ABSTRACT

Galvanic plating in instrumentation. The development of technological process for hard wear resistant chromium plating on steel parts.

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Diploma project, 2019. Number of pages - 94, tables - 22, pictures - 4, literature - 31.

A wide range of applications of electroplating coatings causes their use in many industries. Electroplating coatings are often designed to protect against corrosion and / or surface coatings of certain functional features such as high hardness, surface reflective ability, wear resistance, antifriction properties, etc. The advantages of the galvanic coatings are the thickness adjustment and some other parameters (shine - eliminates the need for polishing, the color - the use of black nickel in optics, the structure - decorative coating "crystallite") layer of metal, which is applied. As a result, economic efficiency increases (no overhead of components).

The use of chrome coatings is due to the following features: chemical resistance, wear resistance, high hardness. Also, the chrome wear-resistant coating can be used to restore the size of the part, which is important when working with products that have rigid tolerances in size. Under the action of oxidizing agents and in the open air, a thin passive oxide film is formed on the surface of the chromium coating. This film protects against corrosion.

The purpose of the diploma project is to develop a technology for applying hard wear-resistant chrome coating on steel parts with a productivity of 7 000 m^2 per year. The optimum conditions of the process have been selected, in which a qualitative coating is obtained, which protects the parts from corrosion and increases their wear resistance.

A wear-resistant protective chromium coating is applied to a steel shaft. The item is a blank offset roller.

According to its purpose, the component is operated under constant moisture, under the action of load and abrasion. The water contacted by the shaft has the following characteristics: hardness – 0.89-2.67 mmol/l Ca^{2+}, pH 4-6, conductivity 800-1500 μSm. The features of the humidifying system and the offset machine itself lead to the fact that water specifications in the printing process are changing. The main reasons for this are the pH and the structure of the paper - when the paper is contacted with an offset shaft, a piece of paper in one or another amount is separated from the web and is transferred to the humidifier by an offset shaft. To adjust the amount of moisture transferred to the offset shaft, the dosing chrome shaft is pressed against a roller shaft with a certain force. In turn, the shaft shaft is also pressed with a certain force to the offset shaft, the shaft of the humidifying and dyeing apparatus. When manufacturing a shaped shaft, the thickness of the chromium coating depends on the future relief of the pattern. The drawing itself is applied to the surface of the shaft using a laser.

For the covering of the part according to DSTU 9.303-84 for all operating conditions, the thickness is regulated by the intra-industry documentation, according to which we choose the deformity of a luminous coating of 17 microns with the previous application of copper (20 μm) to ensure corrosion protection of the base of carbon steel shaft.

The use of chrome coating is due to the following features: chemical resistance, wear resistance (in comparison with steel increases 2-20 times), high hardness (HV 750-1200). Chromium wear-resistant coating can also be used to restore the size of the component, which is important, since the offset machine is not insured against ingress (and as a consequence, between the shafts) of a variety of solid components (wrenches, rods, other tools used in the printing), which are able to significantly damage the shafts. Under the action of oxidizing agents and in the open air, a thin passive oxide film is formed on the surface of the chromium coating. This film protects against corrosion.

There are several methods of chromium application: electroplating, chemical, spraying, diffusion method. The diffusion method consists in the saturation of the surface layer of the metal with chromium by the action of mixtures with chamotte and ferrochromium with hydrochloric acid. But this method does not allow to obtain chromium coating with the necessary hardness. The method of vacuum spraying is usually covered with dielectrics. This method provides a uniform, thin chrome coating, but requires complex equipment, and the metal layer is so thin that it is covered with varnish for protection against scratches. Chromium electrolysis is the most optimal option, since it fully satisfies the necessary hardness and durability parameters.

For the project, a two-layer copper-chromium coating has been selected which will provide high corrosion resistance and hardness of the shaft.

Durable metal-base screed with a coating is a prerequisite for obtaining a quality product. In order to achieve this result, it is necessary to clean the surface of the parts qualitatively from the fats, greases and oxides. The high quality of the surface preparation before applying the coating also determines the beautiful appearance of the product.

Since the parts from the machining shop come with traces of the lubricating coolant, they contain on their surface organic pollutants, as well as oxides, hydroxides, salts, mechanical contamination, which fell on the part during transportation. In the preparation of the surface of products used electrochemical and chemical operations.

Electrochemical degreasing. An effective way of cleaning the surface from greasy contaminants is electrochemical degreasing. It combines the sapulating effect of alkaline solution with the separation from the surface of the part of the fat contamination by gas, which is formed on the surface of the electrode. Electrochemical degreasing allows you to process in less concentrated solutions than chemical. This reduces the cost of reagents and sewage treatment. Such processing can be carried out both on the cathode and on the anode. The problem of the cathode process is the flooding of the part requiring subsequent heat treatment. Therefore, electrochemical degreasing is carried out in a stationary bath at anode polarization of parts. The details are hung on an anode without a current.

Composition of the solution for degreasing:

1) NaOH tech. GOST 2263-79 10-20 g/dm^3

2) Na_2CO_3 tech. GOST 5100-85 20-30 g/dm^3

3) Na_3PO_4 tech. GOST 201-76 30-50 g/dm^3

4) Glass of sodium liquid GOST 13078-81 3-5 g/dm^3

The mode of electrochemical degreasing: t = 70-90 °C, and = 2-10 A/dm^2. Processing time: 15-20 min.

Degreasing is carried out until the surface is completely wetted with water. To check on the part pour purified water and, if the water flows through a uniform film - degreasing is carried out successfully and the surface is cleaned.

Washing. Details are washed in hot running water. Apply the drinking water DSanPiN 2.2.4-171-10. Water temperature: t = 60-75 ◦C. Processing time: 0,25-0,5 min.

Digestive Chemistry. Conducted after removal of fatty deposits from the metal surface to remove oxides, hydroxides and other chemical compounds that appear on the surface during storage in the warehouse due to interaction with the surrounding environment. Conduct in a stationary bath with local exhaust ventilation. Since in chloride acid dissolves mostly oxides, we use it precisely.

Composition of the solution for digestion:

1) HCl GOST 857-95 200-250 g/dm^3

2) Urotropin inhibitor 3-5 g/dm^3

Process temperature: t = 18-25 °C. Processing time: 20-40 min.

Control. The surface of 100% of the parts is checked for boring (it is not allowed to have coarse pores, broad bands with a distinctly different crystalline structure, flaking, the presence of slag formations on the surface, visible areas of different degree of etching are visible to the naked eye - visible light and / or dark, etching cracks, through openings) with a visual overview and comparison with reference photographs.

The literature describes a large variety of electrolytes of chromium. It is known that the deposition of this metal is impossible from the solution of chromium oxide without the presence of foreign ions. Often, such an ion is SO_4^{2-}, but there are also electrolytes with F-containing yones, sulfate-silicon fluoride (SO_4^{2-} and SiF_4^{2-}), tetrachromatous (complex, intended for application of protective and decorative plastic coatings), electrolyte with additives of zinc and cadmium cations, and electrolytes with additives of organic compounds.

Fluoride electrolytes. F-containing electrolytes are used for cold chrome plating in bells and drums, as well as for wear-resistant chrome plating. Compared to sulfate electrolytes, fluorides have better scattering and coating capacity, greater current output (up to 30%), permitting a process at lower current densities (0.5-2 A/dm^2). But at the same time they are more aggressive, passive anodes with the formation of lead fluoride film (has a high electrical resistance). Precipitates derived from such electrolytes have less hardness and greater plasticity than those obtained from conventional sulfate electrolytes.

Sulphated and super sulphate electrolytes. Sulphate electrolytes of chromium allow to get matt precipitate of dairy and hard chromium. They are easy to prepare, but have a low current output of chromium (up to 13%), and the quality of the coating strongly depends on the concentration of the components of the electrolyte. Precipitation is carried out at a temperature of 35-70°C, maintaining a constant ratio of chromic anhydride to the content of sulfate ions 100:1.

The superphosphate electrolytes in the composition are close to the cathode layer. They are recommended for fast application of thick brilliant chrome coatings (up to 1 mm), but require constant adjustment of the composition and use of special suspended devices, which have low scattering ability.

Sulfate-silicon fluoride electrolytes. These electrolytes are capable of maintaining a stable ratio of chromic anhydride to the content of sulfate ions due to the insoluble salt $SrSO_4$. K_2SiF_6 ensures the stability of the electrolyte. But the presence of F-containing ion results in the destruction of a steel bath of chromium and other equipment.

Electrolyte "Limeda X-3". Today, the most common electrolyte of hard wear-resistant chromium is "Limeda X-3". The electrolyte is low concentrated, consists of chrome anhydride and additives of Limeda X-3, which is consumed only when carrying out the electrolyte. This electrolyte allows coating on steel, copper, copper and zinc alloys, nickel, cast iron and aluminum. Hardness of chrome coatings with a layer thickness of 1 μm is 1000-1100 kgf/mm^2. The electrolyte is stable in operation, easy to prepare and operate. Advantages: reduction of environmental contamination due to lowering the concentration of chromic anhydride; saving of chemicals both for the process of chromium plating and for further neutralization of washing waters; increase of precipitation rate in 1,5-2,0 times; Possibility of coatings up to 800 microns; Possibility to exclude polishing at a thickness up to 60 microns; higher scattering capacity of the electrolyte compared to other electrolytes; The resulting microcrystalline layer of chromium, starting with a thickness of 0.3 microns, provides high corrosion resistance of parts; the possibility of covering a large thickness in several stages. The process temperature is 30-55 °C. The current density is 7-30 A/dm^2.

Since the coating requirements are to provide hardness, wear resistance and corrosion resistance, then choose an electrolyte based on chrome anhydride "Limeda X-3". It makes it possible to obtain a hard wear-resistant chrome finish that does not require polishing to a thickness 60 microns, has a beautiful appearance and fully satisfying requirements.

Component	Contents, g/l	Deposition mode
CrO_3	80-120	30 - 55 °C 7 – 30 A/dm^2
«Limeda X-3»	2-3	

Anodes are used from lead alloy and stibium (≈6%). During the electrolysis, the anodes are coated with a PbO_2 film that catalyzes the oxidation of trivalent chromium and protects lead from further fracture.

The anodes use a rectangular shape, a thickness of 5 mm, a length of 1100 mm and a height of 234 mm. On 1 rod we place 1 anode.

On the surface of the anode, reactions take place:

1. $H_2O \rightarrow \frac{1}{2} O_2 + 2 H^+ + 2e$ ($O_c = 95\%$);
2. $Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e$ ($O_c = 5\%$).

Rinse in the bathtub trapping. When working with the electrolyte of chromium binding is the operation of capturing the maximum amount of chromium from washing waters. This is achieved by the use of a catching bath. Details are washed in cold water for a period of 0.25-0.5 minutes in a stationary bath. Subsequently, the water from the bath of capture is used to adjust the composition of the electrolyte of chromium.

Drying. Dry parts by hot air in the drying cabinet. The operation is performed until the moisture is completely removed at a temperature below 70 °C. Drying time: 10-20 min.

Control. Check the surface condition of 100% of parts in accordance with GOST 9.301-86. The presence of uncovered places is not allowed, the color of the coating should be silvery with a blue hue. The coating must be firmly glued to the substrate. The hardness of the coating is checked.

Hardness of coverage. The hardness test is performed according to ISO 410-82: a solid alloy ball with a diameter of 5.0 mm with an effort of 7355 N is pressed in the coating for 10 seconds. If the print is within 0.24-0.6 D (diameter of the ball), then the test is passed. The check is carried out with the help of the Brinells TB 5005A.

The strength of the clutch is determined by an electronic adhesive for GOST 28574-2014 by the method of normal separation of a steel disk. The adhesive PSO-1MG4 has been selected to control the adhesion strength. A steel disk is glued to the surface of the tested specimen; the time required for gluing is removed, the excess glue is removed; the edge of the disk on the surface of the sample is cut; The device employs the effort to tear off the steel disk from the surface of the sample. The data on the strength of the coupling are displayed on the electronic scoreboard. The measuring range of the grip strength value is from 0.1 to 35 mPa.

Control of the appearance of the coating is made on 100% of the parts by inspection with the naked eye in a room with lighting not less than 300 lux at a distance of 20 ± 5 cm from the monitored surface. On the surface of the covered part there is no shortage of the following features:

1. unevenness of light and color;
2. traces of water stains.

Low-quality chromium coating is removed in a solution of H_2SO_4 80% anode dissolution for a current density of 3-5 A/dm^2.

The actual annual operating time of the equipment is 3828 hours.

Annual production program - 7210 m^2, hourly – 1,88 m^2/hour.

The duration of the chrome is 40 minutes, and the production cycle is 133 minutes.

A bath of chromium was developed, based on the size of the part (diameter 273 mm, length 1000 mm). The bath has the following dimensions: internal length - 1300 mm, internal width - 1600 mm, internal height 640 mm; bath volume 1,33 m^3.

Two annual duplex baths are required for the annual program. The download factor is 0,8.

To select the power source, the balance of current and voltage was calculated. Since chromium is produced at a current density of 25 A/dm^2, the current strength is 2207 A. Based on the difference between the electrode potentials of the anode and the cathode under the current, the ohmic drop in the voltage in the electrolyte, in conductors of the first kind and in the contacts, the voltage in the bath was calculated - 10,61 V. The selected rectifier unit has a thyristor rectifier with a pulse current mode and a transformer connection to the network. The overcharge factor for the rectifier unit is 0,62.

The energy balance, which consists of electric energy supplied to the electrolyzer, chemical energy and thermal energy, was compiled.

A heat dissipation was made to determine the need for heating or cooling the bath during operation. Since a large amount of thermal energy is emitted, the maximum heating temperature of the bath was determined - 300 °C. This means that there is no need to install electric heaters in the body of the bath, but it is necessary to bring the cooling down. Taking into account heat consumption for the heating of the electrolyte, bath material, anodes and heat losses to the environment through the body of the bath and electrolyte mirror, the amount of water required for maintaining the operating temperature of the bath at 40 °C is calculated at 10,33 kg/hr.

The cost of anodes for starting equipment is estimated at 45,3 kg, and for the implementation of the annual program, taking into account the annual program of chromium plating, 13 kg. Altogether for a year of work 58,3 kg of andnd material is necessary.

The consumption of chemical reagents for the launch of equipment and the implementation of the annual program together is: CrO_3 - 868 kg, "Limeda X-3" - 25,9 kg. In total, for a year, washing operations, preparation of electrolytes, decomposition at electrolysis, removal with gases, evaporation from the surface of the electrolyte and cooling costs 15591,9 m^3 of water.

The complexity and high speed of the technological processes in the chemical industry, their sensitivity to the violations of the regime, as well as their increased explosive and flammable and harmful working conditions, leads to increased attention to the issues of automation of chemical and technological processes. Automatic control and control of technological processes ensure high quality of products, rational use of raw materials and energy, lengthening of equipment repair intervals, reduction of technical staff numbers.

In this diploma project, for the purpose of obtaining information on the values of the main parameters of the technological process of hard wear-resistant chromium and automatic maintenance of the values of these parameters, within the limits set by the norms of the technological regime a system of control and measuring devices and control devices is introduced. Automatic maintenance of the process of chromium plating is provided both from the central control panel and the place where the devices are installed.

The purpose of automation of this production is the application of hard wear-resistant chrome coating on steel parts with the specified quality indicators.

The decision of the set goal is achieved by the following requirements:

1. Correspondence of the cost of electrolyte technological regulations.

2. Correspondence of the given temperature in the bath to the technological regulations.

3. Correspondence of concentration of electrolyte components to the technological regulations.

4. Correspondence to the regime of electrolysis technological regulations.

To meet these requirements, it is envisaged to control the level of the bath, control the amount of electricity lost, monitor the content of chromic anhydride and the current and voltage in the bath with the appropriate control circuits.

Qualitative coatings from the electrolyte "Limeda X-3" are received in the frame of 30 to 55 °C. In the electrolysis process, the electrolyte can heat up to 300 °C, so it is necessary to maintain temperature constancy.

In the process of chromium plating, the composition of the electrolyte and its volume may vary. The volume of the electrolyte may vary when sprayed during the unloading of the parts and the carving of the parts themselves. With regard to the change in the composition of the electrolyte, this fact can lead to deterioration of the quality of sediment, poor adhesion to the metal surface. That is why the constant composition of the electrolyte (by density) and its level should be automatically maintained.

The basic technical and economic parameters of the shop for obtaining protective chrome coating on steel parts and the full cost of production were calculated.

The profitability of the designed workshop is 19.74%, at a productivity of 7713 m^2/year with a cost of 375.82 UAH/m^2.

The obtained results of calculations indicate the expediency of creating an enterprise, since the products produced by the designed shop can meet the needs of consumers while ensuring profit. Thus, the creation of this enterprise is a feasible and cost-effective project.

Sewage formed during application of electroplating coatings, in the chemical and electrochemical treatment of metals, contains various toxic chemical products. The discharge of these waste water into open water or in urban sewage networks without proper cleaning is prohibited.

The reagent method of sewage treatment can be used without limitation on the concentration of hexavalent chromium.

To restore hexavalent chromium we use sodium sulfate Na2SO3.

The reaction of hexavalent chromium recovery proceeds rapidly in an acidic medium at a pH of 1-2:

1. $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
2. $Cr_2O_7^{2-} + 3HSO_3^- + 5H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

Next, the Cr3 + ion binds to insoluble chromium hydroxide (III) by adding to the solution of technical sodium hydroxide.

$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3$

Insoluble chromium hydroxide is deposited in the settling tank.

Chromium, acid and alkaline sewage are fed into a sandwich.

Acid and alkaline effluents fall immediately into the neutralizer. Chrome-containing wastewater is treated with sodium sulfite in an acidic medium (recovery to a trivalent state) in the reactor, and then enters the neutralizer.

To deposition of heavy metal ions, a solution of alkali through a dispenser is added to the neutralizer. After this, the solution is directed to the settling tank, where the hydroxides precipitate is separated from the neutralized water.

The precipitate passes through a precipitator, a vacuum filter and enters the drainage of dehydrated sediments from where it is transported to the sludge platform.

The neutralized water is fed to a reverse osmosis system, where concentrate and purified water are formed. Refined water returns to production. The concentrate is discharged into drainage (mixed with the household wastewater of the enterprise for the normalization of the salt composition in accordance with the requirements of the MAC, then discharged into the city sewerage system).

The standardized working conditions in the projected workshop are carried out at the expense of mechanization and automation of heavy and labor-intensive works, rational placement and thermal insulation of equipment, aggregates, communications and other sources, radiating in the workplace heat.

Workers are provided with personal protective equipment - respirators such as "Petals", overcoats of type "P", disposable rubber gloves, protective eyeglasses, disposable ear plugs and footwear. Once a week, using a sawmeter, the content of harmful substances and their parameters in the air of the working area is monitored.

In order to remove harmful substances from the air, and to provide clean air, a mechanical general-purpose tidal, local exhaust ventilation is provided in the galvanic workshop. Minimum multiplicity of air exchange is not less than 5. Tidal ventilation serves to supply clean ventilated air instead of sewage. The tidal air is subject to special treatment (heating, cleaning, wetting, etc.) to maintain the parameters of the microclimate. Exhaust ventilation removes contaminated from the workshop and heat up exhaust air. Ventilation efficiency is balanced taking into account the possibility of air supply to or from adjacent premises. The air balance for the electroplating chrome plating unit is negative by 10-15%. Emergency ventilation is provided for the production: in the case of sudden emission of toxic fumes. It is actuated only in the event of an accident and is carried out by exhaust ventilation to create a dilution inside the premises thereby preventing harmful substances from spreading to adjoining premises. Emergency ventilation is included both from sensors of gas detectors adjusted to the magnitude of the MPC of controlled substances, and manually. Multiplicity of air exchange for emergency ventilation 8 hours together with the worker. Baths with harmful emissions are equipped with on-board suction (baths for electrochemical degreasing, etching, coating).

The shop is equipped with a drinking water cooler outside the production area in an accessible location. Replacing tanks with water and disposable cups is provided as needed.

To reduce the airborne working area of harmful substances, the following measures are foreseen:

1. In order to reduce the evaporation of harmful substances and reduce the amount of vapors that are inhaled by workers, preparation and adjustment of baths is carried out with localized ventilation enabled. The surface of baths is blocked by the evaporation of fluoroplastic balls.

2. Replacement of the possibility of harmful and combustible substances with less toxic, non-combustible materials. Replacement of degreasing solutions such as benzene, toluene, benzene chlorine derivatives.

3. In the process of preparing pickling solutions, introduce the acid into cold water with a thin stream, thoroughly mixing.

4. The operator stops above the bath at a time so that the maximum amount of electrolyte from the surface of the glass part is reduced to reduce the removal of electrolytes from the bath.

5. The intervals between baths are covered with fluoroplastic canopies to prevent the solution from entering the floor.

6. To reduce the amount of electrolyte which enters the sewage, immediately after the bath of application of the coating an impermeable catching bath is provided. The water from this bath is used to adjust the composition and volume of the electrolyte.

Keywords: electroplating, chromium, galvanic baths, stationary electroliser, voltage balance, electrolysis, wastewater.