A Comparison of Copper **Bar Anodes**

by Paul T. Forde

Competition in the PCB industry encourages platers to examine anode features.

Until recently. anodes were not an issue for the PCB industry. As far as most of the platers were concerned. copper was copper, and anode composition had little or no effect on operations. Current competition throughout the industry, however. has made platers more aware of every factor impacting their products. A study comparing three of the major brands of phosphorized copper anodes illustrates how anode variations can affect plating quality and cost.

Copper anodes are cast in different conditions. The anode manufacturer may further mechanically process the copper to various other forms, presenting the plater with several types of bar anodes to choose from-—cast. forged, rolled, and to a lesser extent, extruded.[1,2] Besides different types of anodes, the plater can also choose from several shapes; chunks or nuggets, rectangular, hexagonal, oval. and round are the most common.

For the anode comparison study, three major brands that are commercially available were tested, Brand 1. 1.5” X 3" X 8” hexagonal anodes, was produced by melting and casting high-quality copper cathodes under an oxygen-free atmosphere: Brand 2. 1” X 4“ X 8" rectangular anodes, was manufactured by melting and casting cathodes under an atmosphere of nitrogen; and Brand 3, also 1" X 4" X 8" rectangular anodes, was produced from cathodes melted and cast under a nonprotective atmosphere. and then rolled to the correct dimensions,

Figure 1. *Brand 1 anodes exhibit uniform corrosion after Experiment 1.*

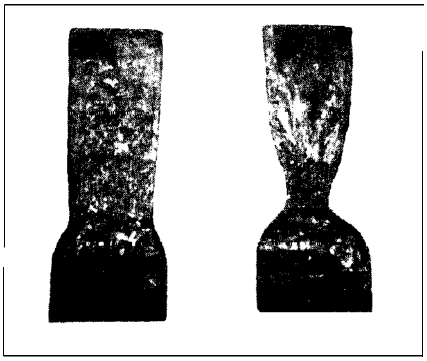

Figure 2. One Brand 2 anode *showed considerable necking after Experiment 1.*

EXPERIMENTAL PROCEDURE

Three tanks in a small-scale plating system were connected in series, Each tank contained four anode bars and one cathode. Anodes were placed approximately three inches from the edge of the tank and two inches from the cathode. Air sparging was positioned on each side of the cathode and located halfway between anode and cathode.

The suggested anode current density was 15 amps per square foot, but due to a slow copper deposition rate, the anode current density was increased to 30 amps per square foot. The system was activated for a two-week period. Voltage and current densities were taken daily, and the system was monitored to ensure that variables (solution level, agitation, temperature, and so on) remained constant. Ancillary equipment, chemistry, and operating conditions are shown in Table 1.

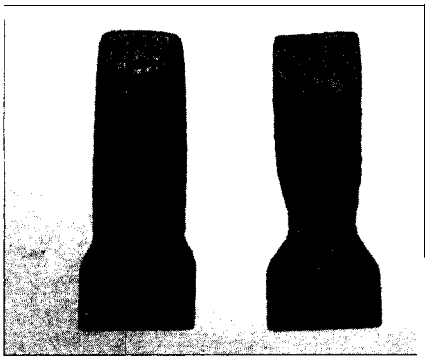

Figure 3. The *Brand 3 anodes after Experiment 1.*

After the two-week period, the anodes had corroded sufficiently for evaluation purposes, The entire test was then repeated with new anodes, solution, and cathodes. In the second trial. no anode bags were used. As in the first trial, bath concentration levels were maintained by adding fresh solution as needed, and periodic voltage adjustments were made.

RESULTS AND DISCUSSION

Prior to the experiment. samples from each brand of anodes were analyzed for impurities. All three brands exhibited comparable levels of’ impurity elements, with the exception

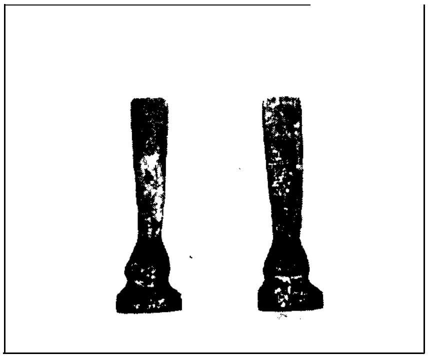

Figure 4. *Brand 1 anodes after Experment 2, with very slight necking.*

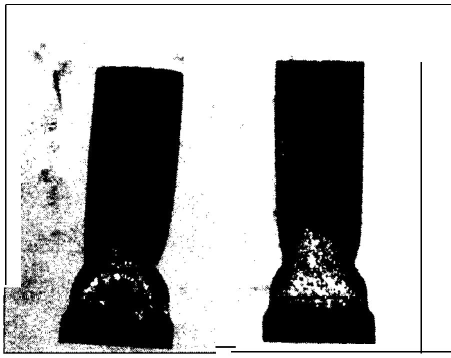

Figure 5. *Brand 2 anodes Experiment 2, slight necking*

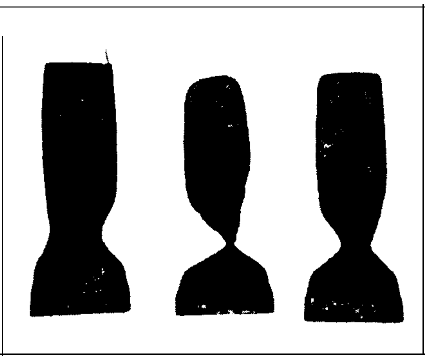

Figure 6. *Brand 3 anodes after Experiment 2 with very pronounced necking.*

Table 1. Operating Conditions for Anode Comparison Experiments.

Cathode		304 stainless steel sheet
Bags		Baker Brothers loosely fitted napped, 2-ply cotton or polypropylene
Chemistry	$CuSo_4\text{-}5(H_20)$	10 oz. per gallon
	H_2So_4, CP, 66Be	12.8 fl. oz. per gallon
	Chloride ion	70 ppm
Cathode current density		25 amps/sq. ft.
Anode current density		15 amps/sq. ft.
Tank voltage		0.5 to 6V
Temperature		75°F
Agitation		Clean LP air

of oxygen and phosphorous (Table 2).

Each of the stainless-steel cathodes plated by the three brands exhibited comparable quality in terms of their srurface roughness. But, appreciably more necking occurred on Brands 2 and 3. That may be attributed to their original hexagonal shape (Figures 1, 2, and 3). The hexagonal shape of Brand 1 approaches a round configuration and appears to lead to more uniform corrosion.

As the neck forms, the reduced area must support greater weight per unit area. This condition constitutes a redistribution of stress, and possibly an area of preferred corrosion that would accelerate the necking condition. The grain size, oxygen impurity content, and distribution of phosphorous also have an effect on the corrosion of the anodes,’ These effects became more apparent when the second test was run, without anode bags.

Figures 4, 5, and 6 show the results of the second plating test. Brand 1 exhibited slight necking down, Brand 2 somewhat more, and Brand 3 was necked down to an even greater extent. The center and in Figure 6 represents the accelerated state of stress-assisted corrosion, which almost reached a point where a piece of the anode would break off and be of no further use. In the second test. without anode bags, considerably less nodular copper growth occurred on the cathodes that were used with Brand 1 anodes (Figures 7,8, and9).

Since each cathode produced from the bagged anodes had comparable surface roughness, therefore, quality, it can be concluded that anode bags play a critical role in trapping impurities that may be inherent to a particular anode brand. Removing the anode bags reveals that a difference does exist among the three brands.

CONCLUSION

in a previous article Brand 1 was shown to have the must evenly dispersed distribution of phosphorous. A metallurgical comparison of the three brands shows that the phosphorous is more evenly dispersed when cast under a protective atmosphere, as opposed to being rolled after casting under a nonprotective atmosphere.

A recent article about phosphorized copper anodes claims that rolled cathodes exhibit more even distribution of phosphorous, in comparison to cast.[1] Basic metallurgical principles indicate otherwise. It seems the rolling operation tends to break up the grains and push the phosphorous to the grain boundaries where they remain locally segregated with oxygen and other impurities. This phosphorous redistribution, along with the higher oxygen content, is the basis for the difference in plating quality among the three brands.

The significant nodular growth apparent in the cathodes produced by

Brands 2 and 3 can most likely be related to oxide levels in the plated copper. While all three brands exhibited comparable levels of impurities (silver, tin, lead, and nickel}, only Brand 1 exhibited a low level of oxygen. With this in mind, it appears that the impurities, with the aid of oxygen, will float to the cathode surface and act as preferential nucleation sites for nodular growth. Copper oxide particles would also contribute to nodular growth.

The smaller grain size of Brand 3, which results from rolling the anode after casting, appears to have little effect on plating quality. Nevers, Hungerford, and Palmer also came to this conclusion while investigating smaller grain sizes than were seen in this evaluation.’ It appears that if purity is questionable and bagging is not used, a large-grained cast structure and fine-grained wrought structure can produce equally poor plated surfaces. Therefore, grain size is of little significance to plating quality.

The shape of the bar has considerable impact on yields, in that the shape of Brand 1, which approaches a round, appears to have the most uniform dissolution in the bath. In the case of Brand 3, the small grain size and the shape of the anode caused necking to the point of anode fracture.

REVIEW

In addition to this article, two other articles examining different aspects of phosphorized copper anodes have run in *PC* FAB. Each of the articles was based on an extensive literature search as well as experimental data obtained through research at Columbia university (New York, NY). The first article concentrated on the dispersion of phosphorous in the anode and the detrimental effects of melting copper under a nondeoxidizing atmosphere and rolling.[1] The impact of rolling is to push the phosphorous and oxygen to the grain boundaries, thereby reducing, restricting, anti segregating this element.

The second article discussed the evaluation of cast vs. rolled anodes without the use of cyclic voltammetry.[2] Again, cast anodes proved to be superior, because they tended to form the desired black, adherent film more quickly than rolled anodes. The results also indicated that the uniform vs. nonuniform distribution of the phosphorous in the cast *vs.* rolled was the primary reason for this behavior.

Finally, this article shows the behavior of the cast and rolled bar anodes in the bath with and without bags. The investigation strongly suggests that rolled anodes behave differently and can result in undesirable plating quality. Also, cast anodes that exhibit higher oxygen content may affect plating quality, but not to the same extent as rolled anodes. ■

Table 2. Comparable Levels of Impurity Elements.

	Brand 1	Brand 2	Brand 3
Oxygen (ppm)	3	16	21
Phosphorous (ppm)	650	740	490

REFERENCES

[1] Forde, P. T. *PC FAB. 8(8),* Aug. 1985.
[2] Forde, P. T. *PC FAB. 11(8),* Aug. 1988.
[3] Walker, W. C. *PC FAB.* 13(8), Aug. 1990.
[4] R. P. Nevers, R. L. Hungerford, E. W. Palmer. *Plating. Nov. 1954,* p. 1,301.

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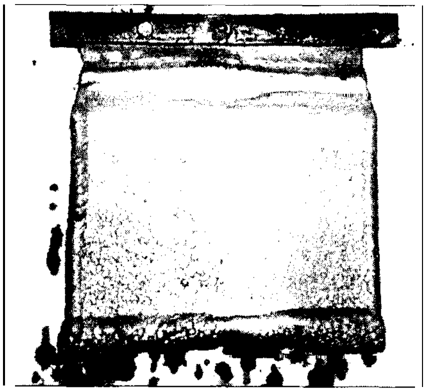

Figure 7. *Cathode produced with Brand 1 anodes in Experiment 2, without anode bags.*

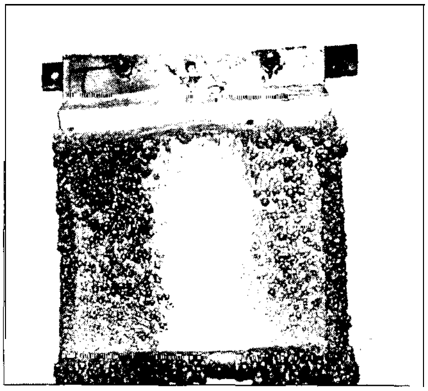

Figure 8. *Cathode produced with Brand 2 anodes in Experiment 2, without* anode *bags, showed extensive nodular growth.*

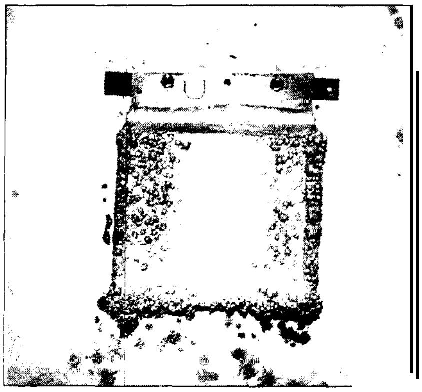

Figure 9. *Cathode produced with Brand 3 anodes in Experiment 2, without anode bags, showed nodular growth.*