

ABSTRACT

Electroplating in instrumentation. The development of silver coating technology of cutlery.

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The process of galvanic silvering of cutlery made of cooper – nickel - zinc alloy was developed in this project. The relevance of this project is that jewelry widely use galvanic processes in making production because of its high strength and economy. Silvered cutlery is becoming popular because it has the same antibacterial, esthetic and anticorrosive properties as pure silver. But silvered cutlery are characterized by greater strength and elasticity, lower thermal conductivity and price than silverware.

Cutlery are used for table setting and ingestion. Cutlery is constantly in contact with corrosive atmosphere, so it is necessary to apply a layer of metal for decorative and protective purposes. Silver coating was chosen to meet these requirements.

Surface area of 2 cutlery (1 spoon and 1 fork) is 2 dm². 24 μm of one-layer silver coating was chosen.

Standard electrode potential of silver (+0,799 V) is more positive than most other metals. This metal is resistant to most cold and hot acids, alkalis and salt solutions, and also into a number of organic compounds.

Silver coatings are used for:

1. high surface conductivity;
2. high electrical conductivity and abrasive resistance of electrical contacts;
3. decorative appearance.

Silver coatings can be created with different properties. It depends on composition of the electrolyte and process of electrolysis.

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One of the main conditions for high counting adhesion and required appearance of a product is high surface cleanness of parts. It's achieved by special preparatory operations before electroplating. The surface of parts can be contaminated with both inorganic (oxides, hydroxides) and organic (natural fats, mineral oil) substances. It influences on the choice of mechanical, chemical and (or) electrochemical methods of surface preparation.

Developed technological process includes the following preparatory operations:

1. two degreasing operations:
 - 1.1. solvent;
 - 1.2. electrochemical;
2. activation;
3. several stages of washing.

Degreasing requires preparatory operations. First stage is solvent degreasing (in tetrachloroethylene) for 0,5...5 min.

Electrochemical degreasing is performed on the cathode at 50-70 °C, current density is 2...10 A/dm² for 3...10 minutes in a solution of composition:

sodium carbonate - 20 ... 40 g / l;
 sodium phosphate - 20 ... 40 g / l;
 sulfonol – 0,1 ... 0,3 g / l.

The aim of activation is to remove oxide film from the surface of cutlery, but at the same time increasing of surface roughness influences on the coating adhesion.

In this case, the activation is performed for 0.5 ... 1 minutes in a solution of sulfuric acid- 50 ... 100 g / l at the room temperature.

After degreasing operations, the parts washed first in hot, then in cold water to remove reagents from the surface, and after activation – it was done only in cold water. This operation takes place for 0.25 ... 0.5 minutes - for degreasing, 0.15 ... 0.25 min - for activation.

Only complex electrolytes with high polarization of reduction silver are used for galvanic silvering. The most known electrolytes of silvering are:

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1. cyanide;
2. iron-potassium-ferrocyanide-thiocyanate;
3. thiocyanate;
4. iodide;
5. ammoniasulfosalicylate;
6. sulphite;
7. pyrophosphate-thiocyanate.

Cyanide electrolytes are characterized by high dispersive capacity, homogeneous fine-grained deposits, they also have a simple composition. But such electrolytes are very dangerous and toxic, so it is necessary to develop and put into production non-cyanide electrolytes.

The process of silver electrodeposition consists of two stages:

1. previous silvering;
2. principal silvering.

The previous silvering is performed in pyrophosphate-thiocyanate electrolyte that contains the following components (g/l):

silver nitrate –	2,5 – 3;
potassium pyrophosphate –	600;
potassium thiocyanate –	300.

The process lasts for 8 minutes, in standard conditions, current density: 0,5 A/dm² for the first 2 – 3 minutes, 0,1 A/dm² – for the last.

The pyrophosphate-thiocyanate electrolyte was chosen for principal silvering. It consists of (g/l):

silver nitrate –	50;
potassium pyrophosphate –	200;
potassium thiocyanate –	300;
sodium thiosulfate –	5;

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polyglyceride of alkenyl succinic acid – 0,6.

The process lasts for 78 minutes, in standard conditions, pH – 8,5 – 9,5; cathode current density – 0,6 A/dm².

The recommended method of silver depositing from potassium-pyrophosphate electrolytes intensifies and simplifies the technological process, provides high quality of silver deposit on the cooper and cooper alloys.

This electrolyte has a several advantages:

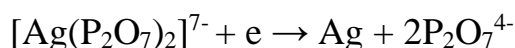
- high cathode polarization;
- fine-grained, bright deposits;
- insignificant internal stress of cathode deposits;
- high dispersive capacity;
- standard conditions of process (18 – 25 °C);
- absence of free cyanide;
- maximum cathodic and anodic efficiency (100 %).

Silvering cooper-nickel-zinc parts from cyanide electrolytes require additional process – nickel-plating. It's necessary because of high level of pH, which causes passivation of part surfaces. The potassium-pyrophosphate electrolyte has lower pH level than cyanide, so there is no need to deposit another metal layer.

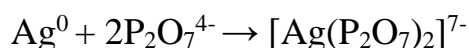
Potassium-pyrophosphate electrolytes for previous and principal silvering have the same compounds, so these two stages can be implemented without washing between them.

Chemical reactions that occur in the chosen electrolyte:

1) cathode:



2) anode:



Polypropylene galvanic bath was chosen for silvering process. It has such characteristics:

- length – 1250 mm;
- width – 710 mm;

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- height – 1000 mm.

Silver marks S 999.9 Ag is used as anodes.

Following operations are envisaged after silvering:

1. washing in standing cold water;
2. washing in running hot water;
3. drying.

Quality control is performed according to the following parameters:

1. appearance;
2. coating adhesion;
3. coating thickness.

Before the silvering 2...5 % of the parts from each bath, but no less than 3 units, are taken to control the surface condition due to require for basic metal.

After the silver deposition visual control is carried out over all details.

The surface of cutlery must be bright and smooth, must not have any flaking, blisters and other defects.

Coating adhesion is carried out by the method of heating. In the course of the measure, they are further heated to a temperature of 200 °C and maintained for 1 hour, after which they are cooled in air. After control, there should not be blisters and flaking.

Coating thickness is measured by non-destructive gravimetric method. It is based on determining the weight of the coating by weighing the parts on the analytical scales before and after the silvering. The method uses a determination of the average thickness of single-layer coatings, which mass can be determined by weighing on analytical scales with an accuracy class not lower than 2.0.

The relative error of the method is $\pm 10\%$.

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Waste water after silvering and other chemical preparations of the parts contain various toxic chemicals. Releasing them into open waters or city sewer without proper treatment is unacceptable.

In this project water cleaning has following order:

1. cleaning electrolyte fouls and waste water from reclaim rinse:
 - 1.1. reagent extraction of silver;
 - 1.2. electrochemical extraction of silver;
2. electrochemical oxidation of thiocyanate ions;
3. biochemical cleaning from phosphates;
4. mechanical and sorption filtering;
5. mixing of acid and alkaline wastewater and their ion-exchange cleaning.

In this project sedimentation of silver (chemical and electrochemical) from electrolyte fouls was developed. Silver is reduced at the steel cathodes at constant current density 0.5...0.05 A/dm² until the concentration of silver decreases to 7...8 g/l. Anodes are made of steel. Following components are added in the electrolyte:

1. 2...5 g / l potassium hydroxide to improve resistance of anodes;
2. surface active agent, which improves silver deposit quality (potassium thiosulfate etc.).

The next step is the electroextraction of silver at a current density of 5...10 A/dm². This process reduces the silver content in the solution to 0.3...0.5 g/l, then increases the concentration of hydroxide in a solution to 10...15 g/l and after that full sedimentation silver on aluminum foil is carried out. Foil with sediment is taken from the electrolyte, washed and treated with concentrated hydrochloric acid to dissolve the remnants of foil. All the silver collected can be washed and dissolved in nitric acid to further preparation of the electrolyte silver.

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Chemical extraction of silver from reclaim rinse is provided by evaporation of water and removing silver using hydrochloric acid and the following method:

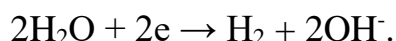
1. silver precipitating as a white gelatinous silver chloride precipitate, which allows to settle for at least one day;
2. checking the completeness of the precipitation of silver chloride by adding acid to the filtered sample solution;
3. filtering silver chloride precipitate through the thick cloth coarse and washing it;
4. drying at 105 ... 120 °C.

Electrochemical oxidation of thiocyanate ions occurs according to such reactions:

- 1) thiocyanate ions are oxidizing to CO₂ i N₂ at the anode:



- 2) reducing of hydrogen at the cathode:



Potassium chloride is added in order to intensify the process in waste water, that additionally oxidize thiocyanates:



Electrolysis takes place in an open non-diaphragm electrochemical bath with class-carbon anodes.

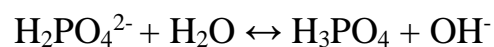
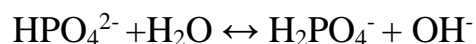
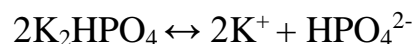
The advantage of this method is the maximum reduction of effluent, the lack of necessary chemicals, compactness and ease of operation of the equipment, the ability to automate the process.

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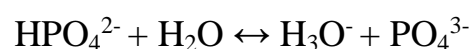
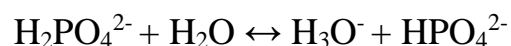
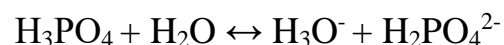
Phosphates from waste water are removed by chemical, physico-chemical and biological methods. The use of chemical and physico-chemical methods is currently limited, as they have a number of disadvantages: high cost reagents, secondary pollution, formed after application of coagulants. Now the biologic method of removal of phosphorus has become the most widespread.

In the process of traditional biological wastewater treatment, phosphates are consumed by microorganisms to increase the biomass of active sludge. Some quantity of the phosphorus complex forms is absorbed by flakes of active sludge. However, the amount of phosphorus, entering the treatment plants, increases the need for active sludge in it, therefore the traditional biological purification in aerotanks is not able to meet the requirements for the concentration of phosphates in purified effluent. That is why the biological method is combined with the chemical, which makes wastewater treatment more effective than with the application of each method separately.

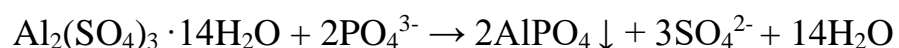
During the process of biological purification in the aerotank a hydrolysis of a complex form of phosphate (pyrophosphate) occurs by the reactions:



Orthophosphoric acid dissociates in three steps by reactions:



$\text{Al}_2(\text{SO}_4)_3$ is added into the secondary clarifier as a chemical reagent:



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One of the methods of chemical purification of acid-alkaline waste water is mutual neutralization. This method consists of mixing acid and alkaline effluents in a neutralizer, which is a container equipped with a mixing device.

The discharging of acid and alkaline waste water is usually different, resulting in the pH value of effluent after mixing usually less than 5. Therefore, to achieve a neutral medium with pH 6.5 - 8.5, it is necessary to additionally introduce alkaline reagents ($\text{Ca}(\text{OH})_2$).

For purification from organic substances, which are part of the electrolytes for basic silvering and electrochemical degreasing, the scheme has available activated carbon filter. Ion-exchange filters provide purification of ions Na^+ , K^+ , NO_3^- , $\text{S}_2\text{O}_3^{2-}$, that have left after the previous processing stages.

The complexity and high rate of flow processes in the chemical industry, their sensitivity to violations of processing and their high explosive and high flammable, harmful work environment leads to increased focus on automation of chemical and technological processes. Automatic control and process control provide high quality products, efficient use of raw materials and energy, extending the run overhaul of equipment, reducing the number of technical staff.

A system of test equipment and facilities management introduced in this project for getting information on basic parameters of the process of silvering provide automatically regulation of the values of these parameters within defined standards of the technological process. Automatic conduct of this process is provided by both the central control panel and the place of installation devices.

The purpose of automation production is the application of a silver coating on the cooper-nickel-zinc parts with specified quality parameters.

Addressing this goal is achieved by completing the following:

1. observance of costs of electrolyte according to the technological requirements;

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2. observance of concentrations of electrolyte according to the technological requirements;

3. observance of regime of electrolysis according to the technological requirements;

4. observance of temperature control of the process.

To meet these requirements assumed control of electrolyte level in the bath, the content of ions $P_2O_7^{4-}$, pH, temperature, current and voltage to the bath electrolyte expenses related regulation circuits.

In automated systems temperature measurement is based on the physical properties of bodies functionally related to the temperature of systems. Silvering process is carried out at temperatures of 18...25 °C. The temperature can be measured by different types of thermometers.

The composition of the electrolyte and its volume may change during silvering. The volume of the electrolyte may vary in its spraying when unloading the parts, that is why level should be automatically kept. With regard to changing the composition of the electrolyte, this fact can lead to poor quality of the formed coating, poor adhesion to the surface of the metal, so it should be automatically controlled.

Equally important process parameters are amperage and voltage, that depend on the current density. If there are problems with current density, the coating will deposit slowly or quickly and it will cause coating defects.

In this project basic technical economic indicators for process of silvering were calculated:

1. profit - 3 186,57 UAH/m²;
2. profitability - 46,77 %;
3. coefficient of economic efficiency - 0,44 UAH/UAH;

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4. investment - 47 164 772,15 UAH;
5. return period - 2,3 years;
6. cost price – 10 000 UAH/m²;
7. number of recruiting staff - 6 persons;
8. number of staff per list - 12 persons;
9. capital productivity - 38,85 UAH/UAH;
10. capital intensity - 0,03 UAH/UAH.

The results of calculations show the feasibility of establishing the company, since outputs of the projected plant is able to meet the needs of consumers and thus provide profit. Thus, the creation of the company is appropriate and cost-effective project.

Key words: electroplating, silver, galvanic bath, current density, previous silvering, principal silvering, pyrophosphate-thiocyanate electrolyte, waste water.

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