

The role and control of chlorides in acid copper plating baths

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This article was developed based on Caterina Borio's thesis at the University of Florence, conducted at the LEA Laboratory under the guidance of Professor Massimo Innocenti and Dr. Walter Giurlani. The work provided an interesting opportunity to further explore analytical methodologies applied to the control of galvanic processes, with an in-depth characterization of the GalvanLab® CDR system.

1. The role of chlorides in acid copper electrodeposition

Acid copper plating baths are widely used in surface finishing processes due to their high deposition efficiency, good leveling ability, and the absence of the cyanurate compounds typical of some alkaline formulations.

The most common composition is based on copper sulfate and sulfuric acid, to which specific organic additives are added to control the morphology, brightness, and uniformity of the deposit. In this system, chloride ions, Cl^- , also play a fundamental role. Although present in much lower concentrations than the main bath components, they significantly influence both the electrochemical behavior of the copper and the action of the organic additives.

In many industrial formulations, chloride concentrations are typically maintained in the 80-120 mg/L range, with target values approaching 100 mg/L. However, the optimal range must be defined based on the bath formulation and the process supplier's specifications.

Chlorides intervene through various mechanisms:

- they contribute to correct anodic behavior and help limit polarization phenomena on the anode surface;
- participate in the modulation of deposition in areas subjected to high current densities;
- interact with organic additives, particularly carriers or suppressors such as polyethylene glycol, PEG, and accelerators such as SPS;
- they take part in the adsorption and charge transfer phenomena that occur at the electrode-solution interface;
- they promote the formation of intermediate species containing copper and chloride involved in the deposition mechanism;

- contribute to the formation of interfacial structures such as PEG-Cl-Cu complexes, which influence the reduction kinetics of copper.

Their function, therefore, cannot be considered independently of the overall chemistry of the bath. The effect of chlorides arises primarily from their interaction with copper, the electrode surface, and the additive system.

2. Why chloride concentration must be monitored

Controlling Cl^- concentration is an important parameter for maintaining the stability of the galvanic process. An insufficient concentration can compromise the effectiveness of the additive system and alter the distribution of the deposit, potentially affecting the brightness, uniformity, and surface quality of the deposited copper. Conversely, excessive concentrations can alter the electrochemical balance of the bath and favor the formation of poorly soluble species containing copper and chloride. Under certain conditions, the formation of CuCl on the anode surface can contribute to passivation or the appearance of unwanted surface deposits. The growth of nodular or dendritic structures can also interfere with the proper functioning of the anode and the overall stability of the process.

Maintaining chlorides within the established operating range therefore allows:

- maintain correct anodic dissolution;
- maintain stable interaction between chlorides and organic additives;
- reduce the risk of surface defects;
- improve process repeatability;
- prevent excessive corrections to the bath composition.

The chloride balance can be further complicated by the composition of the additives used in the process. Some organic

components can be introduced in the form of chloride salts. This is the case, for example, with molecules used as levelers, including Janus Green B.

Periodic additions of these products can therefore introduce additional amounts of Cl^- into the bath, making it difficult to predict its concentration solely on the basis of direct additions of hydrochloric acid or other chloride sources.

For this reason, parameter management should not be based only on theoretical dosing, but on periodic analytical measurement of the concentration actually present in the bath.

3. Analytical techniques for the determination of chlorides

Chloride determination in plating baths can be performed using various analytical techniques. The choice of method depends on the required precision, frequency of testing, matrix complexity, and the need for rapid results.

Argentometric titration

Determination by silver ion precipitation represents one of the most established approaches for **chloride analysis**. In potentiometric titration, the sample is titrated with a silver nitrate solution and the equivalence point is identified through the change in potential measured by a suitable electrode system.

The method can provide high accuracy and repeatability, but requires proper standardization of the titrant, careful endpoint management, and personnel with adequate analytical experience.

Ion chromatography

Ion chromatography (IC) allows the separation and quantification of chloride ions with high selectivity. It is particularly suitable when the simultaneous determination of multiple ionic species or high discrimination is required. However, its application to routine control of plating baths may be limited by the need for sample preparation and dilution, analytical times, and costs associated with instrumentation and its management.

Photometric methods

The spectrophotometric determination of chlorides requires an indirect approach, since the Cl^- ion does not have a sufficiently selective absorbance in the UV-Vis region to allow direct measurement under the operating conditions normally used.

To make its quantification possible, the chloride is then made to react with appropriate reagents, generating a variation in absorbance correlated to its concentration.

Some historically employed methods utilize reagents containing mercury, exploiting the high affinity of chloride for Hg (II) and the subsequent formation or release of colored species, such as systems based on the ferric thiocyanate complex. There are also alternative approaches based on the precipitation of AgCl and the photometric measurement of the generated turbidity.

The main advantage of photometric techniques is the possibility of obtaining a rapid determination using relatively simple instrumentation, a feature that is particularly interesting for process control.

4. Rapid chloride control with CDR GalvanLab®

CDR GalvanLab® is a photometric analysis system designed for the rapid control of the main chemical parameters directly in the production environment.

For the determination of chlorides in acid copper baths, the system uses a dedicated photometric method that allows for simple and rapid results, with automated measurement and concentration calculation management. The approach is designed to simplify routine checks and enable at-line monitoring of the plating bath, reducing the need for complex laboratory instrumentation and shortening the time between sampling, analysis, and process intervention.

Analytical sensitivity

During the characterization of the method the following were determined:

LOD, Limit of Detection: 0.03 mg/L

LOQ, Limit of Quantification: 0.08 mg/L

These values are significantly lower than the concentrations normally found in industrial

acid copper baths and therefore guarantee high analytical sensitivity with respect to the operating range of interest.

Robustness to matrix

One of the most critical aspects in the photometric analysis of an acid copper bath is the matrix. The high concentration of Cu (II) gives the sample a marked blue color, while organic additives present in the bath can introduce further chromatic contributions. The method evaluation demonstrated good robustness to controlled variations in incubation time and to the characteristic coloration due to the presence of copper. The influence of additives used in the bath formulation was also studied. Some yellow-green components, such as Make-Up and Brightener, can cause an extremely small matrix effect. However, at the operating concentrations required by the process, this influence remains limited. This feature is particularly important because it allows the analysis to be performed directly on the actual bath, where copper, acid, and additives are simultaneously present.

To complete the system, CDR GalvanLab® uses dedicated, pre-filled and pre-calibrated reagent kits, ready to use. This configuration reduces preparation time, limits potential variability related to reagent handling, and helps make analytical control simpler, more repeatable and easily integrated into production routines.

Conclusions

In acid copper plating baths, chlorides are a component present in small quantities but have a significant impact on the process equilibrium. Their concentration affects the anodic behavior, the interaction with organic additives, and the final quality of the deposit. For this reason, it is not enough to simply control the theoretical addition: it is necessary to periodically check the actual concentration in the bath. Traditional techniques, such as argentometric titration and ion chromatography, are well-established analytical tools. However, in frequent process controls, speed of execution and ease of operation become equally important factors.

The photometric approach used by **CDR GalvanLab®** allows chloride determination to

be performed directly in the production environment in a few minutes, reducing the time between sampling and the availability of the result.

More frequent monitoring allows you to quickly identify any deviations in concentration, intervene before they affect the deposition and keep the plating bath within the established operating conditions.

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