Electrodialysis in Chromium Plating and in Chromate Treatment

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Electrodialysis is proposed for the recycling of chromic acid from non-flowing rinses (reclaim tanks) as an effective alternative for conventional ion-exchange process, especially in low-output plating lines. A compact membrane cell is placed directly into the reclaimed tank. It removes chromic acid from rinse water and concentrates it. Concentrated solution is returned to the chromium plating or chromate treatment tank. The cell allows the recycling of up to 90 percent of chromic acid from rinse water and correspondingly reduces its output into flowing rinses. No chemicals are consumed, and commercially available inexpensive membranes are used in the cell.

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Major Types of Chromate-based Solutions

Concentrated Solutions

Chromic acid or dichromates are essential components of various solutions used for chromium plating, anodizing, electrochemical and chemical polishing, etching, de-scaling, etc. All these solutions have limited lifetime ranging from a few days up to one or a couple of years. Spent solutions are usually dumped and de-toxicated by chemical reduction of hexavalent chromium to trivalent state followed by precipitation of chromium hydroxide after adding some alkaline.

Diluted Solutions

All kinds of operations, where chromate-based solutions are used, are followed by rinsing. So, rinse water in rinsing tanks is basically the same solution with reduce concentrations of all components. Purification and recycling of rinse water can be accomplished by ion-exchange treatment. It can be done, in principle, for each individual type of rinsing tank and in such a case both water and dissolved substances can be recycled. However, initial and maintainence costs are rather high. Therefore, most of plating shops using ion-exchange treatment prefer to recycle only water from a single unit which treats combined water flowing from all different rinsing tanks. Conventional reagent technology is still most common in plating shops.

Electrochemical Treatment in Non-divided Cells

Electro-coagulation is used in some plating shops in the USA* and Europe for the purification of chromate-containing waste water. The process is efficient and relatively cheap. However, there is no recovery of chromates since all chromium (VI) is converted into chromium hydroxide mixed with hydroxides of iron and other heavy metals.

* Kaspar Electroplating Corp., Shiner, Texas

The following reactions proceed in the electro-coagulation cell:

Anodic Reaction	$3Fe \rightarrow 3Fe^{2+} + 6e^-$
Cathodic Reaction	$6H_2O + 6e^- \rightarrow 3H_2 + 6OH^-$
Chemical Reaction	$3Fe^{2+} + H_2CrO_4 + 2H_2O \rightarrow 3Fe^{3+} + 3Cr^{3+} + 6OH^-$
Over-all Reaction	$3Fe + H_2CrO_4 + 8H_2O \rightarrow 3Fe(OH)_3 + Cr(OH)_3 + 3H_2$

Membrane Electrolysis

Regeneration of chromate-based spent solutions by means of membrane electrolysis[1,2,3] includes the removal of cationic impurities, M^z. Some part of trivalent chromium is re-oxidized to hexavalent state and the rest is removed from the solution together with other cationic impurities. Figure 1 illustrates the principle of the regeneration process. A good example of successful operation of this process is regeneration of solutions used for the chromate treatment of zinc-plated parts in a number of plating shops in Russian, USA* and Germany. The solutions which had been dumped before on a monthly basis have never been dumped since the regeneration was started (now for 1 – 4 years). Economic and environmental benefits are evident: a single make-up costs are usually around $1000 for one tank.

Electrodialysis

Concentrated Solutions

A process reversed to that described above is a recovery of chromate ions from spent chromate-based solutions (see Fig. 2). Efficiency of the process depends mainly on the transport number of chromate ion for the particular type of anionic membrane. This transport number is progressively falling down as the concentration of chromate ions in the intermediate chamber is gradually decreasing in

*Gatto Industrial Platers, Inc., Chicago, Illinois the course of the process. So, complete recovery of chromate ions is impossible, and three-chamber version is suitable for the regeneration only in rare cases.

Another type of three-chamber cell which has two cationic membranes (instead of one cationic and another anionic one) can be used for the regeneration of chloride-type chromate solutions (see Fig. 3). Such solutions are used in the passivation of certain zinc alloys, e.g. zinc-nickel (12 – 14 percent Ni). Second cationic membrane (on the right hand side) prevents migration of chloride ions to the anode chamber. Since the selectivity of membranes is never a perfect one, small impurity of chlorine gas is always contained in oxygen evolving from the anode compartment.

Diluted Solutions

Chromate-containing rinse water can be treated both in 3- and 2-chamber cells (see Figs. 3, 4 & 5). Concentration of chromates and other ionic species in flowing rinse tanks is insufficient to ensure acceptable rates of electrochemical treatment. That is the reason why only reclaim (non-flowing) rinse tanks can be used as a first rinsing step in a combination with membrane electrochemical cells. Concentration of chromate ions in these tanks can be stabilized at levels many times lower than in process solutions by using membrane cells. The input of chromates into subsequent rinsing stages is reduced in this way proportionally. Apart from that, considerable part chromate drag-out from process tanks can be returned back as chromic acid.

Practical Experience

Concentrated Solutions

2-Chamber cells (Fig. 1) with cationic membranes manufactured in Russia are using platinized titanium on anodes and stainless steel cathodes. In some cases lead anodes are used (when process solution contains no nitric acid, acetic or other acids which may cause corrosion of lead anodes). Zinc-chromating solutions are regenerated continuously on a round-the-clock basis irrespective of the schedule of operation of the plating line. Apart from zinc and trivalent chromium, other undesirable cationic impurities, such as iron and copper, are also removed from solutions. They all are concentrated in the cathode compartment which is periodically replenished with sulfuric acid. Technical and economic benefits of the regeneration process are related, on the one hand, with the elimination of periodic dumping and making up of fresh solutions. On the other hand, they are related with reduce consumption of chromic acid or dichromates for the replenishment and other chemicals used in the treatment of wastes (bisulfite, sulfuric acid and caustic soda). Similar process is used in several plating shops in Russia for the regeneration of chromate solutions in cadmium-plating lines. Since the start of these regeneration units, chromate solutions have never been dumped.

Successful industrial regeneration tests have been made also with black-chromate solutions used for the treatment of zinc-iron and zinc-nickel coatings. In the latter case, chromating solution was based on chloride salts. Therefore, 3-chamber cell (Fig. 3) with two cationic membranes was used. Current load was over 300 amps. Anode compartment contained diluted sulfuric acid.

Diluted Solutions

Removal of chromate ions from rinse water in reclaim tanks has been operating continuously in many plating shops in Russia for years. Major types of processes equipped with reclaim tanks and electrochemical cells are as follows: chromium-plating, chromate treatment of zinc, cadmium, steel and brass. According to an approximate evaluation, total input of hexavalent chromium into flowing rinses is decreased by five to one hundred times. Such a wide range of efficiencies is observed since a relationship between the current passed through the regeneration cell and the amount of hexavalent chromium dragged-in is a major factor determining the efficiency for a particular reclaim tank. Higher values (one hundred times or even more) have been achieved on low-output production lines and lower values on those with high output and especially high concentrations of chromates in process solutions (e.g., such as chromium-plating solutions).

Major Problems

Many different problems may appear in the development and in the implementation of the above-described processes. The following two examples are most typical ones and should be especially mentioned here:

(1) undesirable transport of particular ions through the membrane;
(2) absence of ionic transport through the membranes and, consequently, loss of electric conductivity for a certain combination of solutions on both sides of the membrane.

An example of type (1) is removal of cationic impurities from chromium plating solutions or from aluminum anodizing solutions based on chromic acid (all other anionic species are not allowed or should be contained at strictly controlled and low concentrations). Since cationic membranes can never completely exclude the transfer of anions to the analyte, the cathalyte should contain only anions of chromate or hydroxyle. Unfortunately, chromic acid or its salts will soon be reduced at the cathode and will form a non-conductive precipitate of $Cr_2(CrO_4)_3$. An alternative cathalyte, e.g. solution of an alkali is also unacceptable, since cationic impurities cannot pass through the membrane from an acid solution into an alkaline one (except alkaline metals and similar ions). Thus with alkaline cathalyte type (2) may be the case.

Conclusions

1. 2-Compartment electrochemical cells with cationic membranes allow to extend indefinitely the lifetime of various solutions based on chromic acid or its salts.
2. Diluted solutions in reclaim tanks containing chromate ions are treated successfully in 2- or 3-compartment cells in order to recover some part of chromic acid and to decrease considerably the input of hexavalent chromium compounds into waste water from rinsing operations.

References

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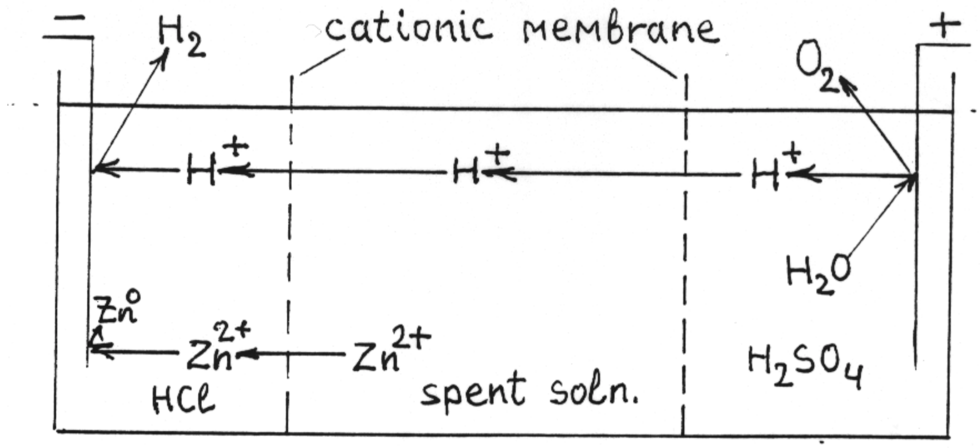

Figure 3

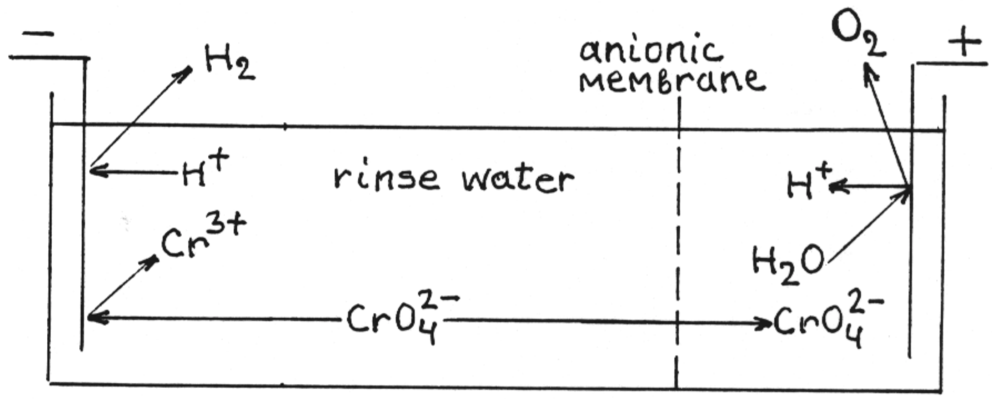

Figure 4

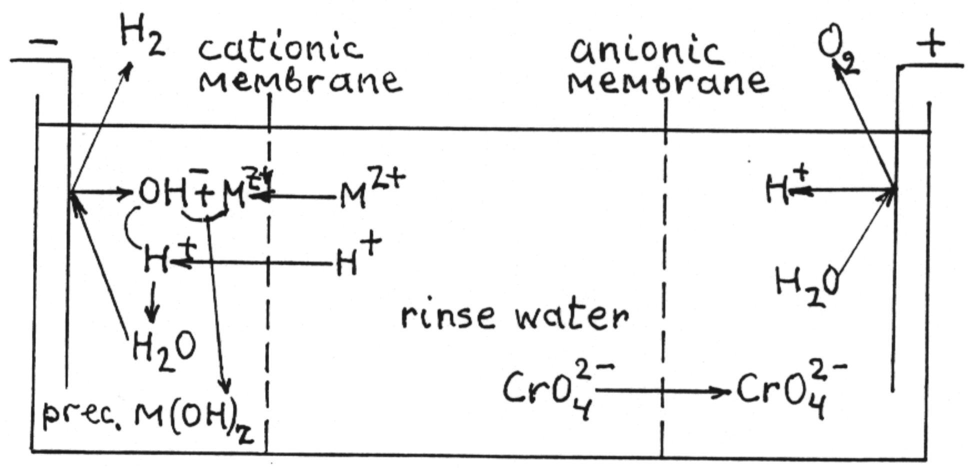

Figure 5