In Tank Removal of Hard Chromium Plating Contaminants

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BASX Systems, LLC has successfully removed contaminants from a hard chromium plating system utilizing a ceramic microfilter. This process uses the microfilter to remove trivalent chromium and iron from the plating solution without reducing the hexavalent chromium solution. The solution is then adjusted back to meet the specifications of the tank and returned to the plating tank. This is performed on a skid-mounted system next to the plating tank. The other solution generated by the hard chromium plating process is a wastewater from the ion exchange system. We were also able to successfully reduce the volume of the wastewater treatment solution from this process by using the microfilter. Volume was reduced from 1,000 gallons of wastewater disposed of off site per week to a solid form of less than 50 pounds per week. This paper will discuss these two processes, what was learned from this research project and what potential this project has for a full-scale system.

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Introduction

Hard chromium plating is an important process in the airline and aerospace industries. This plating process incorporates special features:

- □ Thicker coatings
- □ High hardness
- □ High abrasion resistance
- **Corrorsion resistance**
- □ Heat resistance
- □ Low coefficient of friction

In recent years, the metal finishing industry has found new ways to reduce the effect of hard chromium plating on the environment. New measures have been taken to reduce the amount of mists from the hydrogen generation during the plating process through fume suppressants.¹ One of the concerns for the metal finishing industry is the proposed Metal Products and Machinery (MP&M) regulations, which will require metal finishers to meet new stringent standards regarding chromium and the contaminants in the hard chromium bath.²

Due to contaminants in the hard chromium process, the bath needs to be wasted even though many of the components are still viable. The removal of these contaminants will be the focus of this paper.

Constituents of the Hard Chromium Bath

The deposition of chromium is normally performed with one of two solutions. The two solutions are either trivalent chromium or hexavalent chromium. Hard chromium plating is performed with hexavalent chromium or hexavalent chromium oxide (CrO_3). Chromium plating is operated with insoluble anodes, so that all of the metal deposited is taken from the solution and must be continuously replaced.

No metal can be deposited from solutions of pure chromic acid. Small amounts of foreign anions or catalysts need to be present. These catalysts are normally sulfate. fluoride. silico fluoride or fluoborate. If there is not enough catalyst, then the hard chromium plating process will not operate properly. If there is too much catalyst, then the current density will increase to unacceptable levels. Therefore, it is important to have the correct ratios of catalyst in the plating bath. These conditions are provided in Table 1.4

Table 1		
Condition	Low Conc. Solution	High Conc. Solution
Chromic	250 g/L	400 g/L
Acid		
Sulfuric	2.5 g/L	4.0 g/L
Acid		
Current	31 to 62	16 to 54
Density	A/dm^2	A/dm ²
Temp.	52 to 63 C	43 to 63 C

Note that the ratio for chromic acid to sulfate or sulfuric acid is 100:1. This is an important ratio to keep in balance within the system. This ratio can vary between 80:1 and 120:1.

Contaminants of Concern

There are various contaminants within a hard chromium bath that will cause the plating process to malfunction. Theses contaminants are:

- **□** Trivalent chromium
- □ Lead
- □ Copper
- □ Cadmium
- □ Iron
- Nickel
- □ Zinc
- □ Aluminum

Trivalent chromium results from the reduction of the hexavalent chromium in the plating process and will result in an increase in the current density. The lead results from the anodes used in the process. The remaining metals are normally a result of the basis metal or the metals used in the process.

In order for the hard chromium process to function properly, these metals must be kept below various levels. Normally, the trivalent chromium is kept below 1.5% of the solution strength. The remaining metals should be kept below 100 to 10mg/L.

Experimentation

The experiment was designed to remove these metals and contaminants without wasting the hard chromium bath. This process would take a split stream of the hard chromium bath, raise the pH to precipitate the divalent and trivalent metals while leaving the remaining hexavalent chromium. This can be performed by utilizing a hydroxide precipitation step. Hexavalent chromium will not precipitate to any extent as a hydroxide. In order for this process to be successful, the materials of construction are very important. We utilized a ceramic microfilter for the removal of the precipitants. This is provided in Figure 1.



Figure 1 – Ceramic Microfilter

We were able to successfully remove the divalent and trivalent ions from solution. These results are provided in Table 2.

Parameter	Influent mg/L	Effluent mg/L	Goal mg/L
Aluminum	15.3	< 0.2	<10
Copper	123	2.3	<10
Tri-	6,300	1,170	<15,000
Chrome			
Hex-	55,700	50,000	250,000
Chrome			
Iron	976	0.5	<100
Lead	10.3	< 0.2	<10
Nickel	2.2	0.8	<10

This experiment was performed at a pH of 5.0. The pH was raised by adding a considerable amount of sodium hydroxide. As shown by the table above, we were able

to successfully remove the contaminants of concern. However, during this process, we also diluted the hexavalent chromium. We also added a considerable amount of sodium to the solution, which will eventually become a problem. In order to reduce the amount of chromium needed, we attempted to utilize hydrogen peroxide (H_2O_2) to precipitate some of the metals and reduce the amount of sodium hydroxide needed. This reduced the metals to below 10 mg/L, but did not work as well as the hydroxide precipitation.

As shown by the results, this solution can be readjusted to meet the 100:1 ratio of chromic acid to sulfuric acid. However, we did not believe this would be economical.

Reduction of Ion Exchange Solution

The second aspect of this research was to reduce the amount of waste that was being generated. As part of the waste solution process, approximately 1,000 gallons per week were being wasted from this facility. We were attempting to reduce the amount of solution or waste from this process as part of a pollution prevention program.

The experimentation was intended to reduce the hexavalent chromium solution to trivalent chromium and then reduce the amount of solution. The process is provided in Figure 2.



Figure 2 – Ceramic Microfiltration Wastewater System

This process was able to meet the required 40 CFR 433 discharge standards for the local municipality. In addition, the 1,000 gallons of solution that was being discharged off site was reduced to approximately 50 pounds of solid material. Both materials would be classified as a hazardous waste, but due to the volume reduction, this was a much lower cost option. The payback on this type of system is approximately two years.

The above process requires the reduction of the hexavalent chromium to trivalent prior to raising the pH to remove the metals as a hydroxide. We are currently researching a different process utilizing electrocoaguation, which has shown very positive results. This would lower the chemical requirements considerably, due to the precipitation occurring in the hexavalent state and the reduction of hydroxide as this precipitation occurs at a low pH.

Conclusions

There is a definite need to research the reduction of environmental impact by h hard chromium plating. To date, processes have been developed to reduce the fumes from this process. What is needed is a reduction of the effects of the waste treatment solution.

This research provided a proposed method of reducing the need to regenerate the solution of the hexavalent chromium bath by removing the contaminants in-situ. While this process was able to remove these constituents, the cost is not practical at this time.

This research also reviewed the treatment of the waste solution from the regeneration of the ion exchange solution. This process was successful in reducing the waste solution of 1,000 gallons per week to a solid form of 50 pounds per week. This resulted in a payback of two years.

We are currently investigating the use of electrocoagulation for this process. This coagulation step appears to hold great promise regarding the removal and reduction of chemicals utilized in this treatment process.

References

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