

## Aspects of Electrochemical Regeneration of Chromium Containing Solutions from Metal Finishing Industry

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Chromium plating and chromating processes for different metallic coatings are widespread technologies because chromium and chromates surfaces have special properties like hardness and corrosion resistance. Many different electrolytes and bathes exist in industry – due to differences in the basic metals for coating and in the wanted deposition quality. The main components of these solutions are chromic acid and soluble chromates, inorganic acids and organic additives. In the case of a chromating process the deposited or treated metal react with hexavalent chromium components under partial metal dissolution and formation of three-valent chromium ions. The acidity gradually decreases. Side ions are accumulated within the solution and lower the treatment activity with time. Electrolytes or bathes must be replaced. Similar effects are present during chromizing when hexavalent chromium components are cathodically reduced to  $\text{Cr}^{3+}$  ions or non-saved parts of the metal corrode.

For the majority of solutions used in industry and their spare tank waters no technologies for regeneration exist. An electrochemical regeneration including the removal of side ions and the re-oxidation of three-valent chromium can be a way out for lifetime prolongation and saving chemicals for detoxification. It was shown that the electrochemical regeneration could be favorably carried out in a divided cell [1,2] to prevent the cathodic reduction of hexavalent chromium.

This paper describes results from studying three discontinuous processes of bath regeneration from the chromating and hard chromium plating of alumina and alumina alloys. The aim of the research work was to find the technological conditions (cell structure, anode and separator materials, current densities, temperature, concentration ranges) for optimized regenerations with high current efficiencies and low cell voltages. In the experiments two- and three-compartment cells were used. The separator in the two-compartment cell was a cation exchange membrane of Nafion type. The regenerating electrolyte was the anolyte. The separators in the three-compartment arrangement were an anion and a cation exchange membrane in some experiments or a diaphragm and a cation exchange membrane in other experiments. The regeneration solution was filled in the middle compartment. Kinetic studies on several anode materials showed the advantage of lead/lead oxide electrodes. Titanium anodes coated with lead oxide layers proved to be not effective due to material corrosion. Titanium anodes activated with mixed iridium oxide could not re-oxidize the three-valent chromium.

In the case of treating chromium plating electrolytes the starting concentration of hexavalent chromium varied from 120 g[Cr]/l to 130 g[Cr]/l. The starting concentration of  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  was in the range from 3 g[metal]/l to 10 g[metal]/l. The average process temperature was 313 K.

In the first considered chromating system the

concentration values were 28 g[Cr]/l for hexavalent chromium, 9 g[Cr]/l for three-valent chromium, 6.6 g[Al]/l for alumina ions and 5.6 g[Fe]/l for the  $\text{Fe}^{3+}$  ions. A second treated chromating solution contained only hexavalent chromium with the concentration of 6 g[Cr]/l and three-valent chromium with the concentration of 2.5 g [Cr]/l. The following results were obtained with two-compartment constructions in laboratory and industrial scale.

The highest current efficiency with respect to the  $\text{Cr}^{3+}$  oxidation was calculated for the chromium plating electrolyte. The final  $\text{Cr}^{3+}$  concentration of 2 g [Cr]/l was reached with a current efficiency of 45 %. The current efficiency decreases with decreasing Cr(VI) concentration as well as with decreasing  $\text{Cr}^{3+}$  concentration. Furthermore, in chromating solutions with very low hexavalent chromium concentration (6 – 8 g [Cr]/l) and a  $\text{Cr}^{3+}$  concentration of 2.5 g[Cr]/l in the beginning, the final results were 0.8 g[Cr]/l for the  $\text{Cr}^{3+}$  concentration and 16%-20 % for the integral current efficiency. On the other hand, the migration rate of  $\text{Cr}^{3+}$  and other cations into the catholyte increases with decreasing Cr(VI) concentration. It was found that for both plating and chromating systems the transport number for the ion mass transfer through the membrane increases in the order  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ . The obtained values are between 0.28 (alumina) and 0.003 (iron). In all regeneration electrolytes pH decreased and conductivity increased with time. Only copper could be deposited in the metallic form. Other side metals were only concentrated in the catholyte.

When side ions and especially  $\text{Fe}^{3+}$  ions rapidly accumulate during the finishing process the use of three-compartment cells for regeneration purposes is more appropriate. Typical results for the regeneration of chromium-plating electrolytes are a final concentration of 110 g[Cr(VI)]/l in the anolyte and 40%-60% for the integral current efficiency with respect to the chromium transport into the anode compartment. For lower Cr(VI) concentrations lower transfer efficiencies were calculated. Corresponding results for the chromating solutions regeneration are a current efficiency of 16 % (less concentrated starting solutions) and a current efficiency of 30 % for more concentrated chromating bathes. The comparison of the different anion exchange membranes used in the experiments with a polymeric diaphragm resulted to better current efficiencies for the diaphragm. Additionally, cell voltage decreased from 20 V to 9 V at a cell current density of 5 A/dm<sup>2</sup>.

The same three-compartment cell construction can be used for the chromium removal from spare tank waters. The anolyte solution obtained after regeneration can be added to the working bath placed before the spare tank.

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### REFERENCES

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