Chromate-based Solutions Are Not Dumped Any More: Industrial Experience in Russia, USA & Germany

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Chromate-based solutions used for the passivation of Zn, Cd or Cu, for etching, stripping, etc., are usually dumped when the concentrations of metal ions exceed certain critical value. All types of such solutions can be regenerated directly in a process tank or in a separate regeneration unit. Plating shops in the USA and Germany that are regenerating black zinc chromate solutions (silver-containing) have never dumped them for many years. A number of plating shops in Russia stopped dumping different chromate-based solutions used for the treatment of Zn, Cd and Cu.

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1. Introduction

Chromate-based solutions are widely used as passivating solutions, bright dips, etchants and strippers. In all these applications chromate (or dichromate) ions in acid media react with metal surface:

$$2CrO_4^{2-}+3M+16H^+\rightarrow 2Cr^{3+}+3M^{2+}+8H_2O \qquad (1)$$

Here M designates any divalent metal, such as Zn, Cd, Cu, etc.

Gradual built-up of trivalent chromium ions Cr^{3+} and M^{2+} ions produces negative effect on the activity of the solution. Periodic replenishments (additions of chromate and an acid) allow to increase the life time of the solution, however, it should be dumped, when the concentrations of M^{2+} and Cr^{3+} reach certain limiting values. By the end of the operation period actual concentration of chromate in such solutions usually exceeds considerably its value in fresh solutions.

Economic losses related with making up fresh solutions and disposal of spent ones can be avoided, if excessive amounts of trivalent chromium and other metal ions are removed from the solution. There are several ways for the removal of metal cations from solutions containing chromate. Membrane electrolysis is among them one of most efficient and economical one.

2. Principles of the Regeneration

Three versions of membrane electrolysis have been proposed for the regeneration of chromate-based solutions:

(A). Two-compartment cell with one cationic membrane (Fig 1A)
(B). Tree-compartment cell with two cationic membranes (Fig. 1 B)
(C). Three-compartment cell with one cationic and one anionic membrane (Fig. 1C).

(A). Two-compartment cell

The cell (Fig. 1A) consists of a cathode and an anode compartments. Chromate solution is contained in the anode compartment. Composition of the catholyte depends on the composition of the anolyte and on the particular requirements to the regeneration process. In general it should contain only anions which are already contained in the anolyte. Under such conditions their slow transfer into the anolyte will not produce any adverse effect.

In the course of the electrolysis all kinds of cations present in the anolyte pass though the membrane since they migrate to the cathode. The rate of their transfer from the anolyte into the catholyte is directly proportional to the magnitude of electric current. On the other hand, the rate of the transfer of particular cations (at constant current) depends of their relative concentration:

$$t_i=(z_ic_iu_i)/(\sum z_ic_iu_i) \qquad (2)$$

Here t_i is the transport number of ''i'' cations, z_i is their charge number and u_i is their mobility in the membrane. This means that the consumption of electric energy for the removal of a certain amount of given ions from the anolyte will decrease with increasing concentration of these ions in the anolyte, (assuming the concentrations of all other ions constant). Therefore, continuous regeneration is preferable, since it allows to minimize energy consumption by maintaining constant concentrations of cations in the chromate solution at such levels which are high enough, but still not harmful for the successful operation of a particular chromate-based process solution. In many cases the acidity or the pH value of chromate-based solutions is one of critical parameters. In the course of the operation of such solutions hydrogen ions (i.e. an acid) are consumed (see eq. 1). In the course of the regeneration by membrane electrolysis the concentration of hydrogen ions in the anolyte is increasing, since the rate of their transfer into the catholyte by migration is always smaller then the rate of their formation at the anode by the following reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (3)$$

$$n_{H+} = Q/F(1-t_{H+}) \quad (4)$$

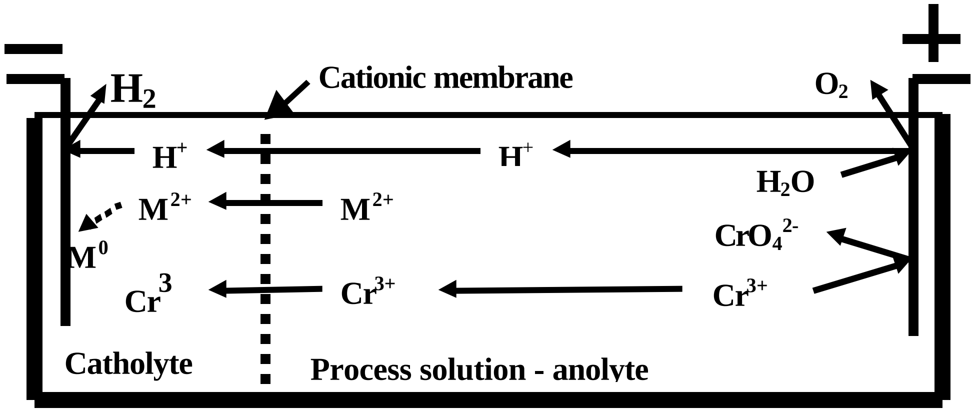

Fig. 1A

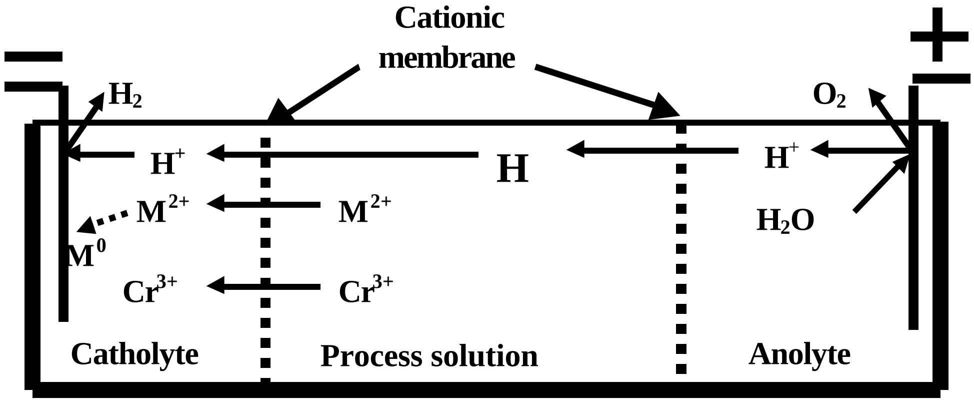

Fig. 1B

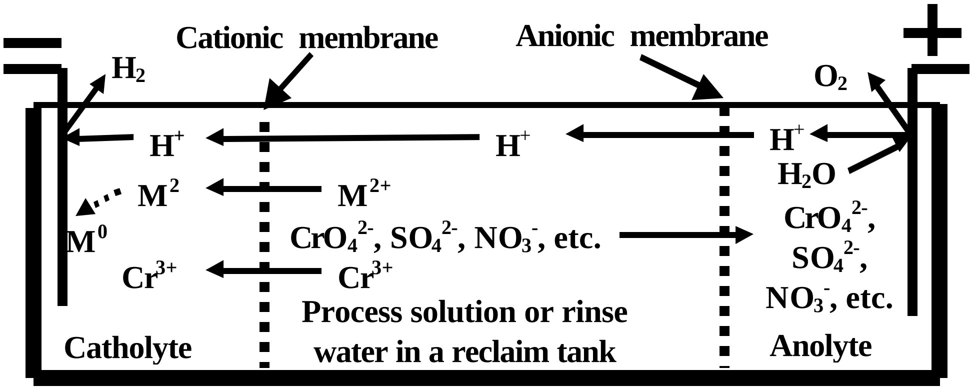

Fig. 1C

Here n_{H+} is an increase in the number of moles of hydrogen ions in the anolyte, Q is electric charge passed through the cell, F is Faraday's number and the expression in brackets ($1-t_{H+}$) is a difference between the current efficiency of the anodic formation of hydrogen ions (equal to unity, or 100 %) and their transport number t_{H+}. Since $t_{H+}<1$, n_{H+} is always a positive value, i.e. the regeneration causes the acidification of the chromate solution. Under favorable conditions the consumption of hydrogen ions by the reaction (1) is compensated by their formation by the reaction (3). If it does not happen, an appropriate amount of an acid or alkali is added to the solution.

Depending on the composition of the catholyte and the type of cations transferred from the anolyte they may be accumulated in the catholyte as soluble salts (e.g. zinc sulfate) or discharged at the cathode forming metal deposit (e.g. copper).

(B). Three-compartment cell with two cationic membranes

This cell (Fig. 1B) is used for the regeneration of chloride-based chromate solutions used for the passivation of Zn-Ni coatings and can be also used for the regeneration of zinc passivating solutions containing trivalent chromium salts instead of chromates. The solution to be regenerated is contained in the intermediate compartment. The catholyte and the anolyte contain respectively chlorides and sulfates. Therefore chloride discharge at the anode and formation of chlorine gas is avoided completely or it proceeds with very small rate, determined by the permeability of the cationic membrane for chloride ions.

(C). Tree-compartment cell with one cationic and one anionic membranes

This cell (Fig. 1C) is usually used for the recuperation of chromic acid (together with other anions present in the process solutions) from diluted chromate-based solutions contained in reclaim tanks installed near chromate treatment or chromium plating tanks. In the course of electrolysis the concentrations of all kinds of ions are decreasing, and in a continuously operating plating line such reclaim tanks allow to reduce water consumption for rinsing operations and to recycle chromic acid.

The use of porous diaphragms

Porous diaphragms made of sintered glass, ceramics or chemically stable plastics (PVC, etc.) may be used instead of ion-exchange membranes in solutions, where ion-exchange resins are unstable. Principal difference between the porous diaphragms and the cationic or anionic membranes is equal permeability of diaphragms for all kinds of ions. This means that the sum in eq. (2), $\sum c_i z_i u_i$ in case of a diaphragm will contain items representing both cations and anions. Therefore, the transport number and the rate of the transfer for a given type of ions will always be lower, if a diaphragm is used instead of a corresponding ion-selective membrane. If a major goal of regeneration process is the removal of Cr^{3+} from the solution, a two-chamber cell with a diaphragm similar to that in Fig. 1A is preferable. It allows to combine the two mechanisms: the transfer of Cr^{3+} into the catholyte and their anodic oxidation into Cr(VI).

A two-chamber cell with a diaphragm may also be used in reclaim tanks, if anionic membrane is unsuitable. As practical experience has shown some types of anionic membranes can lose their permeability for chromate ions even in diluted solutions. If a two- chamber cell with a diaphragm is used in a reclaim tank, the overall rate of the removal of chromate ions is increased. In this case only a part of them is transferred into the anolyte and another part is reduced at the cathode into Cr^{3+}. In this version of the process the relative recovery of chromate and energy consumption are considerably lower than in a three- chamber process.

In certain three-chamber processes only the cationic membranes are sometimes stable enough in particular solutions. So a diaphragm can be used here instead of the anionic membrane. Such a replacement will, of course, reduce the transport number of chromate ions because of greater contribution of hydrogen ions to the charge transfer between the anolyte and the intermediate chamber.

3.Practical examples

Regeneration processes

Several types of regeneration process using the two-chamber cell have been implemented in plating industry by the author. They include:

(a) Zinc passivating solutions
(b) Cadmium passivating solutions
(c) Copper bright dipping solution

(a) Zinc passivating solutions

Regeneration of black zinc-chromate (silver-containing) solution is in operation for few years in continuously operating regeneration cells. Chromate solution is circulating through the passivating tank in the zinc plating line and the anode chamber of the regeneration cell. Sufficiently high acidity is maintained in the catholyte to prevent the electrodeposition of zinc. So only silver sponge is deposited at the cathode and can be easily returned back into the process solution as silver nitrate. ’’Gatto Industrial Platers Inc’’ (Chicago, USA) and ’’Assmus Metallveredelung GMBH’’ (Frankfurt, Germany) job shops are using this process. Before the start of the regeneration the process solution had been dumped once a month.

In Russia in a number of plating shops iridescent- and golden zinc chromate solutions are continuously regenerated directly in the chromating tanks (i.e. in anode chambers). Cathode chambers as membrane half-cells are installed directly in the process tanks. Solutions which do not contain anions causing instability of lead anodes are preferable and are sometimes actually used since the reoxidation of Cr^{3+} proceeds with high current efficiency at lead dioxide. Platinized titanium anodes are used for solutions containing nitric acid.

(b) Cadmium passivating solutions

Cadmium passivating like that of Zn is performed in Russia in chromate solutions containing nitric acid and those containing only chromate and sulfate anions. Both types of solutions are continuously regenerated for a long period without a single dumping. Efficient and continuous removal of cadmium ions from the solution in the course of the regeneration process prevents the cadmium contamination of rinse water in the rinsing tanks after the passivation stage.

(c) Copper bright dipping

A solution containing chromic and sulfuric acids is continuously regenerated for several years without dumping. Cathode chamber with a cationic membrane is installed in the process tank. Lead or platinized titanium are used as anodes. Copper metal is deposited at a stainless steel cathode.

Removal of chromate ions from reclaim tanks

Many plating shops in Russia remove chromate ions from reclaim tanks installed in zinc, cadmium, chromium plating lines. An anodic half-cell is immersed into the reclaim tank and accumulates chromic acid alone (reclaim tanks in the chromium plating lines) or its mixture with other acids (reclaim tanks after chromate treatment). As a result, the input of chromate ions to the next process stage, i.e. into the flowing rinses is reduced many times. Another advantage is the recycling of about 50 % chromates dragged out from the process tanks.

Summary

Electrochemical regeneration of various chromate-based solutions eliminates periodic dumping, allows to stabilize the composition of a process solution and its performance.

The use of reclaim tanks with immersed anodic half-cell reduces the input of chromates into waste water and allows their partial recycling.