Improvement of environmental and economic indicators of the electrolytic chromium plating process

E V Moskvicheva1*, A G Timofeev1, P A Sidyakin2 and L N Chernoshchekov3

1Volgograd State Technical University (VSTU), 1 Akademicheskaya street, Volgograd, 40007, Russia
2 "North Caucasian Federal University” Institute of service, tourism and design (branch) NCFU in Pyatigorsk, 1 Pushkin street, Stavropol, 355009, Russia
3Lomonosov Moscow State University, 1Leninskie Gory, Moscow, 119991, Russia

E-mail: antonio1805@yandex.ru

Abstract. In most cases, the improvement of technological processes is a beneficial measure to reduce anthropogenic impact of production on the environment. However, it is impossible to solve the problem of elimination of production emissions and wastes only by improving the technological process. That is why more and more integrated and complex measures are required to solve the problem, which include both improvement of technological processes and improvement of emissions purification schemes, waste utilization and recycling. At the same time, the measures should be both technically effective and economically feasible. The obtained results allowed to draw a conclusion about the increase of ecological and economic indicators: decrease of toxic chromium anhydride wear and tear by 2-2.7 times; decrease of water volume polluted in the process of technological cycle; decrease of expenses for lead anodes manufacturing and human resources; increase of operational characteristics of manufactured parts - wear resistance, microhardness.

Introduction
Currently, considerable attention is paid to environmental safety issues at hazardous facilities. This interest is stimulated by the unfavorable environmental situation in regions with a high concentration of production facilities that irrationally eliminate their waste as well as by the significant and gradually growing fines paid by companies for hazardous emissions into the atmosphere and industrial waste landfills.

The main solution to environmental problems is to reduce anthropogenic impact of industrial enterprises on the environment. The result can be achieved through the following activities:
- improvement of technological processes;
- improvement of emission purification methods and waste disposal.

Improvement of technological processes leads to improvement of technical indicators (for example reduction of energy intensity, amount reduction of raw materials or product quality improvement) [1].

In most cases, improvement of technological processes is an economically beneficial measure to reduce the anthropogenic production impact on the environment. However, it is impossible to solve the problem of elimination of production emissions and waste only by improving the technological process.
Therefore, its solution requires more complicated and complex measures, which include both improvement of technological processes and improvement of emissions purification schemes, utilization and waste processing. At the same time, the measures should be both technically effective and economically feasible.

Further analysis of decisions efficiency that reduce the anthropogenic impact will be carried out based on measures to improve electrolytic chromium plating production. [2]

At present, the technology of electrolytic chromium plating is improved by changing the composition of chromium plating electrolyte. Chroming electrolyte with thiophosphorus additive (TFA) implemented at the plant allowed:
- to reduce energy intensity of chroming process, as well as chromic anhydride entrainment in 2 - 3 times due to decrease of electrolysis temperature from 55 to 35 °C;
- eliminate the use of special anodes that repeat the surface of parts during their dimensional chroming;
- obtain chrome plates with improved physical and chemical properties (wear resistance increased by 4-5 times, microhardness increased by 1.1-1.2 as compared to currently used standard chrome electrolyte). Based on these data the environmental and economic indicators of the chroming process from the chroming electrolyte with TFA are comparable with the similar indicators of the chrome bath from standard electrolyte. Before conducting such calculation, it should be noted one more economic benefit from implementation of chroming electrolyte with TFA. There are three electroplating-chrome baths at this enterprise; each of them has 1000 liters volume. The baths are powered individually - each bath from its rectifier with a nominal current of 1500 A.

Main part

Originally, the project chromium plating area was designed for application of chrome plates on small parts (handles, caps for ball valves). Currently, the demand for such parts is not high, so there are only two baths of chromium plating in operation. Marketing research has shown that there is a demand for chrome plated ball valve plugs of a larger size (hereinafter - plugs). The plug of such a ball valve has an area of 1.08 m².

For chrome plating from standard electrolyte with minimum possible working current density of 45 A/dm², which provides obtaining chrome plates with high values of microhardness, the surge current (1.5 times higher than the working current) will make up:

\[ J_t = 1.5 \times 45 \text{ A/dm}^2 \times 1.08 \text{ m}^2 \times 100 = 7300 \text{ A} \]

The last value is 4 - 5 times higher than the nominal value of current strength, for which the current source available at the enterprise is designed. In addition, the bulk density of current in the chrome bath will be:

\[ J_v = \frac{7300 \text{ A}}{1.5 - 1000 \text{ l}} = 4.9 \text{ A/l}, \]

This will cause the electroplating-chrome bath to overheat, as the recommended volume current density for chrome plating is 1-1.5 A/l.

As a result, to chrome-plate a plug made of standard electrolyte it is necessary to replace both the power supply and the electroplating-chrome bath. However, such reconstruction as calculations show due to low production volumes (today the market demand is about 2100 plugs per year) is not profitable.

When chromium plating a plug made of chrome plating electrolyte with TFF, the operating current density can be reduced to 8 A/dm² therefore the surge current will be equal:

\[ J_t = 1.5 \times 8 \text{ A/dm}^2 \times 1.08 \text{ m}^2 \times 100 = 1300 \text{ A}, \] and the volume current density in the process of bath operation will be 0.86 A/l. Thus, the introduction of chrome plating electrolyte with TFA allows
to chromium plating the plug without replacing the existing equipment. The calculation also shows that with the required thickness of chrome plates 20 microns, the electroplating-chrome bath will provide the required capacity of 2100 plugs per year, provided its continuous operation [3].

Specialists of the research department of the machine building plant for the implementation of chromium plating electrolyte with TFA made a number of changes in the design of the electroplating-chrome bath. First, they changed the mutual arrangement of lead anodes in the bath, which is necessary for chromium plating one part in it. Secondly, the bath lead cover with expired life was replaced by a by a vinyl plastics cover. For reasons of the low thermal vinyl conductivity, heating and cooling of the electrolyte began to be carried out with a coil of lead pipes lowered into the electrolyte and located on the bath walls. In such a lining not only eliminates the need for lining the bath with lead but also improves the coating uniformity as at least partially excluded the influence of the bath walls and bottom on the passage of current between the anode and cathode [4].

The carried out researches allowed drawing a conclusion that the process of chromium electrodeposition from electrolyte with TFA is most expedient at temperature 35 °C and current density 5-10 A/dm².

Table 1 presents properties of chromium plating electrolyte composition, (g/l): 250 CgO₃ + 2.5 H₂SO₄ + 1.75 TFA, and physical and mechanical properties of coatings obtained from it.

The conducted researches showed that the increase in current density up to 10 A/dm² causes the formation of burn-on along the chrome plates edges. Thus, apparently the optimal mode of chrome plating is electrolyte temperature of 35 °C and current density of 7-8 A/dm² [5].

The question of chromium plating electrolyte correction is important from practical point of view. Carried out researches have shown that TFA decomposes slowly at storage (and consequently at operation) of chromium plating electrolyte with formation of orthophosphoric acid. Calculations showed that chromium-plating electrolyte does not require correction of orthophosphoric acid during the whole period of its operation. Correction for TFA should be made in every 250 Ah/l on condition of continuous operation of electroplating-chrome bath [6].

Adjustment of the electrolyte for FTA is made by adding the necessary amount of "concentrate" to it. The concentrate is a liquid product of chromic anhydride reaction with diisobutyldithiophosphoric acid. To prepare the concentrate of diisobutyldithiophosphoric acid in the amount of 70 g / l is fed into an aqueous solution of chromic anhydride with a concentration of 500 g / l at a temperature of 55 °C then the reaction mass is maintained for 240 minutes at the same temperature to complete the reaction, after which it is cooled. Solid reaction products are separated from liquid ones and washed with water in the amount of 60-70% of the volume of chromic anhydride initial solution. Washing water is combined with liquid reaction products and as a result, concentrate is obtained. The carried out researches showed that the study of chromium plating electrolyte after its TFA correction can be not carried out, if TFA content in the bath before correction corresponds to the working interval of TFA concentrations [7].

The working interval of TFA concentrations depends on chromic anhydride and sulfuric acid concentrations. Decrease of chromic anhydride concentration in electrolyte from 250 g/l to 150 g/l leads to some reduction of working interval of TFA concentrations; increase of chromic anhydride concentration to 350 g/l does not change working interval of TFA concentrations. Thus, it can be considered that the optimal concentration of chromic anhydride in CgO₃ electrolyte is ~ 250 g/l. At this concentration of chromic anhydride the working interval of TFA concentrations, at which shiny chrome plates with microhardness of 11000 - 12600 MPa are obtained can be found from Fig.1, knowing the ratio between the concentration of sulfuric acid and chromic anhydride in the chromic electrolyte. At reception of the hardest chrome coverings (with microhardness not less than 12000 MPa) it is necessary to narrow the working interval of concentrations of TFA and H₂SO₄ (Figure 2) [8].
High wear resistance of chrome plates is explained by the fact that the irradiated chromium coatings have a high value of microhardness as well as are fine crystalline, which is confirmed by X-ray phase analysis presented in Figure 1.

**Figure 1.** Working interval of TFA concentrations as a function of $\text{H}_2\text{SO}_4$ ratio: $\text{CrO}_3$, Anode - lead. $C(\text{CrO}_3)$ concentration $= 250 \pm 30 \text{ g/l.}$ $C(\text{H}_2\text{SO}_4)$ concentration: $100/C(\text{CrO}_3)$ ratio $= 0.76:1.6$. Concentration of TFA 1.1 - 2.0 g/l. Electrolyte temperature is 35 °C. Cathode current density is 8 A/dm$^2$. Microhardness of chrome plates 11000 - 12600 MPa.

**Figure 2.** Operating interval of TFA concentrations as a function of $\text{H}_2\text{SO}_4$: $\text{CrO}_3$ ratio. $\text{CrO}_3$ concentration $= 250 \pm 30 \text{ g/l.}$ $C(\text{H}_2\text{SO}_4):100/ C(\text{CrO}_3)$ ratio $= 0.85:1.38$. Concentration of TFA 1.5 - 1.9 g/l. Anode - lead. Electrolyte temperature is 35 °C. Cathode current density is 8 A/dm. Microhardness of chrome plates 12000 - 12600 MPa.

Figures 1, 2 show that decrease (increase) of TFA concentration in chromium plating electrolyte can be compensated by increase (decrease) of sulfuric acid concentration within the working concentration interval.

Determination of physical-mechanical dependence properties of chrome plates and physical properties of chromium plating electrolytes depending on its composition allowed to reveal optimal composition of chromium plating electrolyte, g/l: CrO$_3$+ 2.5 H$_2$SO$_4$ + 1.75 TFA.
Figure 2 shows that in chromium plating electrolyte that contains 250 g/l of CrO₃, 2.5 g/l of H₂SO₄ the working interval of TFA concentrations is 1.6 - 1.9 g/l.

Operation experience of chromium plating electrolyte with TFA at the electrodeposition showed no difficulties connected with its correction in spite of narrow interval of working concentrations of TFA. The above mentioned achievement is a significant positive result with improvement of environmental and economic indicators. Electrolyte adjustment is accompanied not only by contamination of water effluents, but also by an increase in their volume, which has a very negative impact on the environmental safety of the production under consideration.

It is connected with the fact that low temperature of electrolysis leads to decrease of chromium plating electrolyte entrainment that stabilizes its composition and in the process of chromium plating electrolyte operation there is not only decrease of TFA concentration but also increase of C(H₂SO₄)/C(CrO₃) ratio due to chrome anhydride concentration decrease [9].

This fact, taking into account Figure 2 allows to operate chromium plating electrolyte at wider concentration range of 1.5 - 1.9 g/l TFA.

Concentration of TFA STFA in g/l. In the chromium plating electrolyte is calculated, determining the total phosphorus content of Pcomm. in % and phosphorus content in the form of phosphate ions Pph. in % by the developed method.

\[ C(\text{TFA}) = 324.3 - p \cdot (P_{\text{comm.}} - P_{\text{ph.}}); \]

Where \( p \) is the density of the analyzed chromium plating electrolyte, g/ml.

The concentration of sulfate ions in chromium plating electrolyte is determined by the developed method. Determination of chromium anhydride concentration is similar to its determination in standard chromium plating electrolyte. Adjustment of chromic anhydride and sulfuric acid electrolyte is performed in the same way as in standard chromium plating electrolyte. As in chromium plating electrolyte at correction according to TFA concentrate is added which contains chrome in recalculation to chromic anhydride in amount of 7.43 g CrO₃, it should be taken into account at the electrolyte correction according to the chromic anhydride [10].

Summary
Based on the obtained results, the conclusions were formed showing a demonstrative improvement in environmental and economic indicators of the production under consideration - electrodeposited chrome plating:

- removal of toxic chromium anhydride was reduced by 2-2.7 times;
- the volume of water contaminated during the technological cycle was reduced;
- reduced costs for lead anode production and human resources;
- improved performance of manufactured parts - wear resistance, microhardness.

As a result, the presented results have proved the expediency of the conducted research when the technogenic pollution can be reduced and the quality of the main products can be improved.

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