Technique of Assessment of Environmental Damage Caused by Electroplating Production Facilities (by the Example of Chromium Plating Process Lines)

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Abstract. The use of galvanic chromium plating is accompanied by negative consequences related to considerable damage caused to the environment. The authors have developed new chromium plating electrolytes and methods to obtain chromium-based galvanic alloys which allow reducing the environmental harm and decreasing the morbidity rate of occupational diseases among operating personnel. A technique of assessment of environmental damage caused by electroplating production facilities, which is based on the ecological compatibility criterion has been suggested.

1. Introduction
In spite of constantly expanding sphere of use of electrolytic chromium coatings, chromium electrodeposition that proceeds according to the existing technologies is rather imperfect: it is extremely hazardous for the environment, energy-consuming as well as labor-intensive.

2. Topicality
The use of compounds of Cr(VI) in electrodeposition is limited by the legislative requirements to environmental protection. Debate-provoking provisions of the European Regulation REACH [1], strict Russian legislation in the given sphere have resulted in an abrupt growth in penalties for discharges of chromium-containing waste waters and, hence, to a rise in the costs of wastewater treatment, slag disposal [2], water discharge into sewerage and clean water consumption. These expenses have considerably increased the self-cost of electrolytic chromium obtaining. The direct losses which can be avoided also include the drag-out of solution components with parts and technological equipment as well as inefficient use of water for rinsing, heating and cooling [3-7].

Only 10-30% of chromium is beneficially used, i.e. deposited as metal in the process of electrodeposition of galvanic chromium coatings, the rest of it is subject to entrainment with wastewater discharges and gaseous emissions [8].

The authors have developed new and more efficient ways of chromium electroplating when compared to the existing methods, which simultaneously allow improving the ecological situation caused by production of electrolytic chromium and chromium-based alloys [9 – 16].
3. Task setting
Rational processing of mineral raw materials including solid wastes from electrodeposition production facilities implies the use of initial components to the fullest extent possible, a switch to low-waste and zero-waste technology of production. Based on the amount of wastes generated in the course of this or that technological process, it is possible to judge - to a considerable extent - of the efficiency of raw materials use. At the same time, waste generation is one of the main factors determining the scale of the harmful effect caused to the environment by production, consequently, it can serve as an index of environmental compatibility of a technological process.

At the present time, there is no standard technique to evaluate the ecological efficiency of a technology taking into account the amount of all the types of wastes. Alongside with that, such evaluations are conducted for particular types of production wastes in a series of sectors of the national economy in Russia.

The environmental compatibility criterion was used for the qualitative and quantitative comparative evaluation of the existing and suggested technologies, where one of its parameters (A) determines the \( \text{CrO}_3 \) content in liquid waste discharge. The parameter B of the environmental compatibility criterion determines the \( \text{CrO}_3 \) content in gaseous emissions (the numerical values of the \( \text{CrO}_3 \) concentration were determined under laboratory conditions according to the known technique [17]).

4. Theoretical part
The content of \( \text{CrO}_3 \) in rinse waters was determined through regular methods: photocolorimetric, iodometric and permanganatometric. The analysis of the solutions obtained after rinsing of parts plated with chromium under various deposition conditions was carried out. It was found through laboratory methods and under factory conditions that a larger entrainment of \( \text{CrO}_3 \) with part surfaces from electrolysis bath is observed at higher electric current densities and electrolyte temperatures.

5. Results of the experimental investigation, practical relevance
The method of chromium plating developed by the authors, which is realized at the temperature of no higher than 45°C and at the electric current density of 25-30 A/dm², allows reducing the overall concentration of \( \text{CrO}_3 \) in the rinse water through the use of an organic substance (NF-VglISI) exhibiting the properties of a surface-active agent [18].

The presence of the NF-VglISI additive in the electrolyte increases the operating range of the concentrations of trivalent chromium and ferrum at which the quality of chromium coatings is maintained. While a standard electrolyte is allowed containing up to 4% of \( \text{CrO}_3 \) and 3-7 g/l of ferrum, the suggested electrolytes have up to 9-12% and 25-40 g/l of the abovementioned elements, respectively. Therefore, the electrolyte has to be less often corrected, which results in reduced consumption of water, chemical reagents, and first of all of \( \text{CrO}_3 \).

The calculations [19] show that up to 50% of \( \text{CrO}_3 \) is entrained into ventilation in the course of deposition of wear-resistant chromium coatings. Far from all enterprises use the protection of electrolyte against vaporization and entrainment. Manufacturing of ventilating and filtering elements of materials which exhibit poor corrosion-resistance leads to the fact that the collected chromic anhydride can be contaminated with ferrum and therefore cannot be repetitively used for production purposes without additional treatment.

Taking into account the environmental requirements and the issues of efficient use of resources, the authors investigated the influence of electrolyte temperature, electric current density, organic additive concentration and the ratio of the areas of cathode and anode surfaces on the amount of \( \text{CrO}_3 \) entrainment.

The conducted model measurements showed that the \( \text{CrO}_3 \) entrainment constantly reduces in absolute magnitude in the case if the concentration of organic additive in electrolyte increases (figure 1); it grows with an increase in the cathodic current density at all the rest parameters being constant, but the dependence of the entrainment amount referred to the quantity of the electric current passed on the electric current density is of extremal nature. In all the cases, the maximum entrainment is observed
within the range of \( j = 40-50 \text{ A/dm}^2 \). The largest entrainment of \( \text{CrO}_3 \) was observed at the ratio of the cathode and anode surfaces of 1:1. The reduction in \( \text{CrO}_3 \) concentration in electrolyte, decrease in temperature and electric current density as well as foam formation on the electrolyte surface contribute to the lessening of \( \text{CrO}_3 \) entrainment.

![Figure 1](image-url)

**Figure 1.** The dependence of \( \text{CrO}_3 \) entrainment on the concentration of 4-methylaminophenol at 25°C, at the ratio of \( S_A:S_C = 2:1 \) and the cathodic current density, A/sq:\( ^2: 1-75, 2-50, 3-25. \)

Taking into account the environmental research, the electrolytes with the following compositions are suggested, g/l: 1) 250 \( \text{CrO}_3 \), 3-5 NF-VgISI, 2) 250 \( \text{CrO}_3 \), 50-60 \( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \), 3-5 4- methylaminophenol at the temperature of the solution of 25-35°C and the electric current density of 25-30 A/dm².

5.1. **Environmental compatibility criterion of the technological process of chromium electroplating**

In order to determine the environmental significance of the suggested technology, the authors have calculated the environmental compatibility criterion \( K_{EN} \) [20] according to the formula:

\[
K_{EN} = \sum m_i^L \cdot (C_i^L / \text{MPC}_i^L) + \sum m_i^G \cdot (C_i^G / \text{MPC}_i^G) + \sum m_i^S \cdot (C_i^S / \text{MPC}_i^S),
\]

where:

- \( m_i^L \), \( m_i^G \), \( m_i^S \) - the amount of the i-th toxic component of liquid, gaseous and solid wastes, respectively, kg/kg of product;
- \( C_i^L \), \( C_i^G \), \( C_i^S \) - the concentration of the i-th component in liquid, solid wastes, \( \text{mg/dm}^3 \), and gaseous wastes, \( \text{mg/dm}^3 \);
- \( \text{MPC}_i^L \) - the maximum permissible concentration of the i-th component in the water of fishery water bodies, \( \text{mg/dm}^3 \);
- \( \text{MPC}_i^G \) - the maximum permissible concentration of the i-th component in the air of populated localities, \( \text{mg/dm}^3 \).

The \( \text{MPC}_i^L \) is supposed to be used in order to evaluate the toxicity level of solid wastes since there is a possibility of solid wastes to dissolve in the atmospheric precipitation, in wastewater discharge or subsurface water in the process of storage.

As can be seen from the formula, the environmental compatibility criterion consists of three parts: the parameters determining liquid, gaseous and solid wastes (A, B, C), respectively. The authors do not calculate the parameter C due the inability to obtain the data.

When the parameter A is calculated, the amount of the i-th component in liquid wastes \( m_i^L \) is determined by the formula:
\[ m_{L} = 2.4 \cdot 10^{-5} \cdot C_{i} \cdot Q \cdot n / P, \tag{2} \]

where

- \( Q \) is the volume of liquid wastes, \( m^3/h \);
- \( n \) is the number of working days in the year;
- \( P \) – product output, tonne/year.

When the parameters \( A \) and \( B \) are calculated, all the sources of liquid and gaseous wastes are taken into account. Thus, for gaseous emissions, \( m_{G}^{i} \) is calculated for each \( i \)-th toxic component according to the formula:

\[ m_{G}^{i} = C_{i}^{G} \cdot V_{j} \cdot 10^{-6}, \tag{3} \]

where

- \( C_{i}^{G} \) – is the concentration of the \( i \)-th component in the \( j \)-th source, \( mg/m^3 \);
- \( V_{j} \) – is the volume of emissions in the \( j \)-th source, \( m^3/h \).

The amount of the \( i \)-th toxic component \( m_{G}^{i} \) emitted with gaseous wastes by the \( j \)-th source is determined through summing of \( m_{G}^{i,j} \) over the \( i \)-th component with regard to the working hours:

\[ m_{L} = 40 \cdot m_{L}^{i,j} \cdot n / P, \tag{4} \]

The average concentration of the \( i \)-th component in gaseous wastes \( C_{i}^{G} \) is calculated according to the equation:

\[ C_{i}^{G} = \sum C_{j}^{G} \cdot V_{j} / \sum V_{j}, \tag{5} \]

where \( \sum V_{j} \) – is the total volume of harmful emissions, \( m^3/h \).

The suggested criterion was used for the analysis of environmental compatibility of the chromium electroplating process.

The results of the calculations of the environmental compatibility criterion, of the parameters \( A \) and \( B \) are presented in figures 2 and 3.

**Figure 2.** Proportion of liquid (A) and gaseous (B) production wastes (I, II, III) in the total environmental compatibility criterion \( K_{EN} \).
Figure 3. Comparative indices of environmental compatibility (according to KENV) of electrolytic chromium plating technologies.

As a result of the conducted observations, the tested electrolytes are recommended for implementation since in addition to high technological performance, a decrease in the morbidity rate of occupational diseases among the personnel operating as galvanizers has been revealed at the chromium electroplating facilities.

6. Conclusions
1. The existing methods of air and wastewater treatment aimed at removing chromium-containing components do not allow achieving satisfactory results in terms of MPC. Thus, in order to improve the environmental compatibility of chromium electroplating, it is necessary to use the technological capabilities of the process itself, this means to apply:
   - organic additives and optimal compositions of electrolytes;
   - environmentally safe modes of electrolysis (temperature, electric current density, etc.);
   - technological equipment which allows reducing environmental harm;
   - closed-circuit system of water supply.
2. The conducted model measurements have shown that:
   - the entrainment of chromic anhydride reduces with an increase in the concentration of the organic additive in electrolyte;
   - the entrainment of chromic anhydride grows with an increase in the cathodic current density at all the rest parameters being constant;
   - the dependence of the value of entrainment referred to the quantity of the electric current passed on the electric current density has the maximum;
   - the largest entrainment of CrO₃ is observed at the ratio of the cathode and anode surfaces of 1:1;
   - the reduction in CrO₃ concentration in electrolyte, decrease in the temperature and electric current density contribute to the lessening of CrO₃ entrainment.

Electrolytes with the following compositions, g/l: 1) 250 CrO₃, 3.5 NF-VgISI, 2) 250 CrO₃, 50-60 ZnSO₄·7H₂O, 3-5 4-methylaminophenol at the temperature of the solution of 25-35° C and the electric current density of 25-30 A/dm² are suggested to be used.
3. A comparative analysis of the environmental compatibility of chromium electroplating technologies has been carried out. It has been found that:
   - the introduction of the organic additive decreases the proportion of gaseous wastes from chromium electroplating by almost 8 times, and in the case when Cr-Zn alloys are obtained – by 40 times due to the reduction in the surface tension value, the electrolyte temperature and electric current density;
- the use of the suggested technology allows reducing the value of the environmental compatibility criterion by 4.5-5 times (KEN=0 corresponds to the technology which is completely safe in terms of environmental safety).

4. The suggested chromium plating electrolytes allow reducing the morbidity rate of occupational diseases among operating personnel.

7. References

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