



Pulse Plating

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Pulsed Electroforming

Q In your March 1999 "Pulse Plating" article, you stated, "...there is a positive contribution to increased ionic mobility and concomitant limiting current density (LCD) for cations, like cuprate. The opposite is true for anions, like aurocyanate." Would you please help me set it straight in my head? Would pulse plating have positive or negative effects on heavy deposition (250–2000 microns) of silver from cyanide solution?

A I'm glad you asked this question. There are tremendous advantages to pulse plating. You caught the idea that there would be a negative effect on the limiting current density from plating with negatively charged plating anions, argentocyanates.

When the cathode is negatively charged, it attracts positive ions and repels negative ions. In cyanide-based baths, this effect becomes more significant when more dilute electrolyte is used and small amounts of current are allowable. The limitation only affects the magnitude of current allowable. As anions plate out, their replenishment diminishes because of anodic migration. The effect is small, because migration rate is comparatively not large and increases in more dilute solutions. The greater the charge of the ion the more rapid is its mobility.

Silver cyanide is insoluble in water. As more sodium or potassium cyanide is introduced, insoluble uncharged $\text{Ag}(\text{CN})$ becomes $\text{Ag}(\text{CN})_2^{-1}$ and dissolves. With more "free cyanide" tricyanoargentate $\text{Ag}(\text{CN})_3^{-2}$ forms and possibly tetracyanoargentate. These polyanionic derivatives migrate to the anode. So, in a limited system (low silver and high cyanide) the diminished LCD becomes significant in DC plating. In pulse plating it is less significant because, during off time, there is *no* attraction and repulsion and replenishment occur.

A positive benefit can occur in cyanide-based plating when pulse plating incorporates reverse, like for de-plating. Using periodic pulse reverse plating to make smoother, brighter coatings can result in a more positive effect. The workpiece becomes positive during reverse and attracts the platable anions instead of repelling them. As the platable anions have been migrating to the work and electrochemically dissolved silver just came off the work and is coordinately present at the surface, when the forward pulse is initiated, more current density can be employed. Best

advantage can be employed with one reverse pulse and then a series of forward pulses, with the first few of higher current. Pulse reverse is used for micro-leveling, as well as compensating for primary current distribution (throwing power) deficiencies.

As far as a positive or negative effect on your industrial deposits (10–80 mils), anionic retro-mobility will have an effect on the LCD to some degree, though it may be insubstantial. More important considerations are the use of more conductive potassium, rather than sodium, for higher speed and brightness; sufficient free cyanide for anode corrosion; increased temperature and agitation. All of this gain, however, can also be realized by pulse plating, and if the parameters are combined, including reverse, high-current "treeing" can be minimized. PP allows the anode to corrode during relaxation, and lack of free cyanide is not so much a constraint. This is true of non-cyanide systems also, that missing anode corrosion catalysts like chloride and bromide are not of much consequence.

The contribution to conductivity by potassium over sodium, though larger, potassium is smaller in solution relative to sodium. This is due to the degree of primary hydration, which further influences secondary, etc. (distance of nuclear and outer shell electron charge separation). Lithium is the smallest, but has the highest attraction to the negative portion of water, which cannot "neutralize" it and further requires secondary and tertiary, etc., layers of water. The more tightly bound water gives rise to more drag and lessens mobility and conductivity. Cesium has *no* primary, or secondary waters of hydration and

should allow for the highest conductivity and mobility. Therefore, adding cesium cyanide to the silver bath instead of lithium, sodium or potassium cyanides would maximize brightness, conductivity, speed of plating, etc. Now employ PP or PR to maximize advantage of all of these gains.

Q For the last eight years, I have been doing silver and 10, 14 or 18 kt gold electroforming (Au/Ag) over wax or (Au/Cu/Cd) over fusible alloys. All for decorative applications. Wall thicknesses are between 75 and 250 microns. The bath I used was: Ag 40-45 g/L; KCN 100-110 g/L; K_2CO_3 15+ g/L.

At 8-10 mils wall, I had no problem achieving a smooth, semi-bright deposit using direct current with current interruptions (30 sec ON, 3 sec OFF) with selenium brightener. I am now involved with plating silver directly on rubber molds with thicknesses up to 80 mils. Even though the deposit is semi-bright, I am getting very big nodules, growing out of proportion here and there, and the overall quality becomes unacceptable. My usual approach is failing. This is why I started to look into other options. First and least expensive was to use periodic current reverse. I got a PCR unit and am trying to figure out how to use it correctly (any information on this subject will be greatly appreciated). The second option I wanted to explore was pulse plating. Now you have told me about a third option—a combination of PP and PCR. This is the dilemma I am facing right now.

A No dilemma. Pulse and reverse, that's all. Where or when you introduce the reverse only matters for the type of end plating you need (see my "Pulse Plating" column, January or February *P&SF*). Periodic current reverse means exactly that—periodically you reverse the current. It could be after every pulse and the pulses are 30 sec, or every 30 msec. It depends on the type of PCR unit you have and what it is capable of doing (the length of time before reverse and the length of time for reverse current). You are electroforming. You should be in the region of about 0.1 to 2 sec. on, and the time of reverse depends on how much current you can apply in reverse

mode, assuming you're using the selenium brightener, and how much brightener is in the bath.

Q I have been doing gold electroforming for the last seven years: five years in Providence using Au/Ag chemistry and the next two years in New York City using Au/Cu/Cd. Now I am using a proprietary brightener blend for my silver electroforming. The PCR unit I have does not have a msec setting. It can only go as low as 2 or 3 sec for the de-plate cycle and from a few seconds to a couple of minutes for the plate cycle. The setting I have on now is 45 sec ON and 5 sec OFF.

A Sounds like you may not be able to set the current amount any different for reverse (de-plate) compared to forward (plate). It is possible that you may be getting organic contamination from the rubber process you use (the dissolving of the vulcanized base), so try cleaning the rubber after forming or before plating in Stoddard solvent, mineral spirits or starter fluid, then a

quick dip in acetone or MEK or lacquer thinner. Because this may be a problem, you would need to batch-treat with carbon. As far as getting a smooth plate, make sure you keep the levels of brightener to specifications. In order to plate uniformly, you will want to remove the majority of what you plate each cycle. If you cannot adjust current density differently from forward to reverse, it will make calculations easier.

After cleaning up the bath or otherwise ensuring its correct operating conditions, including constituents, you will want to try altering the ratio of reverse to forward (or PCR-de-plate to plate cycle). If you go 9 sec ON and 1 sec OFF, it would be the same ratio as you now use. So, you might want to try about 9 sec ON and 2 or 3 (maybe more) sec OFF. It will take longer to build, but it will make the work more uniform. It would be equivalent to 45 ON and 10, 15 or more OFF (reverse). The system response improves when you get into the millisecond region with simulated ratios (such as reported in the article). Let me know how it works. *P&SF*