Monitoring of nickel sulfate, hypophosphite and alkalinity in electroless nickel plating baths

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ProcessLab

Summary

The ProcessLab atline analysis system presented here permits the direct determination of the nickel sulfate and hypophosphite concentrations as well as the alkalinity in electroless nickel plating baths. All relevant process parameters are available immediately after sampling and allow an exact replenishment of consumed bath components.

By the use of ProcessLab, electroless nickel plating baths can be operated more economically and ecologically, while at the same time operating and disposal costs are considerably reduced. This also makes a positive contribution to husbanding resources and environmental protection.

Introduction

Nickel deposited from electroless nickel plating baths has excellent properties. The coatings are characterized by outstanding corrosion resistance, good resistance to wear and abrasion and a high degree of hardness. Chemically deposited nickel also forms very uniform layers and is deposited with very good contour definition, even on complicated materials and inner surfaces. As a result, electroless nickel plating baths are very important in metal finishing.

In the process described in detail here, nickel ions are chemically reduced to the metal in acidic electrolyte baths. Sodium hypophosphite is used as the reducing agent; with its help a very corrosion-resistant nickel-phosphorus alloy is deposited on the material surface. A simplified version of the reactions that occur is given below:

$$NiSO_4 + 3\ NaH_2PO_2 + 3\ H_2O \rightarrow Ni + 2\ H_2 + H_2SO_4 + 3\ NaH_2PO_3$$

$$3\ NaH_2PO_2 \rightarrow NaH_2PO_3 + 2\ P + 2\ NaOH + H_2O$$

The decisive reaction is the chemical reduction of the nickel and hydrogen ions by the hypophosphite leading to the deposited nickel and hydrogen gas. Little hydrogen gas formation points to a missing or a slow nickel deposition. The quicker that this reaction takes place, the less phosphorus is contained in the coating and, vice versa, more phosphorus is contained in the coating when the reaction takes place slowly. Coatings with a high phosphorus content (10...14%) are very resistant to corrosion, whereas a higher abrasion resistance is more readily achieved with a low phosphorus content (3...7%).

As nickel ions and hypophosphite are continuously consumed during the deposition process, the concentrations of these components must be kept within defined tolerances and replenished continuously. When the plating bath is in use, the concentrations of sulfate and orthophosphite (NaH_2PO_3) steadily increase; this becomes the limiting factor when the bath is in use for a long time. As more nickel is deposited than phosphorus, more sulfuric acid than sodium hydroxide is formed as the process continues, so that the pH decreases during nickel deposition and must be increased again by the addition of sodium hydroxide or ammonia.

Only exact and reproducible determination of the process-relevant parameters can ensure that the consumed bath components can be replenished correctly in order to guarantee optimal process control.

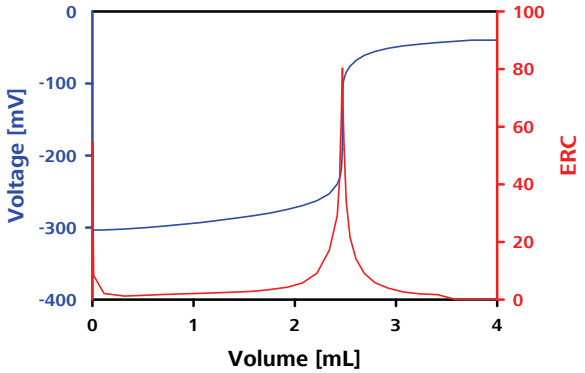
Determining the process parameters

Nickel

A complexometric titration is used for the fully automatic determination of the nickel concentration. A Cu-EDTA buffer solution is added to a bath aliquot and then titrated against an EDTA solution using a copper-selective electrode. The nickel concentration in the nickel plating bath is determined from the EDTA consumption.

Hypophosphite

The hypophosphite concentration is determined by iodometric back-titration. The sample is acidified and then treated with a defined amount of iodine solution. The excess iodine that is not consumed by the hypophosphite is then back-titrated against a thiosulfate solution using Metrohm`s Pt-Titrode. The hypophosphite concentration in the nickel plating bath is calculated from the initial amount of iodine present and the consumed thiosulfate.



Sulfate

In contrast to orthophosphate, considerably greater interference by a product that increases the salt content results from the self-enriching sulfate, which impairs crystal formation and the relevant coating properties such as corrosion resistance, hardness and resistance to abrasion. Sulfate is precipitated as barium sulfate by the addition of barium chloride, and the excess barium is back-titrated against EDTA in the same way as in the nickel determination described above.

Alkalinity

The alkalinity, i.e. the acid-binding ability, is determined by a simple titration with hydrochloric acid using a combined pH glass electrode. The sulfuric acid produced during the coating process reduces the acid-binding ability of the bath and requires the addition of extra sodium hydroxide or ammonia.

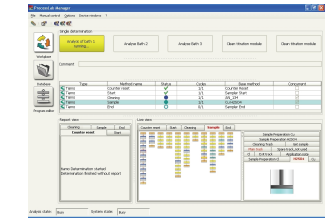
The ProcessLab analysis system

ProcessLab is a modularly designed atline analysis system and for this application it consists of one operating unit and two analysis modules.

Both the analysis modules and the operating unit are contained in a robust, splash-water-protected housing and are therefore ideally suitable for use in a rough production environment. A sample changer with barcode reader is used for completely automatic sample identification and analysis of the bath samples.

The system automatically takes the aliquot required for the particular determination, adds all the necessary reagents and auxiliary agents and then carries out the analysis fully automatically. At the end of the determination the measuring vessel is cleaned, rinsed and prepared for the next determination.

The system is controlled by the user-friendly ProcessLab Manager measuring and control software. Its customized user interface is characterized by its clear presentation and intuitive operation and allows complex analysis sequences to be started by pushing a single button. The system can also transmit status signals, for example when a limit is infringed, or the bath composition can be transmitted in the form of an analog 4...20 mA signal. The simple process integration means that this information is immediately available to the operating personnel in the control center or the process monitoring system.



Advantages of the ProcessLab analysis system

The system is robustly designed for use in a production environment and, thanks to its logical modularity, can be easily adapted to suit the particular process requirements. All the analysis results are stored in a common database and are available for monitoring, measuring and control purposes. The direct determination of the relevant bath parameters and the associated replenishments improve the quality of the finished product and increase the MTO (metal turnover), i.e. the working life of the nickel plating bath. As a result of the reduced operating costs, a ProcessLab system normally pays for itself in less than three years.

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