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Water reclamation and chemicals recovery from a novel cyanide-free copper plating bath using electrodialysis membrane process

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ABSTRACT

One of the industrial concerns is to change procedures into sustainable and cleaner processes. In electroplating, researches have been developed to replace toxic materials for safer alternatives. Cyanide salts are toxic compounds used as complexing agents in alkaline baths. This work focused in a cyanide-free copper alkaline bath developed for copper coating onto zinc alloys. Electrodialysis was evaluated to obtain a concentrated solution from a model rinsing water and simultaneously to treat the effluent for further reuse. Membrane properties after electrodialysis were analyzed, before and after cleaning procedures. Deposition tests were performed using electrolytes containing the recycled inputs and the coatings were analyzed. As results, a solution 5 to 6 times more concentrated than the initial one was obtained. The average demineralization was 90% and the percent extraction of ions was higher than 80%. Interactions between the organic acid and the exchange groups may affect membrane properties. Nevertheless, FTIR analyses and the applied cleaning procedures showed that bonds between phosphorus and quaternary amine may be reversible. Both cleaning procedures presented similar performance and partially restored the membrane properties. The concentrate could be added to the copper bath to compensate eventual drag-out losses without affecting the quality of the coatings.

1. Introduction

Electroplating baths are generally categorized in four main groups: acid baths composed of simple salts, acid baths composed of complex salts, alkaline baths composed of metals forming amphoteric salts and alkaline baths composed of complex salts. The latter represents the most common applications of cyanide salts in plating baths. Cyanide-based baths are mostly used for coating parts with complex geometry because they present greater penetration in comparison with acid baths. They are also used to coat parts in which the substrate is less noble than the coating metal [1]. Because of the toxicity associated to cyanide salts, alternative raw materials have been studied in order to obtain metal coatings with similar properties than cyanide-based baths but using non-toxic compounds. Although cyanide salts are considered low cost raw materials, the replacement of cyanide may be economically feasible if the alternative raw material is possible to be reused. The general treatment of wastewaters containing cyanide complexes involves cyanide oxidation to cyanate, resulting in loss of raw materials. Therefore, if the substituent compound can be recovered and reused, costs may become competitive.

The starting point of this work is a cyanide-free copper alkaline bath developed for copper coating onto zinc alloy die castings in barrel plating systems [2] which composition is shown in Table 1.

Throughout the last years, researches [3–8] have shown that the application of electrodialysis for treating electroplating wastewaters can support the wastewater treatment by promoting water reclamation, recovery of metals and other raw materials and, consequently, enhancing the extension of the bath operational life, since the concentrated solutions can be reinserted in the bath tanks. Moreover, it can be a measure to waste minimization and to the reduction of raw material consumption. Among the membrane separation techniques, electrodialysis is the process that uses an electrical potential difference to separate the solute from the solvent. The choice for the most suitable process is performed based on the size and molecular weight of the particles to be removed. Reverse osmosis and electrodialysis are feasible techniques for metal ion removal, while microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) are suitable for aqueous salts and particles having size between 0.005 μm and 1.0 μm. Depending on the application, electrodialysis may present other advantages over reverse osmosis, such as the operation at low pressure, the possibility of

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Table 1
Composition and operating parameters of the HEDP-based strike copper bath [2].

		Unit
Cu^{2+}	4.5	$g{\cdot}L^{-1}$
HEDP	105.0	$g{\cdot}L^{-1}$
KCl	4.0–7.0	$g{\cdot}L^{-1}$
Salicyl-sulfonic acid (optional)	4.0	$g{\cdot}L^{-1}$
Potassium sulfate (optional)	4.0	$g{\cdot}L^{-1}$
pH	10	–
Current density	0.2–0.5	$A{\cdot}dm^{-2}$
Temperature	25–60	°C
Agitation	present	–

separating cations from anions and the possibility of performing partial desalination [9,10].

The simulated wastewater evaluated in this study contains organic chelates formed between copper and HEDP which is a condition that needs further investigation since researches considering the formation of chelates are scarcer. Therefore, the behavior of copper chelates in a laboratory-scale electrodialysis system was analyzed. The possibility of obtaining a concentrated solution able to replace ions from the original bath was investigated and the quality of the obtained coatings was evaluated. Thus, the main goal of the contributions of the present study is to evaluate the feasibility of the wastewater treatment from the HEDP-based bath aiming at a closed system in which the water treatment and the raw materials recovery could be simultaneously achieved.

In an electrodialysis system, an electric potential difference (or an electric current density) is applied between two poles – cathode and anode. Ion exchange membranes are paralleled positioned between the poles forming individual compartments. The solutions of interest are circulated through the compartments while the electric current density from an external source is applied to the poles. Cations from the solution are transported towards the cathode while anions are transferred towards the anode. The membranes may be cation-exchange (CEM) (allow cations to pass through and retain anions) or anion-exchange (AEM) (allow anions to pass through and retain cations). Consequently, more concentrated or more diluted solutions than the original solution are formed [11]. Fig. 1 shows a representation of the principle of electrodialysis.

The ED stack in Fig. 1 shows two electrodes that are separated from each other by cation-exchange and anion-exchange membranes. The system is fed with the solution to be treated along with an electrode solution whose function is to maintain the electrical conductivity and to protect the electrodes. Cations and anions are transferred from the diluted compartments to the concentrated compartments through the ion-exchange membranes. In the lower part of Fig. 1, the obtained solutions are indicated (treated solution and concentrated solution).

In our previous study [12], the possibility of treating synthetic wastewaters from the mentioned bath by using electrodialysis was proposed. The performed study allowed a percent extraction up to 99% of ions from the synthetic waste and no membrane clogging was observed. Because of the percent extraction achieved previously, this work contains a more detailed investigation for closing the loop in the electrodialysis application for the evaluated bath. The objective of this work is to evaluate the possibility of obtaining a concentrated solution from a synthetic rinsing water based on the cyanide-free copper bath. The results were evaluated in terms of: percent extraction of each component from the synthetic rinsing water, percent demineralization (to analyze the reusable treated water) and percent concentration, that is, the quantitative copper-HEDP recovery. The properties of the anion-exchange membrane were evaluated after electrodialysis and after two different cleaning procedures. Lastly, the effectiveness of returning the concentrated solution to the bath was evaluated by preparing mixtures of electrolytes containing the concentrated obtained by electrodialysis. The mixed electrolytes were applied in electrodeposition tests and the obtained copper coatings were analyzed by means of visual tests, adherence tests and SEM/EDS analyses.

2. Experimental

2.1. Electrodialysis bench system

Tests were carried out in a laboratory-scale bench system containing five individual compartments separated from each other by $16\,cm^2$ rubber spacers and cation and anion exchange membranes ($4\,cm \times 4\,cm$) alternately arranged in a "Cathode-A-C-A-C-Anode" configuration. The characteristics of the membranes were described elsewhere [12]. Five $8\,cm \times 8\,cm \times 1\,cm$ compartments were connected to three 1 L independent reservoirs – *dilute*, *concentrate* and *electrode* – containing 1 L of the working solutions. The solutions under investigation were circulated through the compartments with the aid of centrifugal pumps ($3.5\,L{\cdot}h^{-1}$). Titanium electrodes coated with titanium and ruthenium oxides ($70RuO_2/30TiO_2$) with an effective area of $16\,cm^2$ ($4\,cm \times 4\,cm$) were placed at the extremities and connected to an external power source. The limiting current density was established as presented in a previous study [13]. Electrodialysis tests were carried out at 80% of the established limiting current density. A schematic representation of the ED system is presented in Fig. 2.

2.2. Working solutions

The synthetic solution simulating the rinsing waters from the copper

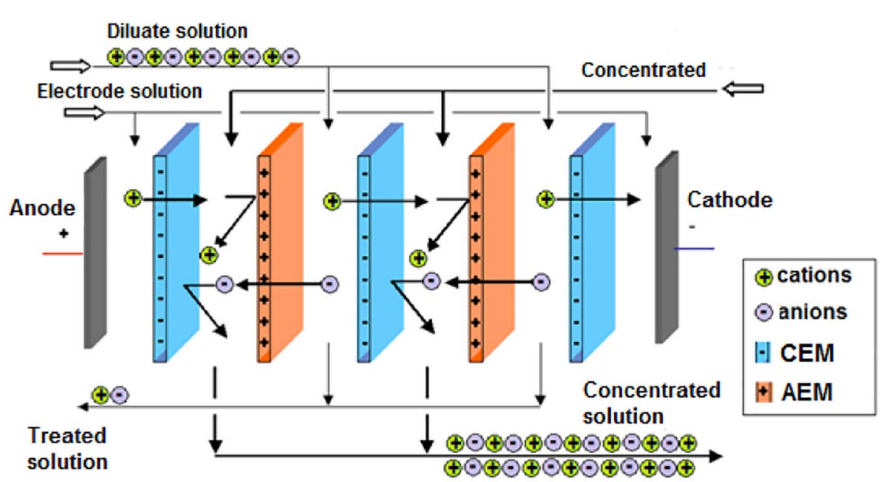

Fig. 1. Representation of electrodialysis [11].