Short communication

Combined sorption technology of heavy metal regeneration from electroplating rinse waters

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Abstract

A novel process arrangement is presented for treatment of electroplating effluents in order to minimise metal losses and prevent environmental pollution. The method comprises three processes: sorption of heavy metals from the catching bath solution, regeneration of sorbent and electroprecipitation of heavy metals in the electrolyser.

Introduction

In recent years considerable attention has been paid to the problem of improvement of electroplating technology in order to decrease the amount of waste water produced and to develop new methods for its purification. Industrial electroplating appears to be one of the most hazardous among the existing technological processes. Its toxic effects on all biological objects are due to the presence of heavy metals in the effluents. As only from 30 to 40 per cent of all metals used in the electroplating process can be effectively utilised (plated) (Alferova et al., 1990), its waste waters are responsible not only for supply of pollutants to the environment but also for the greatest portion of metal losses.

As a rule, after the electroplating operation a plated article is washed in a continuous flow; the same water may be used 1 to 3 times. Average water consumption during one rinse operation is about 100 ℓ per 1 m^2 of the plated surface; at the same time approximately 0.2 ℓ of the electrolyte dragged out from plating bath per each 1 m^2 of the article surface is washed off with rinse water (Nevsky et al., 1993). This leads to generation of large volumes of effluent with low concentration of toxic substances significantly complicating waste water purification processes.

Reagent precipitation, sorption of heavy metal ions, electro- and galvano-coagulation and electrochemical extraction are the most frequently employed methods for the treatment of effluents from first-stage rinse baths, or so-called catching baths. Among the common disadvantages of these methods are:

- secondary pollution of purified water by simple inorganic salts;
- intricacy of separation and utilisation of valuable components; and
- massive losses of non-ferrous metals.

Sorption of cations by an ion-exchanger requires its continual regeneration; in this case the expenditure on reagents is 3 to 4 times higher than the stoichiometric value. Reagent precipitation of heavy metals also requires large amounts of costly chemicals. In comparison with the above-mentioned methods electro-coagulation can be considered as the most advanced one, but high consumption of energy and iron or aluminum restricts its wide application. Despite the simplicity of equipment the recently developed ferrite method also has not found extensive application due to high consumption of alkali and ferrous sulphate heptahydrate as well as difficulties in sludge utilisation. The utilisation of sludges for the production of structural and decorative materials is a difficult task because of their variable composition and gradual leaching of heavy metals by natural waters.

Usually exhausted electrolyte and rinse waters are purified separately (Enger, 1992) with pure heavy metals extracted by electrolysis (Grebenyuk et al., 1989). On the other hand the cascade rinsing of articles has recently become widely used in purification of electroplating effluents (Elinek, 1993). During the first stage of this method the solution regeneration is carried out by ion exchange and vacuum evaporation. The distillate is used for the rinsing operation on further stages. Hard toxic sludges formed during this process are deposited at special dumping sites.

The development of closed cycles of water supply for electroplating production (effluent-free technology) should be considered as an ultimate aim when developing new water purification methods. One of the advantages of the closed system of rinse water processing is the lower level of purification imposed, not by a permitted maximum concentration (PMC), but by requirements of the rinsing operation. For example, concentrations of Ni (II), Cr (VI), Zn (II) and Cu (II) ions in waste waters must be lower than PMC which is 0.01 mg/ℓ. When the closed cycle technology is used the concentration of these ions is allowed to be as high as 10 to 20 mg/ℓ (Golzelmann, 1986). At the same time the volume of treated water decreases substantially.

Among the rinse water purification methods ion-exchange concentration of heavy metals is regarded as one of the most promising (Feksik and Miller, 1993; Shtykov et al., 1991). As far as metal extraction is concerned the regeneration of effluents by electrolysis is considered to be the most effective from an economics and ecology point of view (Langefeld, 1991).

This paper deals with a new technology for rinse water purification combined with utilisation of valuable metals. It results from the investigation into the transport of heavy metal ions across ion-exchange materials with different characteristics. The ions remain in an ion-exchange column when the solution from the catching bath is pumped through it. After the saturation

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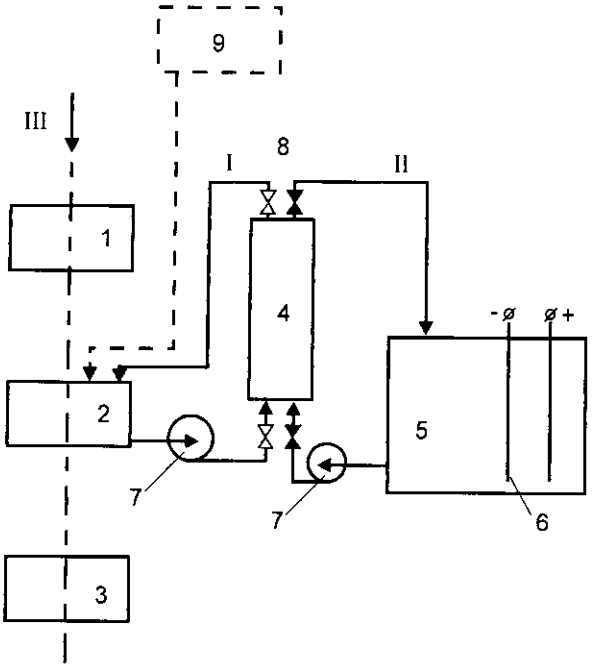

Figure 1

Schematic of installation for electroplating solutions treatment: 1 - plating bath; 2 - catching bath; 3 - rinse bath; 4 - sorption column; 5 - electrolyser; 6 - cathode; 7 - pump; 8 - valve; 9 - softening unit; I - solution flow of catching bath; II - regeneration solution flow; III - movement of articles along production line.

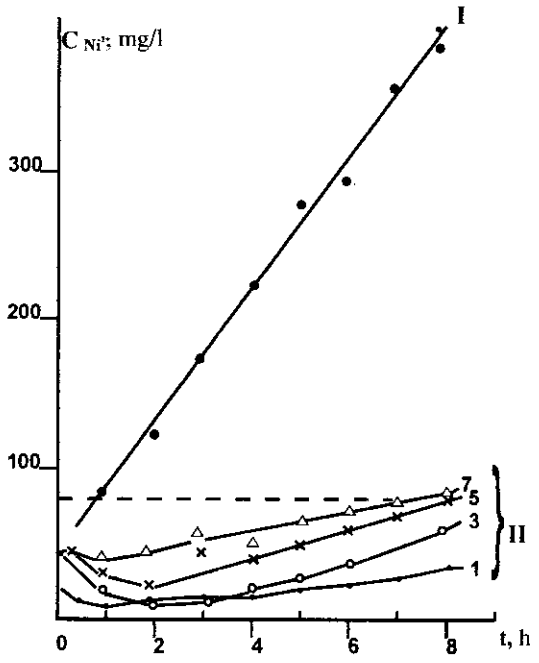

Figure 2

Relationship between nickel-ion concentration in catching bath solution and solution flow rate through regeneration column (I - 2 volumes of catching bath per hour, II - 12 volumes of catching bath per hour) and quantity of sorption-regeneration cycles for column with cation-exchanger KU-2-8; number of cycles 1-7.

of the resin the regeneration solution is run through the column and returned to an electrolyser, where metal is deposited on the cathode. By this means both the regeneration of the sorbent takes place and pure metal is collected, ready to be used as an anode in the plating bath.

Background

According to standard electroplating technology the articles are transported from the plating bath to the catching bath and then to the rinse bath. The amount of electrolyte which is dragged out and, consequently, the concentration of heavy metals in the catching and rinse baths depend on the following factors: composition and concentration of the electrolyte in the plating bath, geometrical configuration of the plated article and the speed of its movement between the baths. Due to these factors the concentration of heavy metals increases up to 1.2 to 1.7 g/ℓ in the catching bath and far exceeds the PMC in the rinse bath during one shift (8 h). One square meter of a plated article loses from 15 to 30 g of metal which reports in either sludges or waste waters. Improvement of the article transportation method cannot completely solve the problem of non-production losses of electrolyte and significantly prolong the life of the rinse bath between discharges.

Proposed new method

According to this newly proposed method a series of ion-exchange columns, one of which is represented in Fig. 1, is situated next to the catching bath. Each column is filled with either cation exchanger KU-2-8 or selective polyampholine ANKB-35 in the Na^+-form. The catching bath solution is continuously circulated through the column by means of a pump. After saturation of the resin in the first column the solution flow is switched automatically to the next column. The saturation speed of the column depends on specific conditions of the electroplating process, volumes of the sorbent and the solution, the solution flow rate, etc. Each column is connected to the electrolyser via the second pump where regeneration of its resin takes place.

The amount of the sorbent is chosen in such a way that the concentration of heavy metals in the catching bath remains not higher than a specially set limiting value during, for example, one shift lasting for 8 h.

Materials and methods

Kinetics of catching bath solution purification from nickel ions was investigated on a semi-industrial pilot plant with a 50 ℓ catching bath. The ion-exchange column for metal-ion sorption was manufactured in a cylindrical form allowing for a radial flow distribution of the solution and with the filter attached to the outer surface of the cylinder. Sorbent volume in the column was 3.2 ℓ. In order to simulate the real transport of the electrolyte by a plated article from the electroplating bath into the catching bath a dosing apparatus was used to continuously introduce 48.6 mℓ/h of the industrial nickel-containing electrolyte.

Nickel-ion concentration in the simulated rinse water was determined regularly. On completion of the sorption process the column was dipped in 9.5 ℓ of the regeneration solution. The regeneration solution circulated through the sorbent with a flow rate of 3 volumes per hour during 3 h. Electrolysis of the regeneration solution with extraction of pure nickel on the cathode was conducted simultaneously until the concentration of

nickel ions in the solution reached 0.5 g/ℓ. After such treatment the column was ready to be used in the next sorption-regeneration cycle.

The change in nickel-ion concentration in the simulated semi-industrial catching bath solution during 8 h in relation to the solution flow rate through the sorbent is represented in Fig. 2. The concentration of nickel ions in the catching bath without purification reaches 1.2 to 1.4 g/ℓ. In order to keep the nickel-ion concentration in the rinse bath (situated directly after the catching bath) lower than PMC and to comply with municipal sewer regulations the concentration of nickel ions in the catching bath solution must not exceed 60 to 80 mg/ℓ (dotted line in Fig. 2). The low circulation rate of the catching bath solution through the ion-exchange columns results in undesirable accumulation of nickel ions in the catching bath. In the case of a high enough flow rate (e.g. 12 volumes of catching bath per hour) this concentration will not depend on the sorption-regeneration process and will always stay lower than the PMC limit.

Another technical novelty of the newly developed combined method of catching bath solution treatment with ion-exchange columns placed directly into the catching bath is represented in Fig. 3. High surface contact of the sorbent with the treated solution can be considered as an advantage of this design though a free space in the catching bath is required. The transportation of a saturated column from the catching bath to the electrolyser is performed by a hoist. The regeneration solution circulating from the electrolyser through the saturated columns removes heavy metal ions from the ion-exchanger. When the concentration of these ions reaches 3 to 4 g/ℓ the metal starts to precipitate on the cathode. The cathode coated with a certain amount of metal according to technological requirements can be used as an anode in the plating bath. Due to the fact that the yield of nickel on cathodes depends strongly on the pH of the solution (at low pH nickel reduction on the cathode does not take place), it is essential to separate the anodes from the remaining part of electrolyser by ion-exchange membranes in order to prevent acidification of the electrolyte (Fig. 3). If Cu, Zn or Cd-containing solutions are treated, a simple electrolyser can be used.

Contents of the catching bath have to be discharged regularly because of the accumulation of basic metal salts which cannot be removed by the described process. This problem is solved by membrane desalination of the catching bath solution after the removal of heavy metal ions from it.

By this means, in the described technological scheme three processes are present: sorption of heavy metals from catching bath solution (saturation of the resin by heavy metal), regeneration of exhausted column and electroprecipitation of the metal on the cathode in the electrolyser.

When a nickel-containing solution is treated, tap water is unsuitable for the rinsing operation. Together with nickel ions the hardness ions present in tap water (mostly calcium) are absorbed in the column. As a result of regeneration by sodium sulphate insoluble calcium sulphate is formed in the ion-exchange resin. It leads to a decrease in the sorbent capacity (desorption) progressing with each regeneration cycle (Fig. 4). This can be avoided by using softened water for the rinsing operation.

The capacity of the cation exchanger in the unit decreases with the operation time also due to the presence of organic compounds, iron and aluminium alkali gels in tap water. This can be prevented by the flushing of the resin with 3.5 N sulphuric acid every two months or after every seven regeneration cycles. Acid from the anode compartment of the electrolyser can be used for this purpose. (This acid can then be utilised for etching of steel articles). After the acid treatment the ion-exchange resin must be flushed with water and transformed to the Na^+ form by immersing in sodium chloride solution.

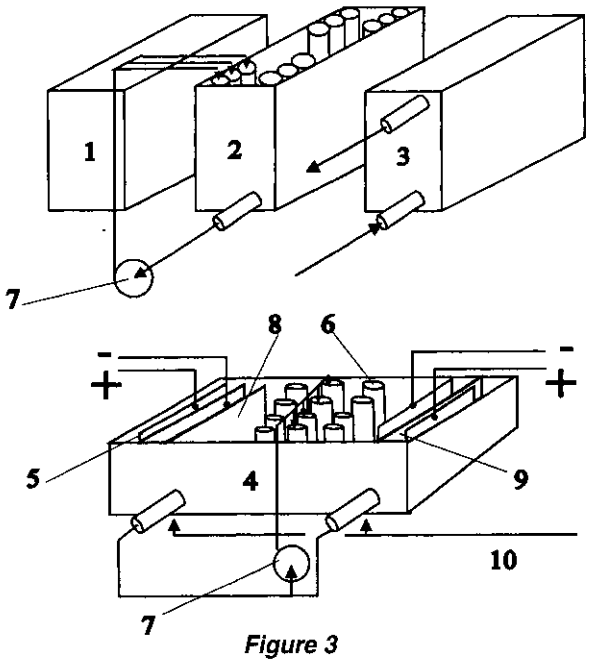

Figure 3

Schematic of installation with columns placed into catching bath: 1 - plating bath; 2 - catching bath; 3 - rinsing bath; 4 - regeneration and electrolysis bath; 5 - anode; 6 - columns; 7 - pump; 8 - cathode; 9 - membrane; 10 - compressed air.

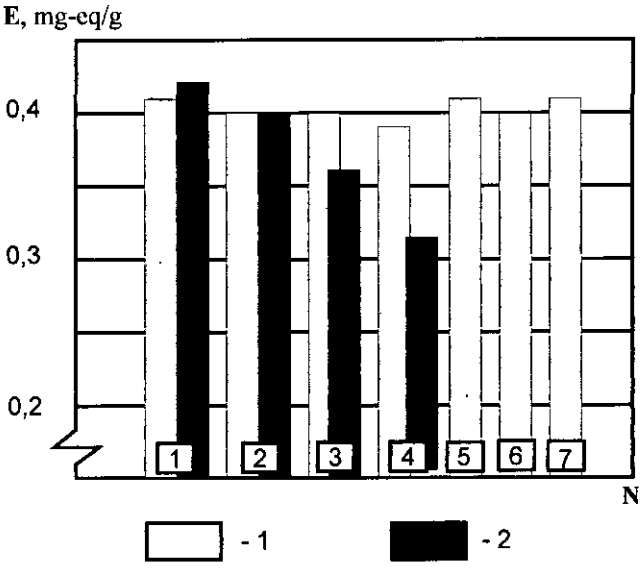

Figure 4

Relationship between sorption capacity E of cation exchanger KU-2-8 in closed circulation system and number of sorption-regeneration cycles N; 1 - softened water; 2 - tap water.

Results

The main advantages of the newly developed technology in comparison with other existing electroplating effluent treatment

methods are as follows:

- heavy metal ions (Cu, Ni, Zn, Cd) are recovered directly in the catching bath;
- recovered metals are pure and can be used in the production of anodes for electroplating baths;
- absence of sludges or other non-utilised substances;
- less rinsing water is required;
- low power requirements; and
- simple installation and maintenance.

Discussion

In comparison with reagent purification significant decreases in energy and reagent expenditure are achieved by this method. The sludge disposal problem is avoided and the hardware is simplified. In addition to these advantages, if compared to electro- and galvano-coagulation methods, no iron or aluminum consumption occurs. Finally this technology requires a smaller ion-exchange column and less regenerant than in traditional ion-exchange effluent treatment.

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