Abstract

Galvanic plating in engineering. Development of technological process of protective copper coating on steel details.

Alabut O. Kyiv: NTUU “Igor Sikorsky KPI”, ChTF, Che-41

Diploma project, 2018. The number of pages – 105, tables – 21, pictures – 8, sourses – 17.

To protect steel parts from corrosion, a technology has been developed for galvanic coating of copper in a galvanic line with a capacity of 13,000 m^2 / year.

The selected part is a steel grounding rod, 1.5 meters long and 10 mm in diameter, on which it is necessary to precipitate 250 μm of copper. The pins have a high tensile strength (600 N / mm^2) and can be immersed in the soil with a jackhammer to a great depth - up to 40 meters. To ensure corrosion resistance, cathodic protection with copper coating is used. Copper coating should have good adhesion to steel, be solid and without pores. Therefore, to precipitate copper directly to the steel, 9 μm of copper from the cyanide electrolyte is first deposited, and then the precipitation is conducted from the cheaper and higher-speed sulfate electrolyte.

The composition of copper cyanide electrolyte:

CuCN	40...50 g/l
NaCN	45...55 g/l
NaOH	3...5 g/l
Na_2CO_3	10…15 g/l

Conditions of electrolysis:

1. temperature 40-45 ºC;

2. cathode current density up to 1,5 A / dm^2;

3. pH 11-12;

4. Rocking cathode rod.

The following electrochemical processes take place in the cyanide electrolyte of copper plating on electrodes:

$$(K) : [Cu(CN)_3]^{2-} + e^- \rightarrow Cu + 3CN^-$$

$$H_2O + e^- = 0,5\ H_2 + OH$$

$$(A) : Cu + 3CN^- = [Cu(CN)_3]^{2-} + e^-$$

The current output at the cathode is 70%.

The key factor in the manufacture of high-quality copper plating for the grounding pin is the creation on the steel billet of a strong homogeneous copper coating of the required thickness with minimal impurities. The main characteristics of high-quality copper plating are:

- plasticity of the coating: high-quality copper coating ensures no cracks in the deformation of the grounding prong, which can occur during installation in the soil;

- adhesion (adhesion) to the substrate: a high adhesion value of the copper coating to the steel base ensures that the coating does not exfoliate at high mechanical loads, for example, when the grounding pin is immersed in the ground. Such adhesion makes it possible to extrude threads on pins after copper plating with the use of rolling technology, ensures the preservation of the thickness of the copper layer on the thread (250 µm), which can not be done using threading technology before copper plating *;

* Features of creating threads

The "correct" thread is applied after the copper plating by knurling, because only this method allows to achieve a high overall quality of the pin.

The alternative "technology" of copper plating with the already existing thread (before coating) is cheaper, but it shows the worst (and dangerous in the operation) result.

This is due to the peculiarity of electrolysis: the thickening of the coating in depressions / depressions, through which the base material (steel) on the thread can be covered only with a thin (0.03-0.05 mm) copper layer.

Such a thin coating is easily damaged when mounted by impacts and friction in the coupling. Later, during the operation of an electrode grounding with such disturbances, electrochemical corrosion (copper-iron) centers appear, leading to its complete destruction within 2-3 years.

- thickness of the copper layer: for the earthing pins, a layer thickness of at least 250 μm (0.25 mm) is needed. Such a value characterizes the mechanical resistance of the coating - during the immersion of the pin it is subject to friction and damage by solid elements in the soil, as a result of which the thickness of the copper decreases. The layer remained to guarantee the service life of the grounding pin for at least 30 years in aggressive soils (100 years in ordinary soils).

So, the part is used in soils (conventional, aggressive or hard with the presence of gravel or small building debris). During installation, it can be mechanically damaged. Consequently, the operating conditions can be referred to as complex.

Advantages of cyanide electrolyte copper plating - a sufficiently high dissipative capacity. When used, copper settles directly on iron and steel parts, and has good adhesion to the base metal. Precipitation of copper from cyanide electrolytes occurs at high cathodic polarization. Precipitation from cyanide electrolytes is characterized by a fine crystalline structure and a low porosity. However, cyanide electrolytes are prepared from poisonous, scarce and expensive salts and require frequent adjustments. In addition, cyanide electrolytes are characterized by a low current yield.

Cyanide electrolytes can work at room temperatures and low concentrations only at sufficiently low current densities. The current yield in cyanide electrolytes usually does not exceed 60-70%. To increase the current density in this graduation project, a swinging cathode rod is used and the temperature of the electrolyte increases to 40 degrees.

For the application of copper coating in the project developed a technological process, the scheme of which is shown on the poster number 1.

To provide conditions for obtaining quality coverage, preliminary preparation of details is carried out:

1. Degreasing is designed to remove from the surface of the details of the layer of grease contaminants that were formed during the manufacture and storage of details. Conducted at a temperature of 60-80 ^oC, for 3-20 min.

The solution contains

NaOHtech.	5-15
Na_2CO_3tech	15-35
Na_3PO_4tech	15-55
Sodium liquid glass	25-30
Syntanol DS-10	3-5

2. Degreasing Electrochemical:

Mode of electrochemical degreasing: t = 70-90 ° C and = 2-10 A / dm2. Reverse current is used to prevent the flooding of steel parts.

Processing time: 15-20 min.

NaOHtech.	5-15
Na_2CO_3tech	15-35
Na_3PO_4tech	15-55
Sodium liquid glass	25-30

3. Since the steel parts have a rust layer, it is necessary to carry out chemical etching of the parts. Conducted within 0,5-2 min. In solution containing:

HCl GOST 857-78 200-250 g/l

Inhibitor 3-5 g/l

4. Activation is intended for removal of thin layers of oxides from a surface. Conducted within 0.25-1 min. In solution:

NaCN	3-5%

5. Electrochemical coppering. Carry out a meeting in the center of $Cu(CN)_2$

$Cu(CN)_2$	40-50
NaCN	45-55
Na_2CO_3	10-15
NaOH	3-5

5. The neutralization is then carried out

NaOCl	180-200 g/l

6. Activation is intended for removal of thin layers of oxides from a surface. Conducted within 0.5-1 min. In solution:

HCl	30-50 g/l
H_2SO_4	30-50 g/l

7. Basic Copper

H_2SO_4	50-70 g/l
$CuSO_4$	150-250 g/l

8. Next, washing and drying

To fulfill the annual program of 13 000 m^2, a PVC bath with a wall thickness of 40 mm with a dimensions of 2000x630x1000 mm was chosen. The bath is equipped with airborne ventilation, heated electrolyte tents and a swinging cathode rod with an amplitude of 10 cm. The parts are suspended on a frame-type suspension. The current in the bath is 74,18 A, the voltage is 3,63 V.

The quality of the coating obtained must comply with the requirements of GOST 9.301-86.

Quality control is carried out according to the following parameters:

The porosity of the coating is determined by the immersion method. During the inspection, the part is immersed in a solution of the following composition (g / l) [6, p.10]:

$K_3[Fe(CN)_6]$ ... 3

NaCl ... 10

It is held in it for 5 minutes at a temperature of 18-30 ° C. On the monitored surface, the number of blue dots formed corresponding to the number of pores is counted. Control of the appearance of the coating is carried out on 100% of the details by inspection with the naked eye. The coating should be firmly adhered to the base metal without peeling, splitting, blinding and cracking.

The coupling force is controlled by the heating method of 200 ° C and an elongation of 1 hour, followed by visual control of the coating surface. No swelling or peeling of the coating should be observed on the monitored surface.

The coating thickness is controlled by destructive or non-destructive methods. In this graduation project, the coating thickness is determined by a non-destructive method using thickness gauges - instruments designed to measure the thickness of non-magnetic galvanic coatings on a ferromagnetic basis without destroying the coating. In devices based on the principle of detachment of a magnet, use a permanent magnet, a calibrated spring and a graduated scale. There is an attraction between the magnet and the steel base. The coating weakens it. The thickness of the coating is determined by the amount of peel force.

The thickness and strength of adhesion is monitored for 0.1-1% of products, but not less than 3.

To optimize the process of applying copper coatings, reduce the cost of manual labor and strictly follow the rules of the process, the bath is equipped with an automatic regulation and regulation system.

The main parameters associated with debugging an automatic line are:

- temperature;

acidity of the electrolyte;

- the level of electrolyte in the bath;
- current and voltage in the bath.

The automation scheme includes measurement, automatic control and registration of these parameters.

The automation scheme includes measurement, automatic control and registration of these parameters.

In economic and organizational calculations, the department was calculated as an object of the economy: the optimal type of movement of labor objects was calculated, the number of employees and their schedule, technical and economic indicators of production:

- the prime cost of coverage is 849 UAH/m^2;
- investment 2560700,27 UAH;
- profit is 1147523 UAH/year;
- profitability 11,3%;
- period of return of investments 2,23 years.

This project provides for the treatment of sewage, which is formed during application of galvanic coating. This project involves the treatment of wastewater, which is formed by the application of galvanic coating. Sewage entering the treatment after the process of copper plating and contain acids, alkalis, copper ions and cyanides with small amounts of copper fall into the tanks settling tanks.

For neutralization of acidic and alkaline waste drained from the sumps of the tanks in the neutralization reactor, there is also provided H_2SO_4 and CaO to maintain the reactor pH 8 ... 10. In the neutralization reactor is also fed effluent from the settler tank containing copper ions to convert them into soluble hydroxide $Cu(OH)_2$. Then the reactor is fed into the neutralization mixture clarification tank where precipitates $Cu(OH)_2$ with a small amount of $CuSO_4$, and $Cu_3(PO_4)_2$. The wet slurry enters the filter press. Sludge after dehydration is withdrawn in special containers and sent for processing.

In the clarification tank remains a solution containing NaCl with a pH of 8 ... 10, which fall further into the reactor neutralizer.

Sewage waters of the sedimentation tank containing CN^- ions with a small content of copper ions enter the oxidation reactor, NaOH and NaClO are also fed there. Oxidation of simple and complex cyanides of active chlorine occurs in an alkaline medium at a pH of 11 ... 12 translation process occurs cyanides and cyanates to convert the cuprous ions in soluble hydroxide $Cu(OH)_2$.

When treating cyanide-containing effluents with hypochlorite, the following reactions occur:

$$CN^- + OCl^- \rightarrow CNO^- + Cl^-$$
$$2[Cu(CN)_3]^{2-} + 7OCl^- + H_2O \rightarrow 6CNO^- + 7Cl^- + 2Cu(OH)_2\downarrow$$

The solution is then fed to a filter where the $Cu(OH)_2$ precipitate is removed, and the solution remaining is fed to the hydrolysis and decomposition reactor where HCl is fed to form a pH of 4 ... 6.

The reaction in the reactor is as follows:

$$2CNO^- + 3ClO^{2-} + H^+ \rightarrow 2CO_2\uparrow + 3Cl^- + 2N_2\uparrow + H_2O$$

After hydrolysis and decomposition reactor obtain a solution of NaCl, which, together with alkaline and acidic waste effluent enters the neutralization reactor, there is fed the HCl and NaOH to maintain the pH in the reactor 5,5..7. Further, the effluents are fed to a mechanical filter to remove suspended solids, and then to an activated carbon filter to remove organic impurities from the solution.

Subsequently the solution enters the apparatus for reciprocating osmatichnogo purification, whereby we obtain desalted water, which subsequently returns to manufacture, and the resulting solution is NaCl at a concentration of 20 ... 100 g / l is electrolysis, where the following reactions occur:

At the cathode: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

At the anode: $2Cl^- \rightarrow Cl_2 + 2e$

$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e$

$\sum NaCl + H_2O \rightarrow NaClO + H_2\uparrow$

As a result, we obtain a solution of sodium hypochlorite, which again enters the oxidation stage of cyanides.