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Regenerating Etching Solutions for Circuit Boards while Extracting Copper

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ABSTRACT

The examination of sludge derived from electroplating manufacturing, printed circuit board production, and paste-like residue from sludge collectors uncover elevated levels of chromium, nickel, copper, cadmium, and various metals. The considerable saturation of water in the region and diverse soil compositions complicate the identification of suitable waste disposal sites, specifically for electroplating byproducts, limiting available spaces and fostering conditions conducive to soil and water contamination by heavy metal ions. The retention of used etching solutions within industrial facilities contributes to environmental pollution, necessitating substantial expenditures for proper disposal at manufacturing sites. Industrial waste, notably from processes such as printed circuit board etching, represents a significant threat to water quality, encompassing various essential technological processes for the production of diverse electronic equipment serving both civilian and military purposes. This article aims to present research outcomes and conducted experiments geared towards developing eco-friendly equipment. Also, the research delves into specific procedures for obtaining concentrated copper precipitates during the regeneration of etching solutions, with the extraction process reducing the generation of waste in the form of a paste-like structure saturated with water on industrial premises. The treatment of wastewater from etching printed circuit boards can be achieved by establishing a closed production cycle for board manufacturing and extracting copper for industrial applications. Finally, the research strives to design equipment for regenerating used solutions with metal extraction in a form suitable for remelting, contributing as an element to environmental conservation. The results facilitate the establishment of a printed circuit board etching line that incorporates the reuse of spent etching solutions in the manufacturing process. For solution regeneration, it is recommended to utilize a regenerator with a titanium VT1-0 cathode. The outcomes of individual tests provide conditions for regenerating spent etching solutions and utilizing the extracted copper in the national economy.

Keywords: etching solution, titanium, cathode, ion, regeneration, ecological safety, environmental pollution, agricultural industry.

INTRODUCTION

When etching printed circuit boards, approximately 0.5 kg of copper can be dissolved per 1 m^2 of the substrate (glass-textolite, copper-clad). The total consumption of the etching solution is calculated based on discharging 100 litres of spent solution during the dissolution of 10 kg of copper (resulting in the dissolution of around 0.5 kg of copper per 1 square meter of printed circuit board (PCB). This has led to the annual accumulation of hundreds of tons of waste in the form of water-containing substances on the premises, stored in metallic containers and various bags, frequently in undeveloped areas exposed to atmospheric precipitation. For example, we consider the situation with the formation of sludge during the operation of a modern printed circuit board etching line. With the productivity of the etching line of 14 m^2/h, the amount of sludge in 8 hours of work will reach more than 110 kg, which will amount to 2,400–2,500 kg at a monthly one-shift operation. Existing technologies for etching printed circuit boards involve dumping "exhausted" etching solutions and serve as a source of environmental pollution. There is a need to spend quite a lot of money on wastewater neutralization. In addition, the copper dissolved in the etching process is irretrievably lost, and a large amount of valuable chemicals is required to produce a fresh etching solution. All this leads to the deterioration of the efficiency of production of printed circuit boards. The analysis of waste generated from electroplating production, etching printed circuit boards and specific technological processes has revealed elevated concentrations of various copper, chromium, cadmium and other metal compounds (Zaverach et al., 2020). Exposure to the atmosphere and precipitation with high levels of nitric and sulfuric acids results in the degradation of containers and packaging, leading to environmental pollution in the enterprise and surrounding areas (Oliveira, 2007). Agricultural enterprises and their utilized territories for cultivating agricultural products, characterized by soil structures unsuitable for industrial waste disposal, limit the options for establishing waste disposal sites. Consequently, challenges in selecting and establishing landfills for industrial waste, particularly from electroplating and PCB manufacturing, contribute to problems of surface and groundwater contamination, as well as soil pollution (Petryk et al., 2018).

Companies are required to utilize diverse purification methods, yet the flaws in current approaches permit the infiltration of heavy metal ions into wastewater, potentially resulting in environmental pollution (Pohrebennyk et al., 2018). The practice of diluting industrial effluents with water is no longer acceptable due to the escalating volume of industrial effluents and the surpassing of permissible limits, leading to diseases and the depletion of living organisms that can enter the food chain, ultimately affecting human health (Grizzetti et al., 2017; Ishchenko et al., 2018). Enterprises in the electronics sector, including those engaged in circuit board production and employing analogous technological processes, impact the ecological conditions around their production sites (Pohrebennyk et al., 2019), as dominating industry enterprises actively extracting valuable minerals for the country (Semenikhina, 2011). Copper, alongside other metals, finds extensive use in both Ukrainian and global industries. Its broad utilization in industry is attributed to its low electrical resistance and high thermal conductivity. In the manufacturing of electrical products, microelectronics and radio-electronic devices, high-purity copper is indispensable. The application of copper in today's PCB constructions involves etching to attain specific characteristics, leading to the presence of wastewater, which, under current technologies, can pose environmental risks to soils and water horizons (Pohrebennyk et al., 2017). The disposal of industrial waste in landfills compounds the challenges faced by Ukraine, which is already grappling with numerous polluted areas, presenting difficulties in the present and for the years to come. The situation is exacerbated by the proliferation of military actions within the country's territory (Alekhya et al., 2013; Pohrebennyk et al., 2016). To predict the soil and rock salinity within the aerated zone of a printed circuit board manufacturing facility on a man-made disturbed production site across different phases of the enterprise's operations, the authors of this article employed the analytical solution proposed by Carslaw and Jäger. This method facilitates the assessment of environmental damage. The projected analysis of soil contamination due to waste from printed circuit board production within the salt storage area indicates that, within a year, the upper soil layer (0.5 m) will reach a salinity level of 0.499%. This practically results in the absence of living organisms and the diffusion of salinity to neighbouring areas, leading to corresponding adverse consequences.

The forecasted assessment of soil contamination over 10 and 50 years from the onset of salinization reveals that within a decade, a contamination mound will develop above the groundwater level, replicating the configuration of the discharge area on the surface. This mound, situated in such a location, bears the primary burden of environmental pollution, influencing the groundwater quality near the enterprise and potentially extending beyond its borders. The estimated water mineralization in the mound is 28.2 g/dm^3, projected to increase to 108.9 g/dm^3 after 50 years. Such processes contribute to climate change, particularly impacting developed countries (Bloomberg et al., 2014; Nester 2016). Based on assessments of several Ukrainian enterprises, the authors of this article evaluated the risk of accidents that could occur during the storage of galvanic waste. Determining the hazard class of complex waste involves calculating the toxicity index based on the average lethal dose of the chemical ingredient, its solubility coefficient in water, volatility coefficient, the quantity of the ingredient in the total waste mass and the specific ingredient number. The findings indicate that for priority pollutants in galvanic production waste, the hazard index is unacceptable, and pollutants present in galvanic sludge, entering the environment due to an accident, would have adverse effects on human health. Health survey processes also highlight pollution (Karaeva et al., 2018).

The treatment of wastewater from the etching of printed circuit boards can be achieved by establishing a closed production cycle for board manufacturing and extracting copper for industrial purposes (Nester, 2016). Several questions in this context warrant investigation to identify optimal methods for electrode coating and separating the extracted copper during the regeneration of spent solutions. The spent etching solution emerges as the main source of copper for use in the electrical industry, practically eliminating wastewater contamination with copper compounds and sludge.

ANALYSIS OF RECENT RESEARCH AND PUBLICATIONS

Detailed scrutiny of patents and current technical literature indicates that addressing the challenge of spent etching solutions involves a shift towards a production method incorporating a closed-loop etching-regeneration cycle within a unified technological process. Concurrently, wastewater from enterprises lacks sufficient research, and dependable designs and technologies for specialized treatment, particularly in heavy metal removal, remain undeveloped.

It is noteworthy to highlight specific studies that explore metal extraction alongside solution regeneration (Trokhymenko et al., 2020; Nester et al., 2020).

Attending to previously unaddressed aspects of the overall issue

The unique characteristic of solid waste production is its minimal environmental impact in small quantities. However, it transforms into an ecological threat in large concentrations. The challenge of industrial and household waste disposal has intensified due to the continuous increase in waste generation, paired with insufficient processing rates. As a result, hundreds of millions of tons of diverse solid wastes have accumulated, requiring proper processing and disposal. Nevertheless, there is a noticeable gap in research related to the extraction process of solid residues and their suitability for further use following industrial processing. The aim and objectives of paper are to present the research findings and experiments conducted for the development of environmentally friendly equipment.

MATERIALS AND METHODS

Description of research methodology (structure, sequence)

The research employed an alkaline ammonia copper chloride solution commonly used in the etching process of substrates for printed circuit boards. The process of purifying wastewater from copper ions and reusing the aqueous solution (regeneration) was carried out through a setup that concurrently utilized the metallization process. The investigations indicated that titanium, and to some extent, 08X17TM steel, were the most suitable materials for the current collector, owing to their high chemical and electrochemical resistance. The selection of materials was carried out on the basis of working processes and materials, our research and the possibility of their real use to ensure the necessary etching speed of printed circuit board substrates, specific characteristics. For example, an important criterion for choosing titanium for use as an electrode is extremely high corrosion resistance, lightness (the density of titanium is almost 2 times less than iron) and easy separation of deposited copper from the electrode surface. The possibility and research of using steel (a cheaper material) as an electrode was considered, but the difficulty of separating the precipitated copper, which should practically be a complete process, did not give the opportunity to choose steel for the manufacture and use of this function in the regenerator. Etching solutions were chosen as a means of ensuring high etching characteristics and the possibility of regeneration compatible with the etching speed to ensure the simultaneous execution of these operations. The laboratory setup executed the process of galvanic copper plating using the extracted metal from spent etching solutions for both flowing and stagnant electrolytes. The schematic representation of the setup is depicted in Figure 1, featuring a rectangular electrochemical cell (1) with dimensions of 0.8×0.8×1 m, constructed from transparent plastic and mounted on a container holding the spent etching solution (electrolyte) (9). The container (9) is fitted with a submersible centrifugal pump (8), capable of generating pressure in the pipeline up to $1.5 \cdot 10^5$ Pa and maintaining a flow rate of spent etching solution up to 1.6 m^3/hour. It incorporates an electric heater (10) with a thermal regulation system, comprising the heater itself, a water cooler and a control relay with a contact thermometer. A valve is positioned between the pump outlet (8) and the cell inlet (1) on the pipeline, enabling the control of fluid supply. A measuring diaphragm (a constricting device in the form of a disc with a hole) (5) is linked to a manometer for overseeing pressure differentials (7). The pump conveyed the spent solution from the tank to the lower part of the cell, where it naturally flowed back into the solution container (9) due to gravity. A sample cathode cell (3) measuring 0.7×0.7 m, intended for the deposition of copper extracted from the spent etching solution, was positioned in the upper part of the electrochemical cell along its axis, opposite sheet anodes made of copper sheet material grade M1 or corrosion-resistant titanium grade VT1-0 with a thickness of 3 mm. The length of the 0.25 m inlet section was chosen to establish a speed regime for the spent solution, ensuring a consistent velocity along the anode, maintained at 1.5–2.5 cm/s. The regulation and maintenance of a constant speed were executed using an

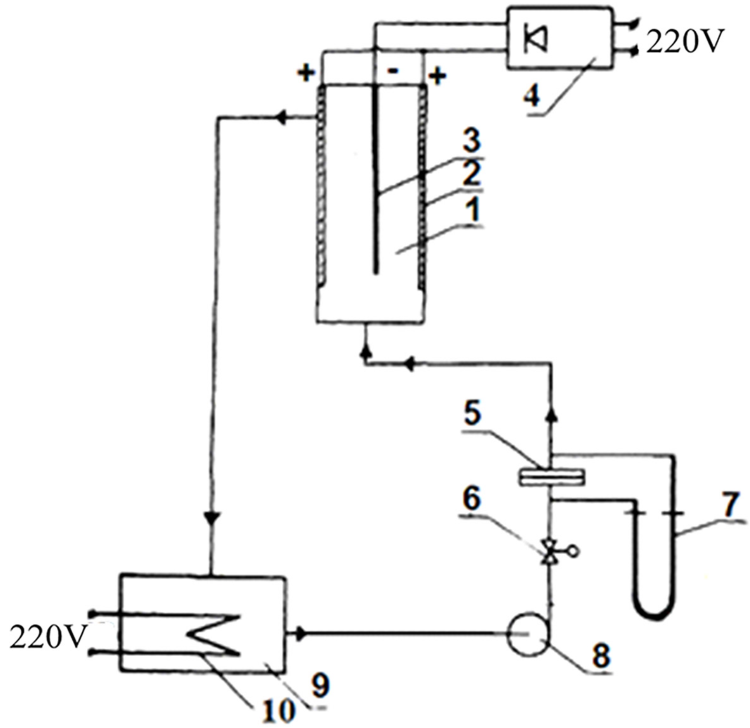

Figure 1. A scheme of the setup for regenerating used solutions and applying galvanic coatings in continuous electrolytes; 1 – electrochemical cell acting as a regenerator; 2 – anode of the cell; 3 – cathode of the cell; 4 – power source; 5 – measurement diaphragm; 6 – valve; 7 – differential manometer; 8 – centrifugal pump; 9 – container with solution; 10 – electric heater for temperature control

RMS rotameter, designed for measurements in environments with uniform flows of clean or slightly contaminated substances. The average flow rate of the electrolyte was gauged and adjusted based on the readings of the differential manometer (7), designed for measuring fluid flow using the diaphragm method of pressure drop. The electrochemical process of copper removal from the spent etching solution and its delivery to the cathode were facilitated by the involvement of the TVR1-3150/12T rectifier (straightener) in the process.

RESULT AND DISCUSSION

Overview of the primary material and the scientific results obtained

The research followed a systematic approach:

- Preparing the cathode's working surface.
- Weighing the cathode plate before initiating electrolysis.
- Preparing the anode's working surface.

The experimental setup operated under the specified conditions detailed below. Regular weighing of the anode were conducted every 30 minutes of operation. To execute this procedure, the cathode's working surface underwent cleaning with a soft brush, and subsequent weighing was carried out to quantify the dense copper deposit and calculate the current efficiency. Further investigations into the physical and mechanical properties of the electrolytic coatings were conducted using the methodology delineated below. Electrical and technical indicators were recorded using a KSP potentiometer, capable of documenting temperature and direct current voltage readings. Additionally, measurements employed a saturated silver chloride electrode known for stability at elevated temperatures, suitable for application in aqueous environments. The hydrogen scale of electrode potentials was utilized in this context. To study spent etching solutions, the authors utilized solutions from the operational etching setup within the enterprise. These solutions, in turn, were prepared using "chemically pure" and "pure for analysis" chemicals. The container (9) dedicated to this purpose was connected through a pipeline to the etching setup container. The following is a compilation of various indicators used to monitor copper coatings derived from spent etching solutions, accompanied by specific definitions and characteristics that provide insights into the practicality of utilizing deposited copper in the national economy. The investigation into the physical and mechanical properties of electrolytic coatings involved methods such as metallography (for studying the macrostructure and microstructure of metals), measurement of the contact angle of wetting (formed on the surface of the examined solid body), flexible cathode, a pendulum (Mendeleev's pendulum) and scanning electron microscopy (for studying individual elements of the substructure of a solid body) along with microhardness measurements. The application of copper deposited on the cathode in the electrochemical cell as secondary raw material introduces practical considerations for both the material and the electrode work. The composition of the cathode material and the cleanliness of its surface treatment are crucial factors (Nester, 2016). To identify a material facilitating the easy removal of deposited copper from the electrodes without significant effort, relevant investigations were conducted. The research employed constructions of cathode plates crafted from I2XI8HT stainless steel and VT1-0 titanium with a thickness of 3 mm, along with GE-FFF graphite anodes. The current density on the cathode electrodes ranged from 15 to 25 A/dm^2. During the operation of the regenerative setup (the installation for depositing copper from spent solution), the reactive surface of the cathodic electrode expands, leading to a reduction in the actual current density and causing the amalgamation of the cathode metal with the deposited copper during the setup's operation. Titanium samples exhibited the best results in detaching the deposited copper from the electrode. In simple bending of the titanium plate, the deposited copper on the cathode easily detached due to internal stresses. The deterioration of copper detachment from the electrode requires additional mechanical processing of the electrodes. Yet, this work does not include information on the correlation between copper detachment and the number of deposition cycles. Another equally significant aspect is that the initial surface's roughness consistently reduces the density of the cathodic deposit. Accordingly, particles of extracted metal (copper powder) emerge on the electrode surface, naturally expanding the cathodic area and diminishing the actual current density. This process also fosters the rise of micro-asperities at distinct locations on the surface of the extracted copper, resulting in additional roughening and, consequently, the creation of powders.

Studying the surface morphology

The primary tool utilized in this regard is a scanning electron microscope (SEM) designed for capturing images of the coating, revealing its composition, structure and specific layer properties. The interaction between the electron beam and the layer of deposited copper in the metal regeneration setup facilitated a detailed examination of the finer details of the extracted metal settled on the cathode. Irradiating copper samples on the cathode permitted the acquisition of the elemental composition, contributing to a conclusive determination of the fate of the metal extracted from spent etching solutions. Visual observation and electronic photographs for comparison carried out with copper from electrolytic (industrial) refining, demonstrated that grain sizes, grain boundary shapes, transitional zones and crystal sizes were practically indistinguishable from copper extracted from spent etching solutions (i.e., wastewater). It is crucial to emphasize that electrolytic refining, containing 99.9–99.95% Cu, is a more advanced method for purifying copper and marks the final stage of production. The findings indicate that the galvanic method enables the provision of clean metal coatings on components, along with ease in achieving diverse coating thicknesses, porosity and effective adhesion to the surface of the coated part.

Investigating the intricate structure of galvanic copper

The research involved a comprehensive analysis of the texture of coatings obtained from deposited copper using the conventional method of metallographic etching. This approach facilitated the identification of crystal dimensions, shapes and their typical arrangement, as well as other irregularities, including inclusions collectively referred to as non-metallic. The etchant employed for scrutinizing etching patterns, effectively dissolving cracks, porous areas and weaker sections, primarily the base metal, is detailed in Table 1. To unveil etching patterns, the etching process took approximately 2.5–3 minutes. Both an optical microscope (MMU) with 370x magnification and a scanning electron microscope (SEM), a more straightforward alternative to a transmission electron microscope (TEM), were utilized to capture images of the etching patterns. The scanning microscopy method not only allows the researcher to observe a considerable depth of focus but also conveys a three-dimensional impression. The fundamental principle of this etching method involves treating the crystal surface with the aforementioned etchant, namely, a deliberately slow solvent chosen to variably dissolve regions where the lattice is distorted or structural defects are present. The action of the etchant on the copper layer's surface leads to the formation of small pits or bumps, known as etching patterns. These patterns also manifest at locations where dislocations emerge on the crystal surface. The density of dislocations is determined by the number of etching patterns per unit surface area. However, not every etching pattern necessarily corresponds to the emergence of a dislocation. The association of etching patterns with dislocations is established through repeated etching, subsequent photography and chemical polishing of the surface. Given that dislocations are linear defects extending into the crystal's volume, the pattern from repeated etching should mirror the initial one. This congruence is absent when etching reveals randomly placed defects of a different nature. The application of layer-by-layer selective etching of the crystal surface, interspersed with chemical polishing (where the dislocation structure remains undisturbed), facilitates the tracking of dislocation lines within the crystal's depth and the examination of individual dislocation loops. Crystals of deposited copper exhibit numerous defects within their authentic ordered atomic arrangement. Notable instances of planar defects in copper crystals encompass grain boundaries and the crystal surface. These defects elucidate the distinctive properties of the crystal, notably its ionic conductivity. In deposited copper, the appearance of vacant lattice sites signifies an escalation in electrical resistance, a critical factor for the application of copper in electrotechnical contexts. Consequently, the dislocation density was ascertained through the following expression:

Table 1. Etchant composition

1. $FeCl_3 \cdot 6H_2O$, g	2. HCl, ml	3. H_2O(distillate), ml
5	30	100

$$\rho = \frac{n}{S_{\partial i \ddot{i}}} cm^{-2} \tag{1}$$

where: n represents the number of etching pits in deposited copper; $S_{\text{of action}}$ denotes the surface area of the substrate under the assumption of conditional (ideal) smoothness;

$S_{\text{of action}}$ is calculated using the Wenzel equation, a scenario that is rarely encountered ($S_{\text{action}} = r \cdot S_{\text{sample}}$)

$$r = \frac{\cos Q_2}{\cos Q_0} \tag{2}$$

where: Q_2 signifies the actual equilibrium contact angle of the liquid on deposited copper; Q_0 denotes the equilibrium contact angle of the liquid on a specially prepared smooth substrate (Class Δ14 cleanliness), metallized through vacuum deposition with metal of the same chemical nature as in electroplating.

The examination of the metal structure is executed using a microscope in reflected light. The metal sample undergoes meticulous processing to achieve a flat surface on a metal-cutting machine, followed by grinding and polishing. Post-preparation, the sample reflects light akin to a mirror. Untreated grinding reveals cracks, pores and non-metallic inclusions. To unveil grain boundaries and distinct structural elements, the sample undergoes etching after grinding.

Exploring the microstructure of copper coatings through the etching method of metallographic slides

This step involved the preparation of samples using a specialized technology allowing the use of epoxy resin. This resin possesses the crucial feature of curing within a day and resistance to corrosion. The grinding process utilized abrasive cloths made from twill cotton fabric and pastes as tools for precise grinding.

Directional changes in grinding by 90 degrees occurred during the transition between different abrasive materials. Following the polishing phase, the microslide underwent rinsing with water and alcohol and was dried to ensure cleanliness for the study. During the etching process, components with electronegative electrode potential became anodes on the microslide surface, dissolving, while the cathodes remained unchanged, forming galvanic elements. Microrelief, manifesting as pits and protrusions that scatter light differently, was created. Pits at grain boundaries scattered light more intensely, appearing as dark lines. The slide was examined using the common method of studying metal structure, employing an optical microscope. The polished sample surface was etched using a solution composed of $(NH_4)_2S_2O$ – 10% solution (4 parts) and H_2O_2 – 3% solution (1 part), revealing the non-uniform areas of copper under the microscope.

Subsequent studies were conducted to ascertain the equilibrium contact angle, which could vary from 0° to 180°. This angle was determined by analysing the equilibrium state of surface tension forces for liquid droplets on the solid surface of the deposited copper in a gaseous environment. The wettability of the metal (solid) surface when three phases intersect is generally described by the magnitude of the equilibrium contact angle. This angle is formed by the surface of separation between the two phases and the surface of the third phase. To measure the contact angle, a drop of liquid from a chromatographic syringe was applied to the object of study. Using a tangent at the point of intersection of three phases, the equilibrium contact angle was determined by measuring the geometric dimensions of the drop, involving mathematical calculations for precise determination.

$$\text{Q} = 2\ \text{arctg}\left(\frac{2в}{a}\right) \tag{3}$$

Determining the micro-roughness of the coating

This stage implies evaluating the surface condition of the extracted copper deposit along the entire length of the metal sample, achievable with a simple tool. This crucial element for technical applications was quantified using the model 201 profilometer. The device, featuring a pointed probe, facilitates the monitoring of nominally rectilinear profiles of external and internal surfaces, such as those on the cathodes where copper is deposited in the setup. The roughness parameters consist of R_a (the arithmetic mean deviation of the profile) and R_z (the height of profile irregularities at ten points determined by profilometers using the profilometer and defined base dimensions). In this context, the arithmetic mean deviation of the profile was determined by the following expression:

$$R_z = \frac{\sum_1^5 |y_{pi}| + \sum_1^5 |y_{vi}|}{5} \tag{4}$$

where: y_{pi}– the height of the i$^{\text{th}}$ highest metal profile peak, y_{vi}– the depth of the i$^{\text{th}}$ deepest metal profile valley.

The arithmetic mean deviation of the R_a profile, which stands for the average of the absolute values of profile deviations within the base length, is calculated using the following expression:

$$R_a = \frac{1}{\ell}\int_0^2 | y(x) | \, dx \tag{5}$$

Determining the expansion coefficient of the deposit

One recognized method of waste utilization involves extracting pure metals from slags, which must possess specific characteristics. It is crucial to ascertain the expansion coefficient for various applications, such as copper plating and other growth processes. The coefficient of deposit expansion can be determined utilizing the MIS-II microscope, specifically for a thickness of deposited copper (coating) measuring 15 µm. The calculation was conducted using the expression provided below:

$$K_h = \frac{\Delta d}{2b} \tag{6}$$

where: $\Delta d = d_2 - d_1$, d_2 – width of the copper conductor after the deposit coating, µm; d_1 – width of the conductor before the deposited coating, µm; b – thickness of the deposit coating, µm.

The calculated coefficient, derived from the measured parameters, falls within the range of 0.45–0.85, which is considered acceptable. However, the irregularities result from the stratification of the working solution, both in the height of the cathode and in the horizontal component, and can be mitigated through structural and technological adjustments to the operational process.

Determining internal stresses

The internal stresses within the deposited metal were assessed utilizing the flexible cathode method. A metal plate, 0.08 µm thick and 60 mm long, was securely positioned in a vertical arrangement to serve as the cathode. The attachment of the element and current supply were executed at the lower end. Insulating lacquer was applied to one side of the cathode (opposite the anode), prompting the deposition of the extracted metal (copper) on the uncovered side. The resulting internal stresses induced bending in the cathode from the thin plate, and their magnitude was determined using a horizontal microscope equipped with a micrometric scale. Maintaining constant values for the deflection of the cathode plate, geometric data were employed to calculate the internal stresses, as outlined in the expression:

$$б = \frac{E \cdot d^2 \cdot \Delta}{3 \cdot \ell^2 \cdot h} \quad kg/cm^2 \tag{7}$$

where: E – elasticity modulus of the cathode material, kg/cm^2; d– thickness of the cathode base, cm; Δ – deflection of the cathode plate, cm; h – thickness of the deposited metal coating, cm.

The hardness of the electroplated coatings was determined using an indirect method, specifically Mendeleev's pendulum. This pendulum in the form of a horseshoe is supported by a diamond prism on the sample being tested. The hardness of the electroplated deposit (H) was calculated using the expression:

$$H = \frac{1}{(\frac{d \ln A}{dt})} \tag{8}$$

where: H – hardness of the deposit; $d\ln A/dt$ – logarithmic decrement of oscillation damping; A – amplitude of oscillations; t – time.

The hardness of the deposit on a known mineral hardness scale was 3 units (hardness determination by scratch method involves applying force to a diamond cone with a vertex angle of 90°, moving across the sample surface and leaving a scratch, the diagonal of which determines the hardness).

Researching extracted copper during the regeneration of aqueous solutions

In this investigation and selection of electrodes, characteristics necessary for operation in regenerators and other galvanic facilities were taken into account. Materials such as 08Kh17TM grade stainless steel (a corrosion-resistant alloy) and VT1-0 titanium (which has sufficient lightweight and good corrosion resistance) were identified for these purposes. Practical work with electrodes determined a thickness of 3 mm for practical usage. Preliminary studies of the parameters of metal extraction processes from spent etching solutions allowed determining a current density in the range of 15 to 25 A/dm^2.

The surface of the electrodes and its roughness were periodically mechanically treated during the tests, as confirmed by the 283 model profilometer. These measurements also allowed for determining roughness values, crucial for practical use in active installations. Microstructural investigations allowed for a continuous assessment of the quality of the deposited material and its further utilization in electrical engineering and other sectors of the national economy. For the convenience of conducting the studies, small plates (10×10 mm) were cut and filled with epoxy resin.

At the same time, microstructural studies were conducted on cut abrasive wheels and levelled plates of deposited metal. Prepared grinds were cut from characteristic parts and had dimensions convenient for research and result evaluation. Microslides were treated with sandpaper transitioning from larger to micron-sized grains to achieve a mirror-like surface. These operations aimed at reducing irregularities on the sample surfaces. The final mechanical treatment concluded with polishing using materials (felt with chromium oxide) and methods to achieve such a delicate operation. Further investigations to determine the microstructure of selected areas were conducted using degreasing with alcohol and a two-minute etching operation with a solution containing hydrogen peroxide and an aqueous ammonia solution. Subsequent microstructure studies were conducted using the MIM-7 microscope, designed for observing the microstructure of metals in normal light. The obtained results revealed that the surface of the copper deposit obtained during the deposition process is clean, free from electrolyte residues, and devoid of galvanic deposits. Dendritic growths of the fungus and other forms, as well as growths of porous deposited copper, are absent. This indicates the purity of the copper coating, suitable for coating various substrates of printed circuit boards using additive technology in production and as an electrical material for the production of conductive material after industrial remelting. The separation of the extracted copper during the regeneration process showed that cathodes made of VT1-0 titanium yield better practical results (copper easily separates from manually bent cathode plates), allowing titanium to be identified as the main element for use in the regeneration process and providing structural parts of the regenerator with strength.

To check the reproducibility of the results, the research was carried out using an electrochemical cell with dimensions of 0.25×0.25×0.5 m and correspondingly selected sizes of VT1-0 titanium electrodes and graphite anodes. The experiments were carried out under conditions similar to those given above. Reproducibility of parameters was established by mathematical processing of results; the results were considered acceptable because the difference between the average values of the deviations did not exceed the average deviation. After analysing the setup and developing a mathematical model for the electrochemical regeneration process, the operational parameters for the installation using a copper-ammonia solution have been established. Additionally, specific structural and technological aspects of the regeneration setup have been pinpointed, with the following specifications:

- Flow rate of the spent solution – 2 cm/s.
- Temperature of the spent solution – 40 °C.
- 3. Electrode gap distance (inter-electrode distance) – d = 20 mm.

CONCLUSIONS

Upon analysing the research outcomes, it can be affirmed that the implementation of a regeneration setup and the establishment of a sophisticated equipment complex, coupled with the simultaneous etching of printed circuit board substrates, will substantially diminish the discharge of spent solutions into wastewater treatment facilities. Additionally, it will reduce sludge accumulation in areas where enterprises engage in the production of printed circuit boards for radio-electronic applications and other associated technologies.

The research findings indicate that copper recovered in the regeneration process of spent etching solutions from printed circuit boards closely resembles copper obtained through electrolytic (industrial) refining. The metal's purity, grain size, grain boundary shapes, transitional zones, and crystal sizes exhibit remarkable similarity between copper obtained from spent etching solutions (i.e., wastewater) and industrially refined copper. The investigation outcomes highlight the efficacy of the galvanic method in coating components with pure metal. This method offers simplicity in achieving diverse coating thicknesses, allows for porosity control, and ensures good adhesion to the surface of treated components.

Despite the installation of a regeneration unit in the etching line, which increases the cost of the line (approximately) by $11,500, the economic effect of implementing new technology for wastewater treatment and reducing the amount of sludge for the estimated period (1 year) will amount to UAH 2,900,000 (> $70,000). At the same time, water saving ensures the process in one line reaches 8,300 m^3/year with the simultaneous release of 12,000 kg of copper. The characteristics of copper recovered from spent etching solutions align with existing standards for industrial-grade copper. These discoveries propose the potential utilization of copper recovered during regeneration in the electrical industry, encompassing the production of conductive materials, power equipment components, and machines.

Implementing systems that integrate the simultaneous etching of printed circuit board substrates with the regeneration of etching solution properties could enhance the operational conditions of specialized industrial facilities. This points toward a direction for similar enterprises to establish waste-free production schemes and reduce their environmental footprint. The suggested approaches to investigate coatings (metal plating) facilitate the development of equipment wherein a regenerator is essential. The primary component in this setup is an installation (electrolyser), where copper is deposited from a used etching solution onto the respective electrode. This research paves the way for crafting a low-waste technological process that utilizes aqueous solutions, thereby minimizing the impact on the surrounding natural environment. The future evolution of this field hinges on refining technologies and equipment based on current scientific knowledge. The introduction of novel scientific and technical advancements into production is essential to bring about improvements and substantial changes in environmental impact.

Among the directions that can also be proposed for further steps, the following can be identified:

- research of electrodes (materials of high precision processing, which will allow easy removal of copper without further cleaning of the surface of the electrode itself after a complex of deposition-taking operations) and in-depth research of the composition of the etching solution, which will allow increasing the speed of etching and regeneration;
- development of the mathematical apparatus for the etching-regeneration process.

The composition of equipment utilized in experiments and testing schemes lays the groundwork for ensuring the process of copper removal from spent aqueous solutions. The subsequent reuse of these solutions in the production process, without discharging them into wastewater treatment facilities and cities, exemplifies waste-free production schemes. Such initiatives should inspire further developments and implementations in manufacturing, ultimately aiming to curtail environmental impact.

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