Innovative solutions to improve the purification method of chromium-containing waste water

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Abstract. The research results showed that the problem of resource saving during the chromium electroplating from standard electrolyte can be solved. Formulated requirements that ensure the implementation of the set tasks without costs for new equipment and chemical reagents. It has been proved that organic compounds of a certain structure introduced into the electrolyte influence the chromium electroplating in such a way that all technological characteristics, coating properties, physical and chemical characteristics of the solution change. The chrome plating process has been optimized using the experimental mathematical planning method, which made it possible to develop methods for obtaining chrome coatings protected by security documents on the basis of experimental data. All the proposed methods allow solving the problem of resource saving and environmental safety. The authors have consistently studied resource-saving and environmental indicators. In galvanic chromium plating technology, resource-saving indicators are: energy intensity; metal intensity; water intensity; and labour intensity. Environmental indicators: industrial emissions: gas emissions, waste water; occupational diseases.

Introduction
The main area of nature protection is the prevention of pollution directly in the technological cycle instead of catching it at treatment plants.

Preventing pollution is always economically beneficial. This is due not only to the reduction of raw material and energy costs in the product manufacturing but mainly to the reduction of waste processing costs.

The modern technical and technological base of industry makes it impossible to carry out deep air and water treatment at industrial enterprises due to the extremely high cost of these measures. The development of new technological processes with reference to which waste-free production can be created will ensure not only high technical and economic performance but also the integrated use of natural resources. However for technical and economic reasons the transition to zero-waste technology cannot be made immediately. The real way to greening technology is to gradually switch first to low-waste and then to waste-free closed cycles. In this way sustainable environmental management and protection can be achieved.
50% of available industrial waste and emissions can be prevented at their source by using technically sound, environmentally friendly and economically viable technologies [1-2].

The electroplating production of chromium is a rapidly growing and major part of a whole range of industries, which may reach a dead end if the main objective: the quality improving of the metal surface is not addressed comprehensively in the close interconnected development of the three areas:
- improving the environmental safety of production, and environmental protection;
- development of resource-saving processes that will increase the efficiency of electrochemical chrome plating by reducing energy and raw material costs not only by using new methods but also by optimizing the process;
- study of the chrome plating process mechanism in order to obtain coatings with predefined (improved) functional properties.

It is necessary to create a process chain of interrelated operations: efficient, environmentally friendly chrome plating and chrome-containing waste water treatment. Today the separation of these operations has resulted in a more complex expensive production process than the main one [3-4]. The treatment plant which is based on the recovery of chromium (VI) compounds to chromium (III) in the form of insoluble hydroxide slurry has become more complex.

Disposing of chromium-containing sludge into building materials is still problematic as there are no statistics yet available to confirm that there has been no change in human health across generations when living in houses whose building materials contain recycled chromium-containing waste.

The widespread use of galvanic chromium plating and the environmental problems it makes pose a pressing challenge: the creation of a new electrolytes generation that will provide a high level of process efficiency with minimal harmful effects on the environment.

Based on the analysis of gas chromium-containing emissions, the water effluents composition and methods of their treatment, the chromium electroplating process, the properties of chromium coatings and chromium alloys based on it the author considers it relevant to create a system of targeted development of resource-saving processes as the basis for environmentally friendly technologies of galvanic chromium plating from water environments.

The research results that are presented in the article are devoted to the search of the main factors influencing the intensification and ecological safety of chromium electroplating and its alloys based on aqueous solutions of chromium anhydride in order to create a method that comprehensively solves the problem of resource saving and environmental protection. Parameters are defined to predict more effective additives, which introduction into the electrolyte will ensure the implementation of environmental and technological objectives [5].

The research made it possible to formulate the requirements that an organic compound - an initiating additive - must meet:
- oxidize in a chromic acid solution to form an organochromic compound with chromium ions;
- regenerated at the anode;
- do not polymerize;
- have an aliphatic substituent with at least ten carbon atoms.

These requirements are met by substances with a cyclic structure:
- carbocyclic,
- alicyclic;
- aromatic with condensed benzene nuclei;
- aromatic with condensed benzene and five-member cycles;
- heterocyclic (six or more carbon atoms, oxygen atom).

Main part
Natural oil is a promising substance that contains a sufficient number of such structures as the structures formed by the interaction of known organic additives with chrome plating electrolyte resemble the aromatic part of some oils first of all Anastasievskoye field. The maximum number of compounds
capable to meet the above requirements is contained in a second vacuum chromium run at temperatures of 350–420°C (spindle distillate) [6].

Solving the resource saving problem of the chrome plating process first of all the conditions are determined under which it is possible to obtain quality coatings at minimum current densities and electrolyte temperature.

Chroming is the most energy-intensive of all galvanic processes and is sensitive to changes in temperature and current density.

The introduction of NF-VGISI additive into the standard chrome plating electrolyte makes it possible to obtain quality coatings at a wide range of current densities at 20 °C and deposition rates that are 2-2.5 times higher than standard. The higher current yield values of chromium in the electrolyte with NF-VGISI additive are explained by a significant increase in hydrogen overvoltage compared to the use of standard electrolyte (without NF-VGISI additive) but also by protonation of organic additive [7-8].

Intensity is an important indicator of resource saving energy. Chromium plating at low temperatures (without special heating) increasing the deposition rate significantly reduced energy consumption.

The NF-VGISI additive promotes the foam formation on the electrolyte surface, which dramatically reduces (by 80-85%) the gas content of chrome anhydride.

In the framework of this task, for the first time studies were conducted on the impact of the organic additive on the physical and chemical properties of the electrolyte solution: density, viscosity, electrical conductivity and surface tension.

It was established that the change point in physical and chemical characteristics of the solution so-called "critical concentration" corresponds to the composition of the solution containing 250 g/l of CrO₃ and 2-6 g/l of NF-VGISI. Sulphuric acid is excluded. The new structure is formed which facilitates the transport of electroactive particles with this composition and certain process modes. It was shown that the maximum current yield of chromium as well as optimal values of some physical characteristics of the obtained coatings are achieved at extreme (first or second derivative) points of functions of physical and chemical properties from the composition of chromium electrolyte solutions [9].

The resulting forecast model is expressed in the following way:

$$F[\left(\frac{d\varphi(C_i)}{dC_i} = 0 \vee \frac{d^2\varphi(C_i)}{dC_i^2} = 0\right) \Rightarrow C_i] = \text{opt}$$

where $F$ is the predicted parameter (BT, microhardness and others),

$C_i$ is the concentration of electrolyte component,

$\varphi(C_i)$ is the function of density, viscosity, surface tension, specific electrolyte solution conductivity,

$\text{opt}$ - optimal value of the predicted parameter (for $BT_{\text{opt}} = \text{max}$).

This expression does not allow the numerical value of the predicted parameter to be obtained but only indicates the area and direction in which it is searched for.

The mathematical process optimization with respect to the obtained data made it possible to recommend the electrolyte composition, g/l: 250 CrO₃, 4 NF-VGISI, electroplating from which will allow obtaining optimal technological indicators [10-12].

As can be seen, an improved composition of chrome plating electrolyte, which lacks inorganic catalyst (H₂SO₄) is the study result.

For the first time, the very strict work dependence of the electrolyte and the coatings quality on sulfuric acid was eliminated. Chromium electroplating from the resulting composition is less sensitive to changes in the concentration of chromium anhydride, chromium ions (III) and iron (III).

The total concentration of Cr³⁺ and Fe³⁺ ions critical for the electrolyte was increased from 7 g/l to 40 g/l.

The results listed in Table 1 allow us to reduce the number of operations performed by the corrector worker to analyze the electrolyte composition by a factor of 2; to facilitate the purification of chrome-containing effluents (the purification stage from SO₄²⁻ has been eliminated) [13].
Table 1. Resource-saving and environmental indicators of the chrome plating from water environment

| Evaluation indicators | Estimated parameters (components) |
|-----------------------|-----------------------------------|
| **Energy capacity**   | Deposition rate increases 2-2.5 times |
| **Metal capacity**    | Electrolyte dissipation capacity increased by 40% |
| **Water capacity**    | Microhardness increased by 30-35% |
| **Labour capacity**   | Wear resistance increased by 3-4 times |
| **Gas emission**      | Internal tension reduced by 30-45% |
| **Water runoffs**     | Porosity reduced by 19-20 times |
| **Occupational diseases** | Lead consumption reduced by 2.7 times |
|                       | Electrolyte heating has been eliminated (t_{\text{pH}}=20-25^\circ\text{C}) |
|                       | Foam creation on the electrolyte surface |
|                       | Corrections frequency reduced by 1.8 times |
|                       | Deposition rate increased by 2-2.5 times |
|                       | Electrolyte heating is excluded (t_{\text{pH}}=20-25^\circ\text{C}) |
|                       | Foam creation on the electrolyte surface |
|                       | Utilization of used electrolyte |
|                       | Exclusion of sulfate ions from aqueous effluents |
|                       | Deposition rate increased by 2-2.5 times |

In view of the foregoing conclusions are drawn which undoubtedly confirm innovative solutions for improving the treatment of chromium-containing waste water:
- the deposition rate of chromium is increased by a factor of 2-2.5 that reduced electricity consumption (energy consumption) by a factor of 2-2.5, the electroplaters number by a factor of 2 (from three-shift operation to one-shift operation), reduced the rate of solution removal from CrO_3, and reduced occupational diseases;
- electrolyte heating is eliminated, which reduced steam consumption, electrolyte evaporation, occupational diseases level by 100%, number of electrolyte adjustments by 1.5 times, amount of water consumed, number of electroplaters - adjusters, chemical reagents consumption;
- foam is formed on the electrolyte surface, which prevents electrolyte drift, reduces gas emissions by 70%, leads to the saving of chemical reagents, man-hours, electrolyte correction is reduced by 1.5 times that reduced the volume of industrial effluents;
- the dissipation electrolyte capacity is increased by 40% that made it possible to reduce the number of locksmiths producing special lead anodes and to save lead (100%);
- the concentration of Cr^{3+} and Fe^{3+} was increased to 40 g/l, thus increasing the electrolyte lifetime that reduces man-hours (for correction), chemical reagent consumption and the volume of chrome water effluent;
- microhardness increased, wear resistance (94-5 times) that increases the service life of the part and reduces metal consumption;
internal stresses in coatings reduced (by 1.25 times);
- coating porosity reduced by 12-20 times (1-2 pores/cm²);
- corrosion resistance increased by 3-4 times (acts in the annex) that made it possible to eliminate preliminary copper and nickel plating operations, thus reducing electricity consumption (by 1.2 times).

References
[1] Moskvicheva E V 1998 Resource-saving processes as a basis for environmentally friendly galvanic chrome plating technologies from water and non-water environment Dokt. Diss.: 11.00.11, 05.17.03 Moscow 352.
[2] Furtatova O N 2004 Intensification of electrolytic chrome plating and neutralization of chromium-containing effluents Cand.Diss: defended 30.03.2004, 05.17.03 / Oksana Nikolaevna Furtatova. Novocherkassk 127.
[3] Elinany G A, et al. 1976 Polarography of metal-galllic complexes Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 72.3 363-369.
[4] Elynek T B 1992 The Successes of Electroplating Technology An Assessment of the International Literature 1990-1991. Metal plating and surface treatment 1 (3-4) 7-26.
[5] Galkin Yu A, Lotosh V E 1990 Technology of sewage sludge disposal at machine building enterprises Chemistry and water technology 12 (6).
[6] Libreich E 1934 Theorie der Verchromung. Z. Elektrochem 1 73-87.
[7] Ignatiev V I, Ionicheva N S and Mareichev A V 1985 Galvanic coatings in mechanical engineering Handbook. In 2 volumes. Edited by Shluger M A.
[8] Kauspedens D V 1994 Galvanotechnology and metal processing 3 43.
[9] Naidenko V V, Gubanov L I 1999 Cleaning and utilization of electroplating industrial processes (Nizhny Novgorod, Decon) 432.
[10] Unruch Y 1991 Metaloberflaeche 3 107.
[11] Shkurikova E B 997 Environmental safety of electroplating production through reorganization of Consciousness Electroplating and surface treatment (5) 1 42-49.
[12] Kushnina K S, Vavilova A S 1990 Wastewater treatment and disposal of electroplating sludge and sludge from hexavalent chromium production (Moscow).
[13] Smirnov D N, Genkin V E 1980 Wastewater treatment in metal processing processes (Moscow, Metallurgy) 88.