ABSTRACT

Electroplating in instrumentation. Development of technology silvering steel parts in the stationary electrolyser.

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In this project was developed process of galvanic silvering of steel balls for bearings. Diameter of the balls is 5 mm. They are used in instrumentation.

Requirements specification for appearance of counting:

1. uniformity;

2. absence of unevenness.

The parts are exploited in drilling equipment for drilling wells more than 600 m. Conditions of use:

1. neutral atmosphere;

2. temperature is of 65 °C;

3. humidity higher than 60%;

4. adaptable to friction.

In these conditions may local soldering of balls with body of bearing. For solving this problem is rationally to use silver-coating on the balls for improve of thermal conductivity.

It was chose 20 μ m of one-layer silver coating.

Standard electrode potential of silver (0.8 V) is more positive than most metals. This metal has a very high chemical stability in a humid atmosphere, sea water, caustic, chloride and sulfuric acid. It is antifriction material in the atmosphere of a vacuum, inert and some corrosive environments.

Silver coatings are used for:

1. high surface conductivity of parts;

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2. antifriction protection of bearings;

3. high electrical conductivity and abrasive resistance of electrical contacts;

4. decorative appearance.

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

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 as inorganic (oxides, hydroxides) and organic (natural fats, mineral oil) substances. It influence on the choice of mechanical, chemical and (or) electrochemical methods of surface preparation.

Developed technological process includes following preparatory operations:

1. three degreasing operations:

1.1. solvent;

1.2. chemical;

1.3. electrochemical;

2. etching;

3. activation;

4. several stages of washing.

Degreasing is required preparatory operations. First stage is solvent degreasing (in gasoline) for 5...10 min.

Then is chemical degreasing for 5 min at 80 ± 10 °C in a solution of the following composition:

sodium hydroxide - 25 g / l;

sodium carbonate - 50 g / l;

sodium phosphate - 15 g / l;

sodium silicate - 2 ... 3 g / l.

Electrochemical degreasing spends for 3...7 min on the cathode and for 2...3 min on the anode at 80 ± 10 ° C, current density is 2...10 A / dm², voltage is 0.3...12 for 5...10 minutes in a solution of composition:

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sodium hydroxide - $10 \dots 20 \text{ g / l}$; sodium carbonate - $20 \dots 30 \text{ g / l}$; sodium phosphate - $30 \dots 50 \text{ g / l}$; sodium silicate - $3 \dots 5 \text{ g / l}$.

Etching is performed after degreasing. Theme of this operation is in remove oxide films, rust and other inorganic compounds formed on the surface of parts.

For chemical etching steel usually used of chloride or (and) sulfate acids. They have difference mechanisms of influence on the steel. In this way was developed to use a solution of the following composition:

chloride acid - 150 ... 350 g / l;

urotropine - 40 ... 50 g / l.

The process takes for 45 ... 90 s at 20 ± 5 °C.

The aim of activation is to remove oxide film from the surface parts. Meanwhile increase surface roughness, which influences on the counting adhesion.

In this case, the activation is spend for $0.25 \dots 0.5$ minutes in a solution of potassium cyanide - 50 ... 100 g / l at room temperature.

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

For galvanic silvering are used only complex electrolytes with high polarization of reduction silver. It's known following electrolyte of silvering:

1. cyanide;

2. iron-potassium-ferocianide-thiocyanate;

3. iodide;

4. pyrophosphate;

5. ammoniasulfosalicylate.

This process includes two stages:

1. previous silvering;

2. principal silvering.

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First stage spends in cyanide electrolyte with following components:

silver nitrate - 3...4 g / l;

potassium cyanide - 80 g / l.

It works for 10 minutes, in standard condition, pH 10...12 and current density is 2 A/dm^2 .

Cyanide electrolytes have the largest cathodic polarization of silver, therefore these electrolytes have high throwing power. Their advantages also include possibility of intensifying the process by nonstationary electrolyze and (or) mixing. Despite these entire advantages cyanide electrolytes are harmful.

For principal silvering was chosen iron-potassium-ferocianide-thiocyanate electrolyte with following components:

silver nitrate - 25 ... 30 g / l;

potassium carbonate - 35 ... 40 g / l;

potassium hexacyanoferrate - 35 ... 40 g / l;

potassium thiocyanate - 80 ... 10 g / l.

It works for 63 minutes, in standard condition, pH 10..12 and current density is $0.6 \text{ A} / \text{dm}^2$.

This electrolyte is widely used for silvering, because it doesn't have of free cyanide ions. To oxidation of anode silver add potassium thiocyanate. Lacks of the electrolyte:

- 1. difficult for preparation;
- heavy losses of silver during its preparation (upon filtration of iron (III) oxide-hydroxide).

Advantages of iron-potassium-ferocianide-thiocyanate electrolyte:

1. quality coatings;

2. comparative safeness;

3. high throwing power;

4. good electrical conductivity;

5. nearly 100 % of current efficiency;

6. stable in work.

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Method of preparation the electrolyte to reduce losses of silver:

- 1. single dissolution of silver nitrate, potassium carbonate, potassium hexacyanoferrate;
- 2. bring the solutions to a boil;
- 3. mix them and boil for 1.5...2 hours;
- 4. during the appearance of red color is necessary add hydrogen peroxide for acceleration of the reactions:

 $2AgNO_{3} + K_{4}Fe(CN)_{6} = 2K_{2}Ag(CN)_{3} + Fe(NO_{3})_{2}$ Fe(NO_{3})_{2} + H_{2}O + K_{2}CO_{3} = Fe(OH)_{2} + 2KNO_{3} + CO_{2} $2Fe(OH)_{2} + O + H_{2}O = 2 Fe(OH)_{3}$

- 5. filtration of the solution;
- 6. dissolution of the iron (III) oxide-hydroxide in chloride acid and heating for sedimentation of silver chloride;
- 7. silver content analysis.

Poor quality silver coatings are removed by electrochemical dissolution of silver in the electrolyte. As cathodes is used glass-carbon or steel.

Selected drum for silvering has the following characteristics:

- maximum load 8 kg;
- volume 13.5 liters;
- speed 6 / min;
- circumcircle diameter 260 mm;
- length 505 mm.

Then choose a bath with the following dimensions, mm:

- length 930;
- width 610;
- height 800.

As anodes using silver marks S 999.9 An. They are placed in cases of chloride cloth. When anodes are not exploited they get out of the bath, cleaned and kept in a dry place.

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Dissolution of silver depends on the concentration of potassium thiocyanate and current density. To avoid anodic passivation should monitor the concentration of the electrolyte components.

After silvering are following operations:

1. washing in standing cold water;

2. washing in running hot water;

3. dry.

Quality control is performed on the following parameters:

1. surface roughness;

2. coating adhesion;

3. coating thickness;

4. appearance.

To control coating thickness are taken from each batch 0.1...1% of the parts, but not less than 3 units. This parameter is determined by non-destructive methods:

1. weight. This method is performed by direct weighing. With direct weighing coating thickness is determined by the change in weight parts before and after silvering;

2. eddy currents. It is based on the analysis of the interaction of external electromagnetic field with the electromagnetic field of eddy currents given in the object control.

Profilometer determines surface roughness.

Coating adhesion tested by heating. In carrying out the control parts are heated to 200 °C and kept at this temperature for 1 hour, after cooled in air. After monitoring should be no blistering or peeling of the coating.

Control of the coating appearance is performed on the all details that were made visually by light in a room with at least 300 lux at 20 ± 5 cm distance from the controlled surface. Coating should be closely linked with the base metal, without peeling, chip receiver, swelling and cracking. Each of the following sing is not a lack if they were detected on the coated surface:

1. uneven brightness and color;

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2. traces of water.

Plating waste 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 thesis, water purification has following order:

1. sewage from the electrolyzer:

- 1.1. extraction of silver;
- 1.2. oxidation of cyanide ions;
- 2. mixing of wastewater and their ion-exchange purification.

In this project was developed sedimentation of silver (chemical and electrochemical) from used electrolyte. Silver is reduced at the cathode of steel at constant current density $0.5...0.05 \text{ A} / \text{dm}^2$ as far as concentration of silver up to 7 ...8 g/l. Anodes are made of steel. In the electrolyte is added:

- 1. 2...5 g / l potassium hydroxide to improve resistance of anodes;
- 2. surface active agent which are for leveling action (potassium thiosulfate, thiourea, etc.).

The next step is the electroextraction of silver at a current density of $5...10 \text{ A} / \text{dm}^2$. Thus reduces the silver content in the solution to 0.3...0.5 g / l, then increases the concentration of hydroxide in a solution of 10...15 g / l and full sedimentation silver on aluminum foil. After checking the completeness of sedimentation 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.

Removal of silver from rinsing non-flowing baths is provided by evaporation of water and then removing silver from hydrochloric acid is made with using the following method:

- 1. silver precipitated as a white gelatinous precipitate silver chloride, which allow to settle for at least a day;
- 2. then make a check on the completeness of the precipitation of silver chloride by adding acid to the filtered sample solution;

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- 3. silver chloride precipitate is filtered through a thick cloth coarse and washed;
- 4. it is dried at 105 ... 120 ° C.

Electrochemical method oxidation of cyanide ions. At the anode cyanide ions oxidize to CO_2 i N_2 :

 $CN^{-} + 2OH^{-} \rightarrow CNO^{-} + H_2O + 2e^{-};$

 $2\text{CNO}^- + 4\text{OH}^- \rightarrow 2\text{CO}_2 + \text{N}_2 + 2\text{H}_2\text{O} + 6\text{e}^-.$

At the cathode reduce of hydrogen:

 $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$.

In order to intensify the process in sewage is added potassium chloride, which on the anode forms Cl₂, that additionally oxidize cyanides:

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-;$$

 $\text{Cl}_2 + \text{CN}^- + 2\text{OH}^- \rightarrow \text{CNO}^- + 2\text{Cl}^- + \text{H}_2\text{O}.$

When the anode current density of 0.5 \dots 2 A / dm² degree of wastewater from cyanide reaches 100%.

Electrolysis is conducted in an open non-diaphragm electrochemical bath with class-carbon anodes.

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

Wastewater is neutralized by the following reactions:

$$NaOH + HCl = NaCl + H_2O$$

$$Na_2CO_3 + HCl = NaCl + H_2O + CO_2$$

First they are cleaned in mechanical and then in the sorption filter with coal, because there are organic materials (waste coal burning). Next runoff entering the ion exchange column output are purified water.

The complexity and high rate of flow processes in the chemical industry, their sensitivity to violations of processing and their high explosive and high flammability, harmful work environment leads to increased focus on automation of chemical and technological processes. Automatic control and process control

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provide high quality products, efficient use of raw materials and energy, extending the run overhaul of equipment, reducing the number of technical staff.

In this thesis project for getting information on basic parameters of the process silvering and automatically maintain the values of these parameters within defined standards of the technological process introduced a system of test equipment and facilities management. 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 steel parts with specified quality parameters.

Addressing this goal is achieved by completing the following:

1. compliance costs electrolyte technological requirements;

2. compliance concentrations of electrolyte technological requirements;

3. compliance regime electrolysis technological requirements;

4. compliance with temperature control process.

To meet these requirements assumed control of the bath, the content of ions CN-, 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 the latter. Silvering process are at temperatures of 18 ... 20 $^{\circ}$ 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. As the density of the coating will be printed slowly and at too high coverage is poor.

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

- 1. profit 1 500 UAH / m²;
- 2. profitability 27,16 %;
- 3. coefficient of economic efficiency 0,3 UAH / UAH;
- 4. investment 35 680 787,77 UAH;
- 5. return period 3,34 years;
- 6. cost price 5 023,24 UAH / m^2 ;
- 7. number of recruiting staff 3 persons;
- 8. number of staff per list 6 persons;
- 9. capital productivity 77,26 UAH / UAH;
- 10. capital intensity 0,013 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.

Keywords: electroplating, silver, galvanic baths, drum electrolytic balance voltage electrolysis, wastewater.

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