Investigation of porosity on Au/Ni plated contacts

Background
This investigation was a continuation of the one reported on December 11, 2000 Ref:____. A black material was found (from now on known as __s) gold plated contacts after they were removed from storage. The black material was determined to be copper sulfide caused by porosity in the plated layers. The present investigation was initiated to determine the cause of the porosity.

Introduction
Ten (See Diagram 1) contacts each were collected at 7 different stages before and during the gold plating cycle. The contacts were opened by removing one of the tines (See Photo 1) exposing the area inside the female contact. Observations were in this critical area using a Hitachi S2500 SEM with EDS capability and a Hirox Hi-scope KH-2400R optical microscope. The parts were scrutinized to determine at what step in the plating cycle the pore formation was initiated.
**Data**

These contacts were machined and supplied to ____and to a lesser degree by customer's internal operations. The substrate material is a Brushwellman M25 BeCu alloy (UNS-C17300). This alloy contains approximately 2% Be, 0.6% maximum Co+Ni+Fe, and 0.2 - 0.6% Pb¹. The procedure used for manufacturing is:

1. Machining using
2. Cleaning with
3. Inspection
4. Crimping
5. Heat treating:ii
6. Hardness testing
7. Mass finishing
8. Rinsing in water
9. Warm air drying
10. Final inspection.

The parts were then shipped to customer where they were inspected. They were then shipped to their plater, for electroplating. They utilize the following plating cycleiii:

1. Raw substrate*
2. Degrease soak cleaner*
3. Dip in Sulfuric Acid *
4. Bright dip in *
5. Copper flash
6. Cu plate *
7. nickel plate
8. Gold strike *
9. Hard gold *

¹Telephone conversations with Mike Gideon of Brushwellman confirmed the Pb was present in spheres within the alloy for the purpose of increasing the machinability (telephone # 216-383-4928).

ii “Cleaning Beryllium Copper,” Brushwellman Technical Service Department Bulletin #RO4905146

iii As related by Fredrick A. Binda, VP, Purecoat International, LLC on 12/22/00
10. Hot air dry

The contacts were then sent to customer. They were inspected and assembled by hand into a housing with a teflon insulator. Some abrasion of the gold surface occurred during assembly, but under normal circumstances this wouldn't compromise the integrity of the finish. At no time during assembly or inspection was finger protection worn to prevent skin oils from coming into contact with the parts.

**Observations and Discussion**

*Raw Substrate Before Plating*

Part's inspected before plating show pores and machining marks (Photos 2, 3, and 4). EDS spectra reveal that the dark spots contained mainly cobalt [Co], but also some iron [Fe] and silicon [Si] (Figure 1).

*(Photo 2) substrate @ 1.5K X, pores boxed in red*

*(Photo 3) substrate @ 500X showing machine marks*

*(Photo 4) substrate @ 2K X showing porosity*

*(Figure 1) EDS scan of pores showing Co, Si, and Fe presence*

*After each of these steps 10 parts were removed for SEM analysis*
**Hot Sulfuric Activate (HSA)**

The parts inspected after hot sulfuric activate (HSA) also show pores and machine marks (Photo 5 and 6).

![Photo 5] Hot Sulfuric 1.7K X

**Photo 5** 1.7K X Porosity in surface, after HSA

![Photo 6] Hot Sulfuric 150 X

**Photo 6** 150X Machine marks in surface, after HSA

EDS spectra revealed nothing different than those taken of the substrate before plating. A scan of the many pores revealed Co and Fe islands (Figure 2). It is a normal condition to have pockets Co/Fe beryllites throughout the substrate. They add strength and refine the grain size of the alloy\(^\text{iv}\). The problem with using HSA on these parts is that the substrate is an M25 C17300 alloy that contains lead. Following is a note of caution when dealing with any copper alloy containing lead, such as Alloy M25 (C17300). Nitric acid or PNA (Phosphoric, Nitric, Acetic) is used rather than a sulfuric acid system because of the insolubility of lead sulfate.\(^\text{v}\) This insolubility

\(^{iv}\) Telephone conversation with Mike Gideon of Brushwellman 12/22/00. Telephone # 216-383-4928

\(^{v}\) “Cleaning Beryllium Copper,” Brushwellman Technical Service Department Bulletin #RO4905146
can lead to porosity and blistering in the plated coatings. It should be noted that via EDS scans no lead was detected in this stage of the process. This is probably because any lead encountered during machining of the substrate was probably smeared in extremely thin layers so was beyond the limits of detection of the equipment used. It should be noted that in some EDS scans chloride was detected as well. It can only be assumed that these parts were subjected to a chloride activate as well, but chloride also forms insoluble salts with lead.

*Sulfuric and Nitric Acid Bright Dip (BD)*

Parts inspected after BD show some machine marks and porosity of the surface (see photos 7 and 8). EDS spectra (see figure 3) revealed that many of the larger pockets contained lead. It appears that the copper being soluble was removed leaving an insoluble lead compound, probably lead sulfate (see photo 9).

*(Photo 7) 1.2 K X after BD showing Pores and pockets of lead*

*(Figure 3) EDS spectra of bright dipped 451 substrate showing lead peaks.*

*(Photo 8) 200 X after BD showing machine marks*

*(Photo 9) 2.0K X after BD showing lead compound in pore*
"Leaded copper alloys form insoluble salts in either sulfuric or hydrochloric acid, and therefore should be pickled in fluoboric acid, 20 ml/l to 50 ml/l by volume, or nitric acid, 100 ml/l to 200 ml/l by volume."\textsuperscript{vi}

These areas didn't show up under examination of the parts removed after HSA activate apparently because they were covered with copper, but when subjected to the BD several microns of copper were removed exposing the lead and because there is sulfuric acid present in the BD the lead formed insoluble lead sulfate. The only way for the lead particles to be removed with this procedure is for the copper to be removed by the removal of copper, which leaves a crater (see Photo 10).

\begin{center}
\textbf{(Photo 10) 1.2K X after BD showing crater with lead nodule in center[blue box]}
\end{center}

\textbf{Copper Pyrophosphate Plate (CPP)}

Parts inspected after copper plate (see Photo 11) show a marked difference in topography than those after BD. Not only are pores still visible in the surface, but the copper plate is rough and nodular. Nodules range

\begin{center}
\textbf{(Photo 10) 1.0K X after copper plate showing craters}
\end{center}

\textsuperscript{vi} ASTM B281-88; Standard Practice for Preparation of Copper and Copper -Base Alloys for Electroplating and Conversion Coatings; re-approved 1995
and nodules. in diameter from 2 - 7 microns (80 - 280 microinches). puts a cyanide copper flash on the parts before plating them in a pyrophosphate copper. The cyanide copper is an excellent activator for copper alloys containing lead and can only help the porosity situation. The roughness in the copper plate might be due to a process control issue "When the solution [pyrophosphate copper bath] is operated at this high pH [8-9], the tendency toward roughness can be eliminated by increasing the P_2O_7/Cu ratio."

Nickel Plate (Ni)
451's that were nickel plated and gold struck were stripped in a gold stripper to expose the bare nickel and allow a more detailed EDS examination of the surface (the gold and lead peaks overlap). The surface remained rough and still had pores in it (see Photos 11 and 12).

(Photos 11 and 12) 250X and 1.0K X showing rough porous nickel surface

Conversion Coatings; re-approved 1995
EDS examination of pore sites yielded many spectra displaying lead/sulfate peaks (see Figure 4). This helps to strengthen the argument that the cause of some of the porosity is due to an improperly treated substrate that leaves lead compounds behind.

**Hard Gold Plate**

Parts examined after gold plating show the nodules that were introduced by copper plating and the porosity that was in the base metal substrate (see photo 13). EDS spectra collected from these samples displayed little of note because the gold/lead/sulfate peaks all overlap.

However samples of parts plated three years ago were taken from storage and these too exhibited the same anomalies as those plated in December 2000, nodules, roughness and black copper sulfide material oozing.
Conclusions
It appears that the integrity of the plated deposit was compromised before or during the electroplating cycle. Whether this was caused by the quality of the substrate material (M25, C17300) is beyond the scope of this investigation. The problem investigated here was related to using the proper plating cycle to effectively plate these parts. This caused rough plating (nodules) and pitting of the deposit. The problem can be broken down into three main areas:

1. Pitting and nodules caused by presence of silicon
Silicon is a difficult substance to plate on and can cause blisters and skip plating unless properly treated during the pretreatment cycle. On method of pretreatment is a bifluoride or fluoboric acid dip to remove the silicon. Sources of silicon in plating these parts are:
- In plating baths as a contaminant
- Silicon lube used during machining
- Present in the substrate.

2. Pitting and nodules caused by presence of lead
As stated previously lead is present in the substrate to make the copper more machinable. Proper pretreatment is required for electroplating on lead containing alloys. Among the steps that should be taken are to utilize a fluoboric acid activate after alkaline soak clean and to eliminate the use of activators and bright dips that contain sulfate.

3. Pitting and nodules caused by rough copper deposits
During the extensive SEM analysis performed during this FMA the step where the greatest increase in surface roughness was noted was after copper plating. The nodules ranged in size from 1 - 7 microns. It is impossible for 0.5 - 2 microns of sulfamate nickel and another 1 - 2 microns of gold to cover these large nodules. The result is a porous gold deposit that is open to corrosion.

**Recommendations**

1. Use finger cots when handling parts for inspection and assembly. Finger oils are acidic and can cause corrosion of the substrate before and after plating. They also can change the contact resistance by acting as an insulator.
2. Increase the smoothness of the copper deposit to eliminate nodules.
3. Alter the pretreatment cycle to eliminate the use of sulfate based chemistries for activating and bright dipping.
4. Utilize a fluoboric acid dip to treat the lead and the silicon before plating.
5. Try using an alkaline electroclean in addition to the alkaline soak clean
6. Find and eliminate the source of silicon