

DOI:10.47188/0869-5326_2023_31_3-4_25

УДК 544.6;546.56;546.742

Экологические аспекты пассивации цинка в растворах на основе солей трехвалентного хрома

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Электрохимическая регенерация раствора на основе трехвалентного хрома позволяет предотвратить накопление в растворе ионов цинка и продлить срок службы раствора. Другая проблема, которую также можно решить - ограничить вынос тонов фтора в ванны проточной промывки путём установки электрохимического модуля в ванну улавливания после ванны пассивирования с целью извлечения из неё ионов фтора. Одновременная работа двух модулей даёт возможность значительно улучшить экологическую ситуацию в гальваническом цехе.

Ключевые слова: хромирование, погружной модуль, регенерация.

UDC 544.6;546.56;546.742

Environmental Aspects of Zinc Passivating in Solutions Based on Trivalent Chromium Salts

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Electrochemical regeneration of trivalent-based baths allows to prevent the built-up of zinc ions and to extend the life-time of the solution. Another problem which can be solved is the control of the emission of fluoride ions into flow-rinses by introducing a reclaim tank after the passivating tank with an electrochemical module in it which will remove fluoride ions from rinse water. Simultaneous operation of the two electrochemical modules allows to improve considerably the environmental situation in the plating shop.

Keywords: trivalent chrome passivation, immersed electrochemical module, regeneration

Introduction

Various methods including electrochemical ones have been proposed for the regeneration and utilization of spent solutions as well as for the purification in plating lines in order to create "green" electroplating industry [1-10]. The use of zinc passivating solutions, based on trivalent chromium allows to eliminate hexavalent chromium from both protective films on the surface of zinc-plated parts and process solutions. However, the operation of new types of passivating solutions still creates solid and liquid wastes, containing toxic components, such as zinc, chromium, fluoride atc. New types of passivating solutions like old ones can be operated usually for only limited time and should be dumped periodically due to excessive built-up of zinc ions (usually about 10 g/l). Any treatment of spent solutions only converts liquid wastes into solid ones. Continuous regeneration of passivating solutions would provide a radical solution of problems related with spent solutions. Another environmental aspect of the operation of any passivating solution is a drag-out of the passivating solution into rinsing tanks. Ion-exchange with complete recycling of components would be of course a promising technology, however, not economical when applied to a single rinsing tank. Multi-stage rinsing in a combination with the evaporation would be also possible. An alternative approach based on the membrane electrolysis is described below. Membrane electrolysis may be used for both continuous regeneration of the passivating solution and continuous purification of rinse water after the passivating.

Regeneration of passivating solution

The regeneration is carried out in a three-compartment electrolytic cell with two cation-exchange membranes (Fig. 1).

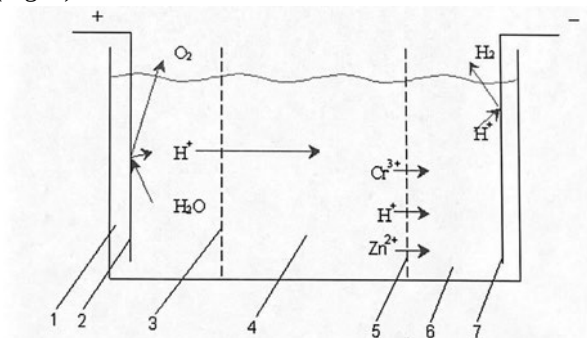
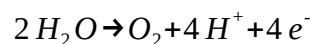


Fig. 1. Regeneration cell; 1, anode compartment; 2, anode; 3, cation-exchange membrane; 4, intermediate compartment; 5, cation-exchange membrane; 6, cathode compartment; 7, cathode.

When electric current passes through the cell, hydrogen ions are formed at the anode (2).



Then, the electric charge is transferred by these ions through the cation-exchange membrane (3). Passivating solution is contained in the intermediate compartment (4). Ions of trivalent chromium are consumed in the course of the passivating and are substituted by zinc ions. In addition to their consumption certain amount of chromium ions is transferred through the membrane (5) into the cathode compartment. Therefore, chromium ions should be added to the passivating solution. The excessive built-up of zinc ions should be prevented by their removal. The removal is accomplished by the transfer of ions from the passivating solution into the cathode compartment (6) through the cation-exchange membrane (5). The relative rates of the transfer of all cationic species through membrane (5) is controlled by the transport numbers:

$$t_j = (c_j | z_j | u_j) / \sum c_j | z_j | u_j \quad (2)$$

Here t_j is the transport number of the particular (j) ions, z_j is their charge number, and u_j is the ionic mobility.

The absolute value of the transfer rate is expressed by the formula:

$$V = (M_j \cdot I \cdot t_j) / (|z_j| F) \text{ g/hr} \quad (3)$$

Here V is the transfer rate, M_j is the molecular mass of ions, I is the current passed through the cell F is the Faraday's number.

It follows from equations (2) and (3) that the input of hydrogen ions from the anode compartment will always compensate their consumption in the process of passivation and their transfer into the catholyte. On the other hand, the transfer of zinc and chromium ions at constant pH in the passivating solution will be controlled mainly by their concentration ratio:

$$t_{Cr} / t_{Zn} \approx (3C_{Cr}) / (2C_{Zn}) \quad (4)$$

Therefore, the loss of chromium ions due to their transfer into the catholyte will be minimized, if the operation of the passivating solution is made with continuous regeneration and the concentration of zinc ions is close to its upper limit.

Following considerations concerning pH changes in the anodic and cathodic compartments should be taken into account. Since current efficiency for oxygen formation at the anode is close to 100%, every Faraday passed through the cell, will produce by the reaction (1) one mole of hydrogen ions in the anolyte. Since transport number of hydrogen ions in the cation-exchange membrane is equal to unity, all hydrogen ions formed are transferred from the anode compartment. This means that the initial concentra-

tion of an acid in the anolyte will not change in the course of the electrolysis.

The balance of hydrogen ions in the catholyte is not so easily predictable, since the electric charge is transferred through the second cation-exchange membrane (5) simultaneously by several ionic species: hydrogen, zinc, trivalent chromium and other cations (alkaline metals, ammonium) which possibly are the components of proprietary passivating baths. Apart from that the cathode current efficiency for hydrogen formation may be less than 100% due to the discharge of metal cations as a result of this process pH of the catholyte may be rising up resulting in the precipitation of hydroxides at the cathode. Therefore, acidification of the catholyte by periodic additions of an acid may be necessary in order to prevent this.

Purification of rinse water

Fluoride is a major anionic component of passivating solution which should be removed from rinse water, while zinc and trivalent chromium are major cationic components. Therefore, a four-compartment cell may be used in this case (See Fig. 2).

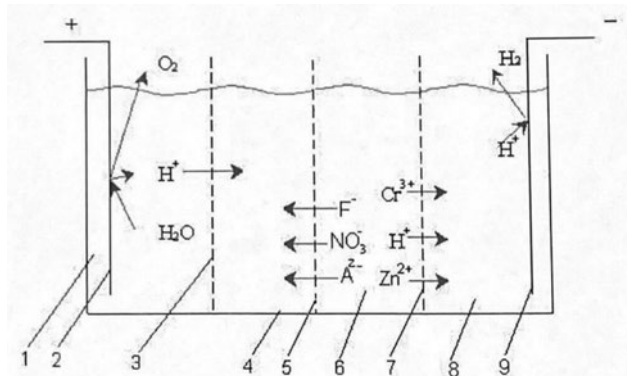


Fig. 2. Four-compartment regeneration cell; 1, anode compartment; 2, anode; 3, cation-exchange membrane; 4, intermediate compartment collecting mixture of acids; 5, anion exchange membrane; 6, compartment with rinse water; 7, cation-exchange membrane; 8, cathode compartment; 9, cathode.

As the anode reaction in the regeneration process is the formation of oxygen (reaction 1), and the electric charge is transferred through the cation-exchange membrane (3) by hydrogen ions, the composition of the anolyte does not change in the course of the electrolysis.

The intermediate compartment (4) accumulates all anionic components of the passivating solution approximately in the same proportions as they are contained in it. Rinse water is contained in the compartment (6), separated from the compartment (4) by an anion-exchange membrane (5). Cations contained in the rinse water are transferred through a cation-exchange membrane (7) into

the cathode compartment (8). Thus, both cations and anions are removed from the rinse water and are accumulated in separate compartments, from which they can be returned into the passivating tank.

Equipment

1. Regeneration unit

Most economical way to implement the regeneration of the passivating solution is based on the use of immersed electrochemical modules 1. Cathodic and anodic modules can be placed in the passivating tank. Their position should meet following requirements: (a) not to interfere with the treatment of work pieces; (b) to minimize the electrical resistance of the passivating solution between the membranes. The width of the space occupied by the two modules may be reduced down to 15-20 cm (Fig.3).

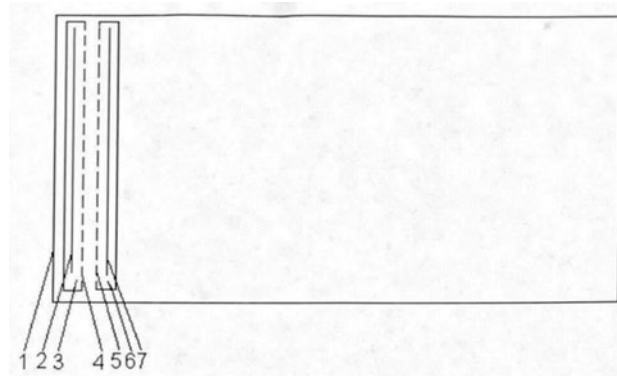


Fig. 3. Passivating tank with two immersed modules; 1, tank with passivating solution; 2, anode; 3, anodic module; 4, anion-exchange membrane; 5, cation-exchange membrane; 6, cathodic module; 7, cathode.

For the successful operation of the regeneration unit it is necessary to ensure effective exchange of the solution in the gap between the modules and in the whole tank.

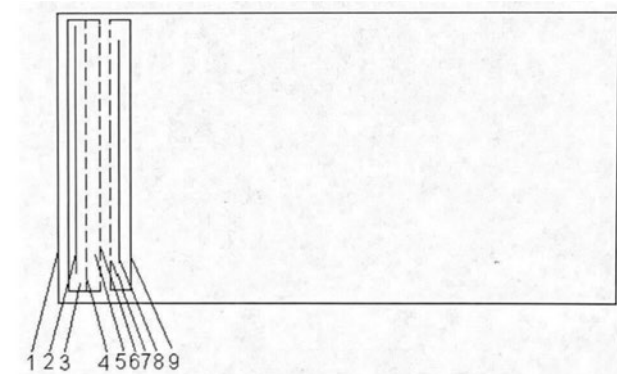


Fig. 4. Reclaim tank with two immersed electrochemical modules; 1, reclaim tank; 2, anode; 3, anode compartment; 4, cation-exchange membrane; 5, intermediate compartment; 6, anion-exchange membrane; 7, cation-exchange membrane; 8, cathode; 9, cathodic module.

2. Purification of rinse water

Like in the passivating tank, effective exchange of rinse water in the gap between the modules and the whole reclaim tank is necessary (Fig. 4).

The operation of the reclaim tank with electrochemical modules and will allow to reduce the amount of chromium, fluoride, and other ions dragged from the passivating solution will allow to return them back. Simultaneously the consumption of chemicals and fresh water as well as the amount of solid waste formed are reduced.

Summary

There are two types of environmental problems related with the operation of passivating solutions based on trivalent chromium salts: Periodic dumping of spent solutions; Drag-out of process solutions into rinsing tanks. The use of membrane electrolysis allows to solve both problems - to eliminate periodic dumping and to reduce considerably the input of the components of the passivating solutions into waste water. The implementation of membrane electrolysis does not need additional floor space in the plating line. The membrane electrolytic cells consist of existing process tanks in the plating lines and immersed electrochemical modules, i.e. half-cells, with cathodes and anodes, separated from the solutions in the process tanks by ion-exchange membranes.

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For citation

Kruglikov S. S. et al. Environmental Aspects of Zinc Passivating in Solutions Based on Trivalent Chromium Salts, *Electroplating & surface treatment*. 2023, vol. 31, no. 3–4, pp. 25–28.

DOI: 10.47188/0869-5326_2023_31_3-4_25