nickel pins per MIL-STD-202 both with and without steam aging, al parts tested have exhibited 100% solder coverage, regardless of coating thickness. These pin will pass any solderability criterion presently imposed on gold pins.

Concern has been expressed in literature over the growth of intermetallics after solderin pure palladium coatings and the effect of the intermetallic on solder joint integrity.[9] An interesting difference has been found between this intermetallic growth documented for pure palladium coatings and the behavior of soldered palladium-nickel surfaces. After aging soldere samples of both pure palladium and the palladium-nickel alloy for 8 months at room temperature cross sections showing the solder/precious metal interphases were made. Using a scanning electron microscope, energy dispersive x-ray dot maps were made to show the locations of palladiu and tin for each coating. These maps indicate that significant intermetallic growth beyond th original deposit can be seen for the pure palladium coating. A marked difference can be see for the soldered palladium-nickel alloy, where no evidence of intermetallic growth can be discerned. As a result, it can be concluded from our data that concern over the growth of intermetallics in pure palladium coatings is warranted; however, these concerns are not valid fo Berg's palladium-nickel alloy.

Bend Ductility

Bend ductility of the contact material is an important consideration for connectors whic are formed or bent in post-plating operations. For these applications, a ductile coating i advantageous because it affords the maximum protection from corrosive attack of the under plat or substrate during storage and use of the connector.

Our tests gauged bend ductility of 1.25 um (50 uin.) palladium-nickel and 1.25 um (50 uin. hard gold pins by counting the number of cracks per inch in each coating after bending the pin around tool steel pins with varying radii.

The data obtained show that hard gold begins to crack when a bend radius less than 6.35 m (0.250 in.) was made. The palladium-nickel coating did not crack even when the bend radius wa decreased to 1.27 mm (0.050 in.). As a quantitative comparison, hard gold shows approximatel 2,000 cracks/inch when bent to the 1.27 mm (0.050 in.) radius. The resulting conclusion of thi study is that Berg's palladium-nickel coating is substantially better than hard gold coating for applications requiring bend ductility.

Wire-Wrap Performance

Most BergPost™ terminals are wire-wrapped after insertion into a circuit board.

Two tests, stripping force and gas tightness, were performed on a standard 0.75 um (uin.) gold post and a 0.75 um (30 uin.) palladium-nickel post with a soft gold flash. Bot tests were performed in accordance with MIL-STD-1130B 5.6.1 and 5.6.2.

Both coatings passed the gas tightness test by showing unattacked gold on more than 75% o the middle five wraps' corners after exposure to aqua regia fumes for ten minutes. In addition both pin groups also passed the 8.8 N (2.0 lb.) minimum strip force, with the results shown i Table 3. It was concluded that a gold-overflashed palladium-nickel post will provide performance equivalent to that demonstrated by standard gold posts.

Wear Resistance

A significant number of pin connectors are mated with box-type connectors in their end use Some of these connector couples must withstand multiple insertions and withdrawals while maintaining satisfactory electrical performance. Most customers, when using this type of connecto system, specify a wear test through 100 to 200 cycles.

To determine the wear resistance of the palladium-nickel and palladium-nickel with gold overflash coatings relative to that of gold, an accelerated wear test was employed. Th following conditions were followed for the test:

- Male pin coatings: 0.75 um (30 uin.) Au, 0.75 um (30 uin.) Pd-Ni, 0.75 um (30 uin.) Pd-Ni + Au Flash
- Female connector: Berg's Mini PV™ with 0.0035 inch thick spring; 0.75 um (30 uin.) Au in contact area
- Number of cycles: 100, 500, 1,000
- Normal force: 2.94 N (300 g)
- Cycle speed: 5.08 cm/min. (2 in./min.)
- Post-cycling exposure: 3 ppm H_2S for 48 hours at 40°C

The results for this test are shown in Figure 1.

As reported earlier,[10] no significant difference between any of the coatings can be see after 100 to 200 cycles, as required in most applications. In an application requiring an unusually high number of cycles, the gold-overflashed palladium-nickel coating would be recommended.

Environmental Resistance

The service environments for many connectors are less than ideal. In most cases, pollutants present in the environment may promote the degradation of the connector at varying rates depending on the types of pollutants present and their concentrations. Particularly for mor hostile environments, it is important to use a coating which is corrosion resistant to prolon the life of the connector.

Three series of tests have been performed or are in progress to ascertain the performanc of the palladium-nickel and gold-overflashed palladium-nickel coatings relative to that of gold The first series followed a classical series of tests commonly used in the electronics industry The second series of tests used flowing mixed gas environments to produce corrosion mechanism found in actual service environments on an accelerated scale. The third series of tests involves placement of connector samples in hostile service environments in a variety of connecto user sites. From these tests, an accurate picture of long term connector performance has bee obtained.

Classical Testing

Three plating combinations of pins and receptacles were exposed to a sequence of environments to compare contact resistances. Pin coatings tested were the following:

- 0.75 um (30 uin.) Au
- 0.75 um (30 uin.) Pd-Ni
- 0.75 um (30 uin.) Pd-Ni plus Au flash

The female receptacle used in all cases was a 0.75 um (30 uin.) gold PV™ with a 0.0035 inc thick spring. The connector couples were exposed to a sequence of humidity, flowers of sulfur and salt spray environments under the conditions found in Table 4. The results of the testin can be found in Table 5. From this data, it can be concluded that all coatings demonstrat equivalent performance. None of the pins tested showed any increase in contact resistanc attributable to contact degradation except perhaps the gold coating, which showed an increase o no more than 0.15 milliohms contact resistance. Both palladium-nickel coatings yielded extremely stable contact resistance measurements throughout the exposure sequence.

Flowing Gas Exposure Testing

Data reported earlier for 0.75 um (30 uin.) Au, 0.75 um (30 uin.) Pd-Ni, and 0.75 um (uin.) Pd-Ni with gold overflash mated with Berg's PV™ have shown equivalence in both chlori and hydrogen sulfide environments which simulate exposure through 10 years by utilizing flowi gas exposures. Test parameters followed were established by the Environmental Studies Grou through work conducted at Battelle Laboratories.[11] A summary of that data can be found i Figures 2 and 3. Both charts show changes in contact resistance as a function of exposure time Each figure represents the compilation of contact resistances for 120 connector couples.

The Type I exposure test (chlorine) typifies a significant number of connector service e vironments where the failure mechanism is pore corrosion. Reports of the performance of palladium and palladium alloy coatings have shown susceptibility to degradation in this type c environment.[12,13] In the connector application study conducted by Berg, the gold-plated coupl showed no appreciable increase in contact resistance. The palladium-nickel couple showed small increase of approximately 1 milliohm over the 10 years accelerated exposure. This increase is much less than normal specifications allowed; however, if this increase is unacceptable for a particularly sensitive application, the gold-overflashed palladium-nickel coatin will provide satisfactory performance. As can be seen on the chart, the performance of palladium-nickel with gold overflash is equivalent to that of the gold coating.

The Type II test shown in Figure 3 exposes the connectors to a hydrogen sulfide environmen which encourages both pore and creep corrosion. All coatings tested showed equivalent performance through 10 years accelerated exposure.

Testing is presently being conducted using a very severe hydrogen sulfide, chlorine, an nitrogen dioxide environment. Since the difference between coating types has not been mad clear to this point, it is hoped that the more harsh environment will demonstrate the ultimat capabilities and performance characteristics of the palladium-nickel coatings relative to golc In addition, creep corrosion data will be obtained which will show relative resistances of thes coatings to this mechanism of contact degradation. As data are analyzed, reports of thi testing will be presented.

Site Studies

The third series of tests is designed around the placement of connector samples at connector user sites. The following sites are being utilized:

- A paper mill in Maine
- An air traffic control center in Pittsburgh, PA
- A petrochemical refinery control center in Houston, TX
- A telecommunications center in Daytona Beach, FL
- A steel mill blast furnace control room in Kentucky
- A steel mill HCl environment in Michigan

All of these sites represent very aggressive environments. Data will be gathered over th next two years and will be reported as it becomes available.

CONCLUSIONS

Several conclusions can be drawn from Berg's gold substitute program. The Berg palladiu nickel alloy provides performance not equalled by any other candidate that has been evaluate Specifically, the alloy demonstrates excellent properties which include low porosity, ductilit low internal stress, solderability, resistance to intermetallic growth, and process stabilit This makes this system the most viable gold substitute we have found. Further testing has sho that the palladium-nickel alloy with a gold overflash is at least equal to gold in every ar tested and actually surpasses gold in many properties considered important by the electroni industry, including porosity and bend ductility.

Our original objective was to find an economical replacement for gold that demonstrat performance equal to the traditionally used coating. Because of the exceptional performance o the alloy system found throughout the testing, Berg is able to offer superior pin connector pro ducts for electronic applications. The use of Berg's palladium-nickel coating in connector sys tems will assure higher levels of performance and reliability without the need for higher costs

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TABLE 1

Porosity of Pin Connectors After HNO_3 Fume Exposure

	Number of Pores/Pin	
Pin Coating	30 Min.	60 Min.
0.75 um (30 uin.) Pd-Ni + Au flash	0	10.0
0.375 um (15 uin.) Au	7.7	30.2
0.75 um (30 uin.) Au	2.4	19.3
1.25 um (50 uin.) Au	3.6	3.2

TABLE 2

Blister Count of Pin Connectors After HNO_3 Fume Exposure

	Number of Blisters/Pin	
Pin Coating	30 Min.	60 Min.
0.75 um (30 uin.) Pd-Ni + Au flash	0	0
0.375 um (15 uin.) Au	8.6	30.8
0.75 um (30 uin.) Au	9.7	25.1
1.25 um (50 uin.) Au	0	1.4

TABLE 3

Wire-Wrap Performance - Stripping Force

Coating	Stripping Force (N) (lbs.)
0.75 um (30 uin.) Au	19 (4.3)
0.75 um (30 uin.) Pd-Ni + Au flash	19 (4.3)

Minimum is 8.8 N.

TABLE 4

Classical Environmental Test Conditions

o Humidity - MIL-STD-202, Method 103

Relative Humidity - 90% minimum
Temperature - 40°C
Duration - 96 hours

o Flowers of Sulfur - BUS-20-25

Test Medium - Flowers of Sulfur
Relative Humidity - 80%
Temperature - 65°C
Duration - 240 hours

o Salt Spray - MIL-STD-202, Method 201

Concentration - 5% (by weight)
Duration - 48 hours

TABLE 5

Contact Resistances After Classical Environmental Exposures

	Contact Resistance (m)		
Pin Coating	After Humidity	After Sulfur	After Salt Spray
0.75 um (30 uin.) Au	+ 0.09	+ 0.15	+ 0.13
0.75 um (30 uin.) Pd-Ni	- 0.02	- 0.07	- 0.04
0.75 um (30 uin.) Pd-Ni + Au flash	0	- 0.01	- 0.04

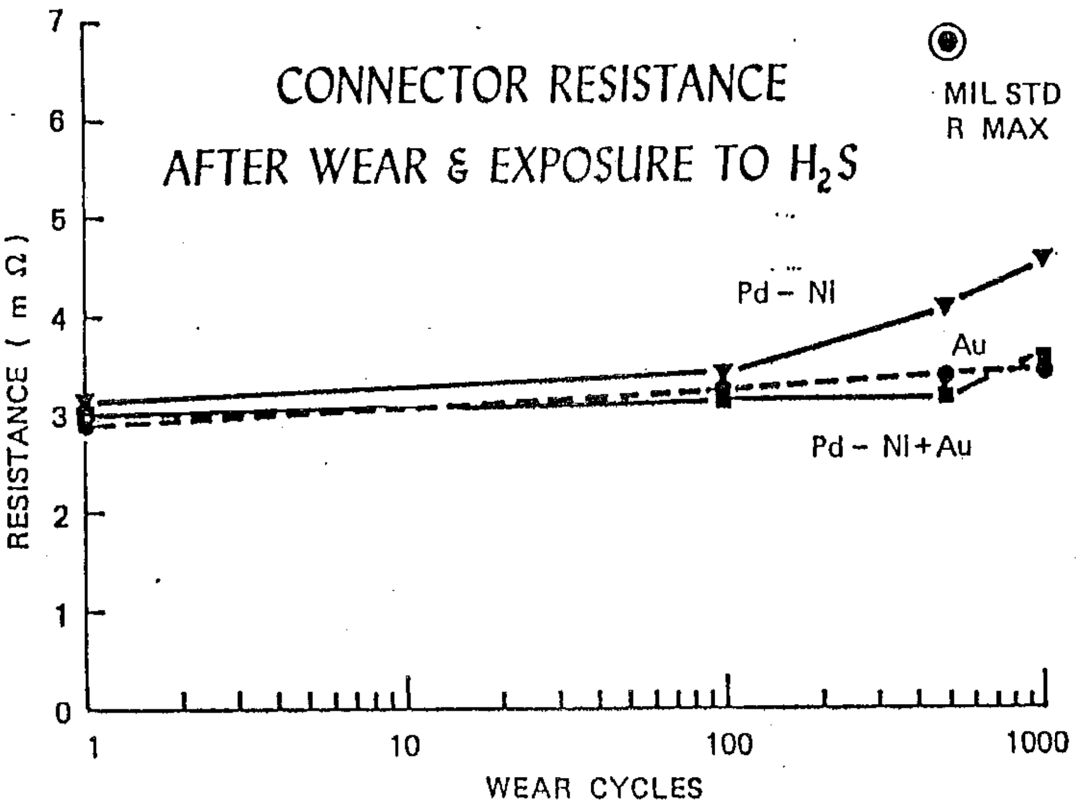
CONNECTOR RESISTANCE
AFTER WEAR & EXPOSURE TO H_2S
MIL STD
R MAX
Pd – Ni
Au
Pd – Ni + Au
RESISTANCE (m Ω)
0
1
2
3
4
5
6
7
1
10
100
1000
WEAR CYCLES

Figure 1