

Electrochemical regeneration of chromium-containing galvanic solutions

Filatova E.G.

Irkutsk National Research Technical University
IRNITU
Irkutsk, Russia
efila@list.ru

Minaev D.V.

Irkutsk National Research Technical University
IRNITU
Irkutsk, Russia
minaev.dimn@yandex.ru

Chugunov A.D.

Irkutsk National Research Technical University
IRNITU
Irkutsk, Russia
chugunovsasha1996@yandex.ru

Abstract—Spent galvanic solutions are highly aggressive and contain substances, suitable for reuse. Regeneration of these solutions represents both an environmental and economic issue of actual problem. The efficiency of electrochemical regeneration chromate electrolyte of anodic oxidation was monitored. The obtained results indicate that the electrochemical module ensures the constancy of the electrolyte composition, so that the controlled parameters (pH, the concentration of H⁺ ions in terms of chromic acid, the content of chromium (VI) ions in terms of CrO₃, aluminum, chloride ions, sulfate ions, unit electric conductivity of the electrolyte) are normal. It is shown that this technology makes possible to achieve the required quality of technological solutions, providing the creation of a local closed system of electrolyte regeneration.

Keywords—Galvanic production; mechanical engineering; anodizing; chromate-acid electrolyte; submersible electrochemical module; electrochemical regeneration.

I. INTRODUCTION

Waste galvanic production, getting into the environment, causes irreparable damage to the ecological situation of the planet. This, above all, is the discharge of insufficiently purified sewage into open reservoirs. As a result, tons of toxic metals (chromium, nickel, copper, zinc, bismuth, lead, etc.), alkali, acids, inorganic salts, organic compounds, etc., fall into water bodies.

In addition to wastewater, waste technological solutions and electrolytes, periodically discharged into rivers and lakes, are dangerous for the environment. Although their consumption is tens and hundreds of times lower than that of wastewater, however, with irrationally organized wastewater disposal, a large part (sometimes up to 70-90 %) of highly toxic substances, discharged into sewerage, fall to the share of spent technological solutions of electrolytes [1, 2].

In galvanic production, technologies of anodic oxidation of metals, including aluminum are widely used. Anodic oxidation allows protecting metals from corrosion and increasing the service life of their products. At the present, in galvanic

production, several technologies of anodic oxidation of aluminum, which have their advantages and disadvantages, are used [3, 4].

The most common oxidation happens in sulfuric-acid, oxalic-acid and chromate-acid electrolytes.

In the sulfuric-acid electrolyte, it is not recommended to apply anodizing of parts, having narrow slits, gaps, riveted or welded joints, to avoid corrosion. When the temperature of the electrolyte rises, the quality of the slick deteriorates, so a deep cooling of the electrolyte is required.

When processing products, low-porous, hard slick films are formed in the oxalic-acid electrolyte to produce hard and electrically insulating coatings. The process of oxidation in the oxalic-acid electrolyte at the cost of consumables and the cost of electricity is less economical than that in the sulfuric-acid electrolyte. The process of oxidation is accompanied by the release of a significant amount of heat. To avoid the corrosion of the oxide and the base metal of the processed products, it is necessary to apply intensive stirring and cooling of the electrolyte. The temperature of the solution should be monitored in the immediate vicinity of the surface of the treated products.

The chromate-acid electrolyte is less aggressive with respect to aluminum and oxide slick than sulfuric- and oxalic-acid. In this electrolyte, there are processed details of the first and second accuracy class. Chromium-acid electrolyte is recommended for the production of protective slick on complex shape details, as well as on products, having welded and riveted joints. Especially it is suitable for processing details from lithium aluminum-silicon alloys. The chromium-acid electrolyte has a significantly less dissolving effect on the oxide slick. Due to its economy, the possibility of processing various aluminum alloys and the production of oxide coatings with good operational properties of chromium-acid electrolyte are most widely used in industry.

With long-term operation of the chromate-acid electrolyte of anodic oxidation, various impurities, ions of aluminum,

chromium, etc. accumulate in it, which adversely affects the quality of the anode slick of aluminum details, increasing the quantity of finished products at the enterprises. If the permissible concentrations exceed the above-mentioned impurities, a partial or complete replacement of the electrolyte is carried out. Spent electrolyte refers to waste of the 1st -2nd hazard class and requires special storage conditions. For one year, the machine-building enterprise produces tens of thousands of liters of spent chromate-acid electrolyte, which is often stored on the territory of the enterprise.

In view of the lack of reliable equipment, intended for regeneration of waste technological solutions, and due to low technological discipline, they are discharged to the sewage structures of the enterprise — a neutralization station for industrial wastewater. Usually used at neutralization stations, the reagent method of precipitation of cations of heavy metals in the form of their hydroxides is intended for detoxification of low concentrated wash waters and can not provide the necessary barrier function of local treatment facilities in the event of admission of volley discharges of highly concentrated etching solutions.

As a result of the discharge of highly concentrated waste solutions into the local sewerage network of the enterprise, there is not only the loss of valuable chemicals and non-ferrous metals, but also the operating mode of local treatment facilities is significantly disrupted. It is owing to the fact that the copper, contained in etching solutions, is in the form of stable complex compounds that transit through the entire technological cycle [5].

What should and can be done to significantly reduce the impact of this negative impact on humans and the natural environment? Analysis of scientific and technical literature showed the following areas of using spent concentrated solutions of electrolytes — it is neutralization and regeneration. Neutralization can be carried out by electrochemical, chemical and other methods [6, 7]. Neutralization requires a significant consumption of reagents and leads to the formation of sediments, containing a large number of valuable components. Further use of these sediments is hampered by their complex variable composition.

The galvanic production solutions are very aggressive and contain substances, suitable for reuse. Regeneration of these solutions represents an actual problem from environmental and economic point of view [8, 9]. Regeneration of waste solutions of galvanic production is a very complex, expensive process [10, 11]. As an intermediate solution to this problem, it was proposed to organize non-draining, non-waste and closed water rotation of galvanic production [5]. Regeneration of electrolytes is to restore their efficiency, but they can withstand only a certain number of cycles of regeneration. In most cases, all this requires the use of complex multi-stage methods, including chemical and electrochemical processing, coagulation and flocculation, ultrafiltration, evaporation, electrodialysis with using ion-selective membranes and adjusting pH and chemical composition, etc. For modern technologies of neutralization of the spent electrolytes, it is possible to carry membrane technologies, submersible electrochemical modules.

The aim of the work was to monitor the efficiency of electrochemical regeneration of chromium-acid electrolyte.

II. MAIN CONTENT

Electrochemical regeneration of chrome-containing galvanic solutions was carried out, using a submersible electrochemical module. In fig. 1 there is a scheme of such installation. The submersible electrochemical module is a chamber with successively alternating anodic and cathodic zones, separated by a membrane. Usually, a submersible electrochemical module is installed inside a galvanic bath with a process solution that needs regeneration.

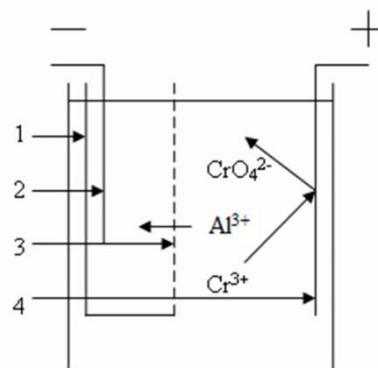
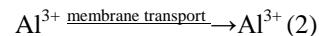


Fig. 1. Diagram of submersible electrochemical module:
1—submersible electrochemical module; 2—internal electrode;
3—membrane; 4—external electrode

When the electrochemical module is immersed with a cationite membrane, an internal cathode and an external insoluble anode in the course of electrolysis, the ions Al^{3+} pass into the submersible module, and the ions Cr^{3+} are oxidized at the anode with a simultaneous acidification of the solution:



By regulating the current, one can arbitrarily accelerate or slow down the reaction (1) and thus maintain a constant composition of the chromium-acid electrolyte, corresponding to the optimal values of the ratio Cr(VI)/Cr(III). At the same time, the correction of the composition of the electrolyte is minimized, namely, for compensation for its drift with parts being processed. With the proper organization of the regeneration process of the exploited electrolyte, periodic discharges of toxic substances into the environment can be completely eliminated.

Table 1 shows the chemical composition of the initial chromium-acid electrolyte, which was regenerated through the submersible electrochemical module. The amount of impurities in the electrolyte was controlled by a chemical analysis method [12].

TABLE 1. Chemical composition of chromium-acid electrolyte (Temperature 298 K)

Controlled parameter	Value by regulatory documents	Analysis result
Chromium ions (VI) in terms of CrO ₃ , g/dm ³	50–120	118.66
Al ³⁺ , g/dm ³	up to 3.0	2.99
pH	up to 1.6	0.73
γ , mS/cm ²	137–185	151.4

As can be seen from the presented data (table 1), the results of the analysis of the monitored parameters correspond to the requirements of normative documents. Sampling of chromium-acid electrolyte anodizing bath was carried out monthly from January 2013 to November 2015. The results of monitoring are shown in fig. 2–5. When using the electrolyte, the content of aluminum (fig. 2) and ions chromium (VI) in terms of CrO₃ (fig. 3) increases. According to the current regulations, the aluminum content should not exceed 3 g/dm³, and the content of ions chromium (VI) in terms of CrO₃ is 120 g/dm³.

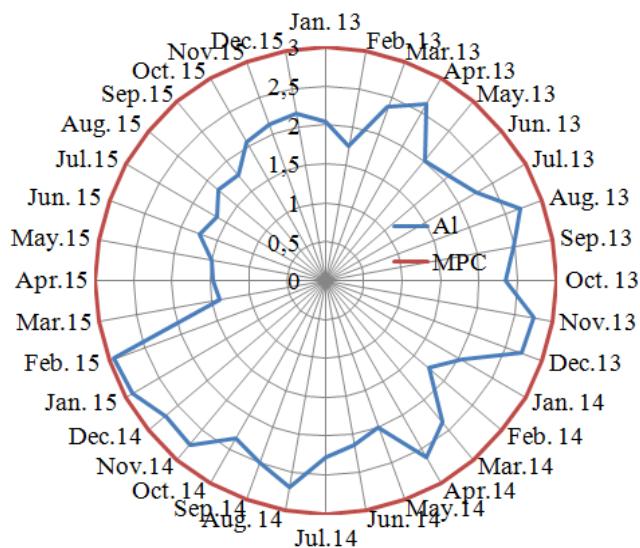


Fig. 2. Content of aluminum ions, g/dm³.

If one pays attention to the change of the concentration of aluminum (fig. 2), the content of this indicator seems to repeatedly approach a critical value.

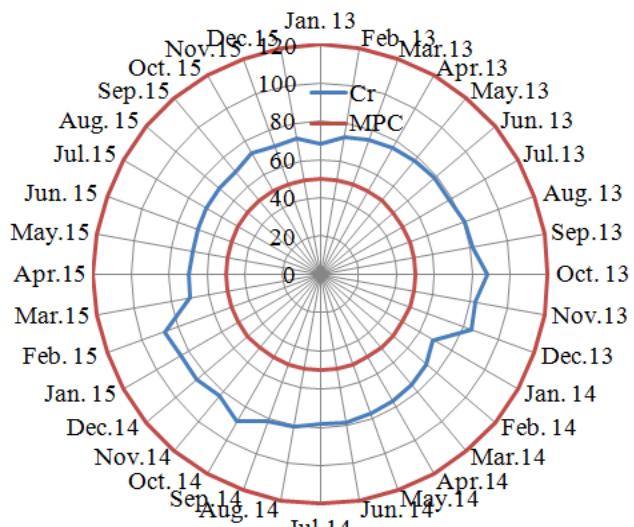


Fig. 3. Content of chromium (VI) ions in terms of CrO₃, g/dm³.

The data in fig. 3 show that the optimum content of chromium (VI) ions in terms of CrO₃ in the electrolyte has minimal and maximum limitations. Moreover, this indicator during the entire controlled period of time practically does not approach the limiting values.

The chloride ions and sulfate ions, present in the chromium-acid electrolyte, are also monitored. The results are shown in fig. 4 and in table 2.

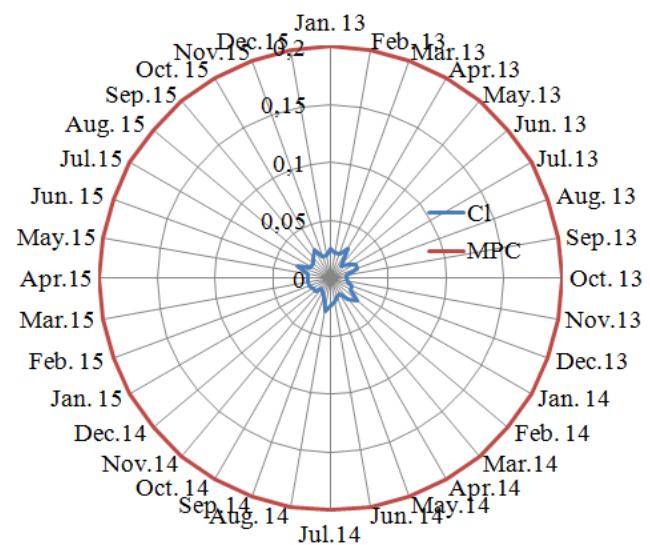


Fig. 4. Change of the content of chloride ions, g/dm³.

As fig. 4 shows, the content of chloride ions remains normal, and it is significantly lower than the limit value throughout the entire regeneration period.

TABLE 2. Results of monitoring the content of sulfate ions

Controlled period	C(SO ₄ ²⁻), g/dm ³	Controlled period	C(SO ₄ ²⁻), g/dm ³	Controlled period	C(SO ₄ ²⁻), g/dm ³
2013		2014		2015	
Jan.	0.16	Jan.	0.26	Jan.	0.09
Feb.	0.15	Feb.	0.12	Feb.	0.09
Mar.	0.11	Mar.	0.13	Mar.	0.12
Apr.	0.13	Apr.	0.12	Apr.	0.11
May.	0.11	May.	0.11	May.	0.11
Jun.	0.12	Jun.	0.11	Jun.	0.11
Jul.	0.11	Jul.	0.13	Jul.	0.11
Aug.	0.11	Aug.	0.11	Aug.	0.1
Sep.	0.15	Sep.	0.09	Sep.	0.1
Oct.	0.16	Oct.	0.098	Oct.	0.09
Nov.	0.14	Nov.	0.078	Nov.	0.1
Dec.	0.12	Dec.	0.1	Dec.	0.08

From the presented results (table 2) one can see that the maximum content of sulfate ions was 0.26 g/dm³ in the second year of exploitation of electrolyte. Wherein, according to normative documents, it should not exceed 0.6 g/dm³. Thus, this controlled indicator is also normal in regeneration.

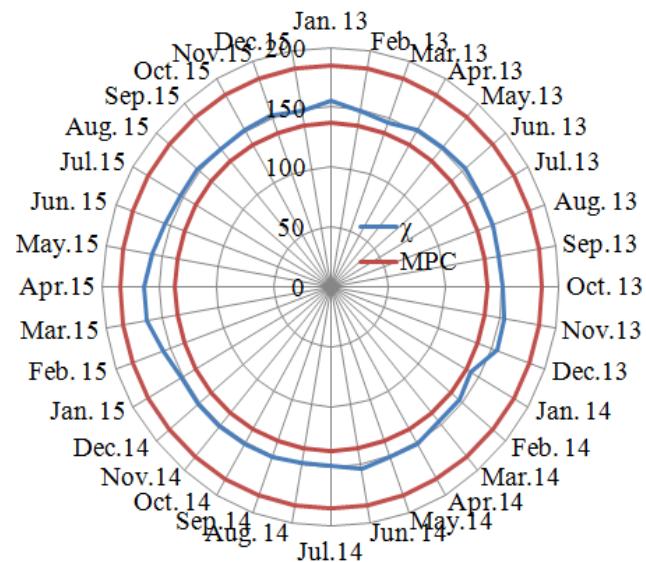
During the monitoring of the composition of the chromium-acid electrolyte, the hydrogen index and the concentration of H⁺ ions in terms of chromic acid were monitored (table 3).

TABLE 3. Sampling of pH values

Controlled period	Sampling of pH values	Sampling of values C(H ⁺), g/dm ³
2013	0.53–0.68	43.1–45.2
2014	0.55–0.68	42.3–45.6
2015	0.57–0.67	43.7–50.0

The pH value remains substantially lower than the required value of 1.6 during the entire period. If one pays attention to the change in the concentration of H⁺ ions, this index most closely approaches limitations 40–55 g/dm³.

Unit electrical conductivity is an expressive parameter of the quality of the chromium electrolyte used for anodizing [12] (fig. 5).


 Fig. 5. Change in unit electrical conductivity, mS/cm².

Unit electrical conductivity of the electrolyte at certain times approaches the upper and lower limits of the norm (137–185 mS/cm²).

If one analyzes the results for all the controlled parameters of the regenerable chromium-acid electrolyte, they can be conditionally divided into three groups.

The first group is the content of aluminum ions, the concentration of H⁺ ions in terms of chromic acid and the unit electric conductivity. These three indicators are the closest to the maximum regulatory values and need more careful adjustment during regeneration. The second group is the content of chromium (VI) ions. The change in chromium concentration during the entire controlled period approaches insignificantly the upper and lower limits of the norm. The third group of parameters is the pH, the content of chloride ions and sulfate ions. The presence of these components in the solution is significantly below normal throughout the entire regeneration period.

Table 4 shows the degree of environmental hazard of electrolytes, containing toxic components that have a harmful effect on natural water bodies during discharge.

TABLE 4. Degree of ecological danger of solutions and electrolytes of anodizing

Purpose of electrolyte	Controlled indicator	MPC of fish. Households, mg/dm ³	Degree of ecological danger (C ⁰ _{max} /MPC)
Anodizing in chromic acid	Cr (VI)	0.02	4.2·10 ⁶
Etching and anodizing of aluminum	Al ³⁺	0.04	0.9·10 ⁶
Neutralization of chrome-containing effluents (repair Cr (IV) to Cr(III))	SO ₃ ²⁻	1.9	Depending on the dosage
	S ₂ O ₃ ²⁻	1.7	
	SO ₃ ²⁻	2.2	

The most toxic are heavy metal ions, so the maximum permissible concentration (MPC) of chromium (VI) ions, when discharged into fishery water reservoirs is 0.02 mg/dm³, and Al³⁺ ions – 0.04 mg/dm³. In case of presence of these ions in the regenerated electrolyte, the content of the Al³⁺ needs more careful correction than chromium (VI).

Electrochemical regeneration technologies are advisable to apply in practice only if they are recouped. Below, there is an estimate of the costs of the electrochemical reduction of the electrolyte chromate.

The installed power capacity of the used equipment was calculated by the formula:

$$N = \frac{P \cdot K \cdot N}{\cos \varphi} \quad (1)$$

where P — a coefficient that takes into account the transformer reserve, 1.5; K — a coefficient that takes into account the electric lighting load, $K = 1.05$; N — power of all working electric receivers; $\cos \varphi$ — the power coefficient of the electric motor, $\cos \varphi = 0.9$. Since $N < 750$ kW, the calculation is based on a one-part tariff.

Annual outgo of consumed electricity is:

$$C_{el,pow.} = \Sigma W \cdot T / 10^3, \quad (2)$$

where ΣW — annual amount of active electric power, kW/h; T — number of hours of operation of electrical equipment during the year, h.

Annual electricity costs are:

$$\mathcal{Z}_{el,pow.} = T_1 \cdot \Sigma W \quad (3)$$

where $T_1 = 2.51$ rubles – single-rate tariff for electricity (in 2016 prices)

Table 5 presents the technical and economic parameters of the two options for the operation of a galvanic bath. The first option is anodic oxidation of parts with complete replacement of the electrolyte. The second option is anodic oxidation with electrochemical regeneration, using a submersible electrochemical module.

The given data (table 5) show that there is a significant reduction in material costs during electrochemical regeneration of the electrolyte. When comparing the two considered options, in the second case, the costs are reduced more than nine times. At the same time, electricity costs for regeneration of one galvanic bath are 29601.94 Rubles.

TABLE 5. Technical and economic indicators of compared options

Name of indicators	First option	Second option
Price of 1 m ³ of electrolyte, Rub.	8006.7	8006.7
Price of electrolyte in galvanic bath, Rub	288 240	288 240
Annual costs of electrolyte with its full change, Rub.	288 240	–
Installed power of used equipment, kW/h	–	13.1
Electricity consumption for regeneration of 1 m ³ of electrolyte, kW	–	327.6
Electricity consumption for galvanic bath regeneration, kW	–	11793.6
Annual electricity consumption for regeneration, Rub.	–	29601.94
Consumption for bath maintenance, Rub.	72 060	9768.64
TOTAL, costs, Rub:	360 300	39 370.58

Based on the analysis of all the results of the monitoring of the main parameters of the regenerable electrolyte, as well as the technical and economic parameters of the galvanic bath maintenance, the following technical solution was proposed.

For the regeneration of the electrolyte and the continuity of the processing of parts, the following is accepted: to include a separate capacity of a smaller volume with a submersible electrochemical module in the process scheme. On average, the volume of the bath is 36000 dm³; the volume of the electrolyte to be purified with using a submersible electrochemical module is 10 dm³. The time of regeneration of one portion is 25-35 min. The regeneration time of the entire bath with an 8-hour mode of the operation is 225 days, and with a 16-hour mode it is reduced to 113 days.

Carrying out the process of electrolyte regeneration makes it possible to create environmentally neat production of regenerated electrolytes, which extends their life from three to fifteen times, and to save significantly material resources by preventing irreversible losses of chemical substances.

III. CONCLUSION

In this way, regeneration of the chromium-acid electrolyte of anodic oxidation with using a submersible electrochemical module provides the possibility of its return to the technological process. Therefore, regeneration can be

considered as the most significant process in the technology of processing concentrated electrolytes and solutions. The obtained results indicate that the electrochemical module ensures the constancy of the electrolyte composition, so that the controlled parameters (pH, the concentration of H⁺ ions in terms of chromic acid, the content of chromium (VI) ions in terms of CrO₃, aluminum, chloride ions, sulfate ions, unit electric conductivity of the electrolyte) are normal. The introduction of low-waste and non-waste technologies into production will allow the most rational and comprehensive use of natural raw materials and energy so that no impact on environment will disrupt its normal functioning.

References

- [1] V.I. Aksenov, I.I. Nichkova, V.A. Nikulin, and N.S. Tsarev, "The problem of galvanic treatment is eternal?", Plumbing. Heating. Conditioning, Issue 2 (158), pp. 23-25, 2015.
- [2] A.A. Pashayan, and M.V. Zerkalenkova, "New slopeless and regenerative methods of water purification from chromium compounds", Ekologiya i promyshlennost' Rossii, Issue 9, pp. 7-9, 2014.
- [3] M.A. Ilyashchenko, "Perfection of the technology for purification of effluents from galvanic plants from chromium ions by the example of LLC Yurginsky Mashzavod", Ecology and safety in the technosphere: current problems and solutions, 2016. pp. 118.
- [4] Sh.S. Nozirzoda, "Electrochemical purification of water", Ecology and safety in the technosphere: current problems and solutions, 2016. pp. 129.
- [5] W.T. Yelinek, "Advances in galvanic engineering. A review of the world-wide specialized literature for 2014-2015", Electroplating and surface treatment, Issue 2, pp. 14-21, 2016.
- [6] T.A. Budykina, "Modern technologies for neutralizing galvanic effluents of machine-building industries", Modern Materials. Technics and technology., Issue. 1(9). pp. 51-56, 2017.
- [7] D.Yu. Turaev, "Extraction of cations of heavy metals from acidic solutions, contained strong oxidants", Achievements in Chemistry and Chemical Technology, Issue 9(114), pp. 11-16, 2010.
- [8] E.G. Filatova, "Review of technologies for wastewater treatment from heavy metal ions based on physical and chemical processes", Izvestiya Vuzov. Applied chemistry and biotechnology, Issue 2(13), pp. 97-109, 2015.
- [9] Filatova EG, and D.V. Minaev, "Estimation of the efficiency of electrochemical regeneration of chromium-containing galvanic solutions", Ecology of industrial production, Issue 1(97), pp. 13-17, 2017.
- [10] M.J. Martinez-Rodriguez, B.L. Garcia-Diaz, J.A. Teprovich, D.A. Knight and R. Zidan, "Advances in the electrochemical regeneration of aluminum hydride", Applied physics a-materials science & processing, vol.106, Issue 3, pp. 545-550, Mart 2012.
- [11] K.L.Huang, and T.S. Chen, "Electro-Regeneration of Ce(IV) in Simulated Spent Cr-Etching Solutions Containing Abundant Ce(III)", Journal of the electrochemical society, vol.156, Issue 12, pp. 192-198, 2009.
- [12] L.N. Solodkova, V.I. Mamaev, V.V. Okulov, and V.D. Skopintsev, "About analytical control of the electrolyte of chromate anodization", Galvanic engineering and surface treatment, vol. XXII, Issue 1, pp. 4-6, 2014.