Closed-loop Chromium Plating Line

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Three-year operation of a chromium plating line equipped with chromic acid recycling system based on the use of immersed electrochemical modules have demonstrated high environmental and economic efficiency. Chromic acid returned into the plating tank is free of cationic impurities (iron, copper, etc.). Operation costs were reduced by 50%, and initial costs were compensated as soon as in thee months. A new version of the system developed recently which allows eliminating any loss of chromic acid due to cathodic reduction will soon be put into operation.

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Introduction

Conventional chromium plating lines in the Soviet Union and nowadays in Russia always included at least one reclaim tank. Some water, containing chromic acid, from this tank is periodically added to the plating tank to compensate the evaporation of water. The steady-state concentration of chromic acid in the reclaim tank is usually relatively high – from 15 to 100 g/l. Lower values are observed in the production of thick coatings and higher ones in decorative chromium plating. Purification of waste water coming from rinsing tanks is relatively expensive. It needs special equipments (evaporators, ion-exchangers, galvano- or electrocoagulators, etc.) and consumes much thermal or electric energy or produces large amounts of solid waste. The use of membrane electrolysis directly in reclaim tanks is the only method with very low initial and operation costs which ensures efficient reduction in the input of chromic acid into waste water. The implementation of this method in tens of industrial plating shops has proved its efficiency both in environmental and economic aspects. Some comparative data on the operation of conventional chromium plating tank with and without membrane electrolytic cell installed in the reclaim tank are given in this paper.

Operation of the Membrane Cell

The membrane cell (Fig. 1) consists of the cathode compartment (the reclaim tank itself), the anode compartment, i.e. a so called immersed electrochemical module (IEM) with an anion-exchange membrane installed in one of its walls and the electrodes placed near the opposite sides of the membrane (the anode – inside the module, the cathode – in the reclaim tank).

In the course of the electrolysis chromate (or dichromate) ions pass through the membrane. Major electrode reaction at the anode is the formation of oxygen which also includes liberation of hydrogen ions:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

A combination of the electrode reaction (1) and the electrolytic transport of ions results in the accumulation of chromic acid in the anolyte. Some part of it is periodically added to the solution in the plating tank and same volume of water is added to the anolyte afterwards to keep its level constant. It should be noted that chromic acid solution in the module is completely free of any metal ions (Fe^{3+}, Cr^{3+}, etc.). Thus the addition of this solution to the plating tank decreases their concentrations in the plating solution.

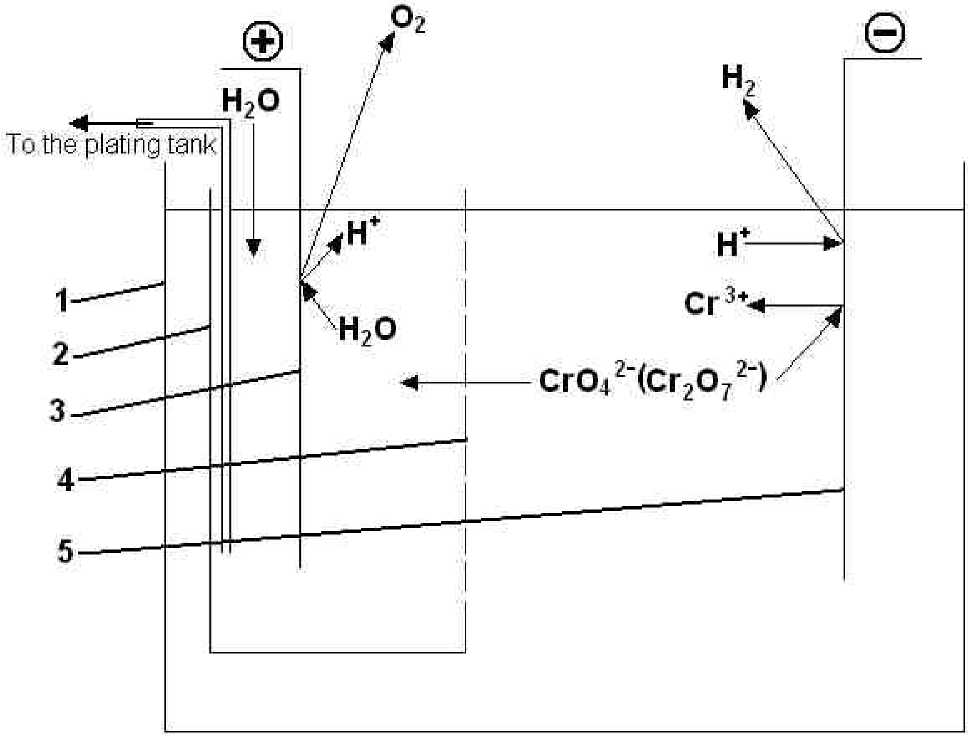

Fig.1. Reclaim tank with immersed electrochemical module.
1, Reclaim tank;
2, Immersed module;
3, Anode;
4, Anionic membrane;
5, Cathode.

There are two parallel reactions at the cathode:

the discharge of hydrogen ions

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

and the reduction of chromate (dichromate)

$$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad (3)$$

Chromate (dichromate) ions are converted into trivalent chromium, thus, ensuring further reduction in the input of Cr^{6+} into waste water. Overall electric energy consumption and the input of Cr^{6+} into flowing rinses are reduced by approximately 50% due to the reaction (3). However, the amount of chromic acid returned into the plating tank is about 50%, and the rest is lost as Cr^{3+} dragged from the reclaim tank into flowing rinses.

Two immersed modules are used in a new modification of the process (Fig. 2). Second (cathodic) module with a cationic membrane prevents cathodic reduction of chromic acid. Therefore nearly 100% of chromic acid dragged out from the plating tank is returned back. On the other hand it will be necessary to install a cathodic module and an additional anodic module in order to maintain same steady-state concentration of chromic acid in the reclaim tank, which is observed in the previous case. Apart from lower productivity the new process consumes about three times more electric energy. All plating shops in Russia which are using membrane cells in the reclaim tanks still have been using single-module version.

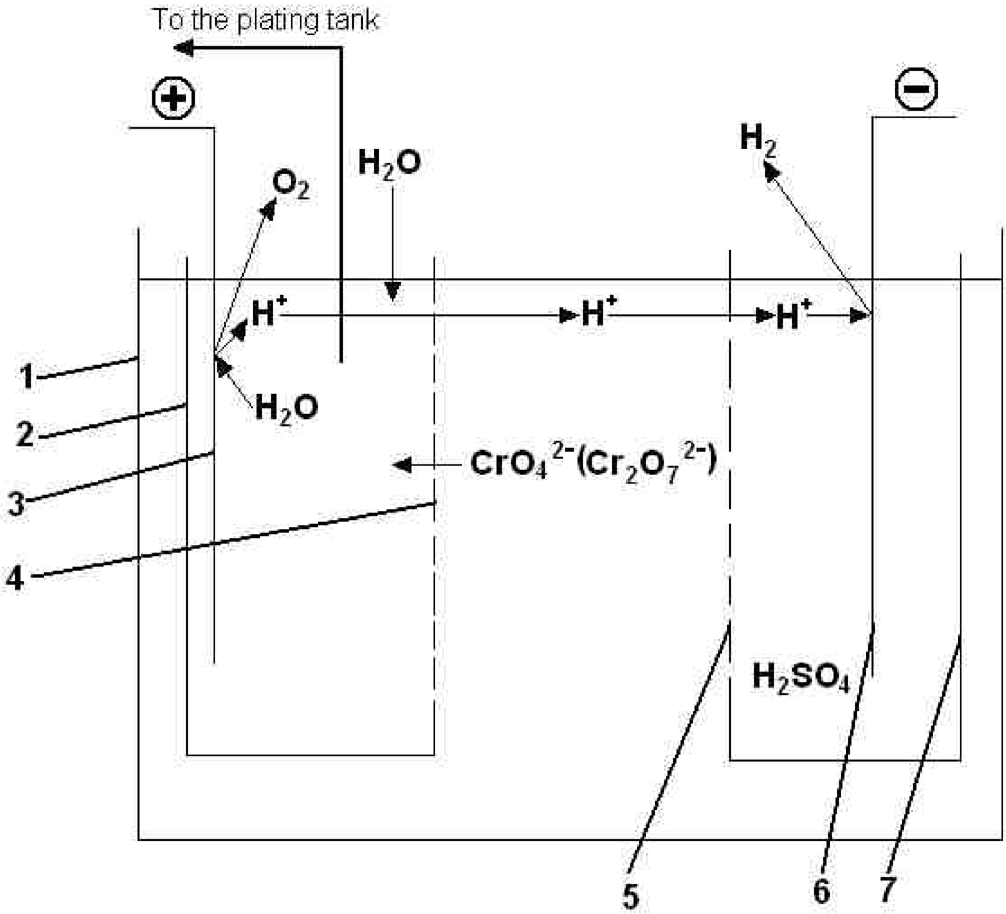

Fig.2. Reclaim tank with two immersed modules.
1, Reclaim tank;
2, Anodic module;
3, Anode;
4, Anionic membrane;
5, Cationic membrane;
6, Cathode;
7, Cathodic module.

Industrial Experience

The results of a one-year operation of chromium plating line in «Uralvagonzavod» are given below. Annual output of plated parts was equal to 1000 m^2 (1 shift, 5 working days a week). In this line the parts after plating were rinsed in the reclaim tank with installed in it anodic module with an anionic membrane. Lead anode was placed inside the module and stainless steel cathode was located in the reclaim tank parallel to the membrane. About half of the solution inside the module was transferred into the plating tank, when the concentration of chromic acid (as CrO_3) reached 40 to 50 g/l. The parts after the rinsing in the reclaim tank were rinsed in a flowing rinse tank. Because of such procedure average concentrations of chromic acid in the reclaim tank and in the following rinse were reduced by many times (See Table 1).

Table 1. Average values of CrO_3 concentrations with and without the module in the reclaim tank

Parameter	Plating line without the module	Plating line with the module
CrO_3 in the reclaim tank, g/l	19.4	2.4
CrO_3 in the flowing rinse tank, g/l	0.2	0.02
CrO_3 returned into the plating tank in one year, kg	–	68

It follows from these data that the use of the module should lead to considerable reductions in the consumption of various chemicals (CrO_3, and chemicals used in the treatment of waste), fresh water and in the total costs.

The structure of the production costs related with the environment protection is shown in the Table 2.

Table 2. Comparison of annual costs related with the environment protection with and without the modules for two plating lines.

	Without the module		With the module	
	Amount	Cost	Amount	Cost
Disposal of concentrated liquid waste	10 m^3	18600 rbl $ 744	3 m^3	3100 rbl $ 124
Consumption of fresh water	27000 m^3	31500 rbl $ 1260	13500 m^3	15800 rbl $ 632
Reagents used for waste treatment		181000 rbl $ 7240		47600 rbl $ 1904
Electric energy consumed in waste treatment	64800 kWhr	50500 rbl	30300 kWhr	23600 rbl $ 944
Total operational costs for waste treatment		281600 rbl $ 11264		90100 rbl $ 3604

Initial costs related with the installation of four immersed modules were equal to 53300 rubles ($ 2132). So they were completely repayed in 3.5 months. Because of high economic and environmental efficiency of immersed modules plant management decided to install them in other chromium plating lines. Total number of plating shops in Russia now using immersed modules in reclaim tanks is over 200.

Summary

The access of chromic acid into waste water from chromium plating line, consumption of water, amounts of liquid and solid waste formed are considerably reduced, if immersed electrochemical modules are used in reclaim tanks.

Chromic acid is removed from rinse water in the reclaim tanks and is concentrated inside the modules being completely purified from all cationic impurities (Fe^{3+}, etc.).

Chromic acid accumulated in the module is returned into the plating tank.

