



## Facts About Anode Sludging

Prepared for IMC-MetalsAmerica, LLC  
By Richard W. Strachan, Ph.D., CEF-SE

### Introduction

The impurities found in copper anodes as well as the structure and manner of dissolving of anodes, continuously cause small quantities of particulates and impurities to be generated. These go into the plating bath. The black phosphorus film which forms on phosphorized anodes in copper sulfate baths winds up in the plating solution as the anodes corrode and get smaller in the normal plating process. Normal filtration practice removes these particulates and precipitates without problem. This so called "sludge" formation is normal and expected.

### "Anode Sludge" Defined

Excessive anode sludge formation occurs as a result of non-uniform corrosion of one or more copper anodes in the plating tank. This excessive anode sludge, hereinafter referred to as "anode sludge", is usually seen as an excessive quantity of copper particulates which have corroded from the anode or anodes and settled into the tank or anode bag. Anode sludge indicates that something is wrong in the plating process. The consequences of anode sludging include reduced current efficiency as a result of anode copper lost from the plating process, product defects due to particulates circulating in the tank and settling out upon the parts to be plated, and filtration and cleanout problems requiring extra time and attention to deal with.

### Non-Uniform Corrosion

Non-uniform corrosion of the copper anodes can take place for a variety of reasons, including poor circulation of electrolyte around the anodes, low anode current density and improper phosphorus film formation. See the notes in the box below for more detail. It is important to ensure good bath circulation, and adequate anode current density. It is also important in acid copper plating baths that phosphorus film formation takes place properly. Lack of this protective coating on the anode allows general corrosion of the anode to occur.

Several conditions can lead to poor formation of phosphorus film:

1. **Dirty or greasy surface.** Make sure the anodes are clean.
2. **Anode current density too low.** Make sure that there are not too many anodes or anode baskets in the tank, and that the current is high enough, say 15 amps/per square foot (*or 1.6 amps per square decimeter*) minimum. If the anode current density is too low, the phosphorus film will not form.
3. **The anodes are in a system with other anodes having low phosphorus.** When the phosphorus is considerably higher in one lot of anodes compared to other anodes in the tank, the electrical conductivity of the high phosphorus anodes will be lower, and less current will pass through these anodes than the rest. Therefore, the current density will be lower and the phosphorus film will not form.
4. **The chloride content of the bath is low.** Phosphorus filming requires chlorides. Chlorides should be 75 to 100 parts per million chloride in the bath (*See note about brightener manufacturer recommendations below*).

Note that in some plating systems such as rotogravure cylinder plating, the electrolyte circulation may be very high and the phosphorus film may not adhere to the surface of the anodes adjacent to the rotating cylinders. In these regions, the current

density will be high, and stagnant, copper-rich electrolyte does not form. Anode polarization will not take place at these locations and so sludging will also not occur.

It is also necessary to maintain the proper plating bath chemistry. Copper and/or acid concentrations which are too high may lead to anode passivation due to sulfate buildup around the anodes. Certain bath impurities at high levels can have a similar effect. Bath temperature must be maintained in recommended ranges for similar reasons.

#### PLEASE NOTE

The above recommendations for anode current density, and also guidelines for bath chemistry must be guided by the brightener system being used. The brightener manufacturer's recommendations should be followed, to avoid problems.

#### Corrosion Mechanisms and Sludging

Why do anodes corrode non-uniformly? We normally visualize that anodes corrode as a consequence of the electroplating process. A potential is applied between the anode and the cathode which are immersed in an electrically conductive plating solution, causing a current to flow. For current to flow, copper ions will be dissolved from the anode and deposited on the cathode, as electrons flow in the opposite direction. We visualize that copper is dissolving from the anode in proportion to the current density, according to Faraday's Law, in a smooth and uniform manner. In fact, the process is likely to be more complex than this, as a result of various processes going on at and near the anode. The most significant of these processes include:

- (a) General corrosion of the anode in the acidic plating solution.
- (b) Formation of a black phosphorus film to protect the anode from general corrosion.
- (c) Copper ion concentration increase in the plating solution around the anode surface as copper is dissolved from the anode. An increase in copper ion concentration can lead to anode polarization.
- (d) Non-uniform current density around the anode due to masking, directional effects, geometry and anode polarization.

A result of these effects may be anode polarization, which leads to non-uniform corrosion of the anode. General or acidic corrosion, which occurs when the anode is polarized and the phosphorus film is broken down, is the cause of anode sludging. General corrosion attacks the copper at grain boundaries more than within the grains. This used to be a concern with hand cast anode bars or shapes, where solidification of the cast metal was relatively slow and grain size could be very large. With today's continuously cast anodes, grain sizes are quite small, grain boundary area is large, and non-uniform corrosion due to this mechanism is not a problem.

On the other hand, holes in anodes and crevices between anodes packed in anode baskets provide locations where the copper concentration in the electrolyte can increase. Corrosion cells can be set up between regions of low and high copper concentration, which leads to accelerated corrosion in the high copper regions. Corrosion in holes, cracks and crevices under these circumstances can be rapid, and create anode sludge, as copper particles, small grains, etcetera corrode out of the metal matrix. This excess corrosion causes the sludging to occur in the copper rich electrolyte regions around the anode.