

CHROMIUM RECOVERY FROM EXHAUSTED BATHS OF SURFACE TREATMENT PROCESSES IN ORDER TO REUSE THEM AT THE TANNING INDUSTRY

Josep Torras Grané¹

Irene Buj Corral²

Joan de Pablo Ribas¹

Miquel Rovira Boixaderas¹

1. CTM Centre Tecnològic. Universitat Politècnica de Catalunya (UPC) (Spain)

2. Department of Mechanical Engineering. Universitat Politècnica de Catalunya (UPC) (Spain)

ABSTRACT

Chromium plating on metallic surfaces (like functional or decorative plating) provides an extremely hard, wear resistant and corrosion resistant layer. Typical thicknesses of the layer range between 2.5 and 500 μm . The chromium electroplating processes use baths containing high concentrations of Cr (VI) with chromium trioxide (CrO_3) as the chromium source. When because of technical or economical reasons a bath gets exhausted, a waste containing mainly chromium in the form of dichromates as well as other heavy metals is generated. Chromium may be purified in order to use it at other industrial processes with different requirements. In this work an economical system for using wastes of the galvanic industry as reagents for the tanning industry is presented. The metals present in a chromium exhausted bath are precipitated using NaOH. Then, the solution containing mainly soluble Cr (VI) is separated. By means of sodium sulfite in acidic conditions, Cr (VI) is reduced to Cr (III). Afterwards a basic Cr (III) sulfate may be obtained, which is one of the most used forms at the tanning industry.

Keywords: chromium recovery, exhausted baths, surface treatment.

1. INTRODUCTION

Hard or functional chromium of metallic parts provides an extremely hard and corrosion resistant layer with low friction coefficient and exceptional wear resistance to parts on which it is plated. It may also be used for rebuilding worn parts like rolls, dies or tools. The usual thicknesses of the chromium layer range between 2.5 and 500 μm [1].

Electrolytic chromium plating baths have a high concentration of Cr(VI) as dichromate and a high acidity because of the presence of chromic acid and sulfuric acid (110-130 g dm^{-3} of chromium, which is equivalent to about 150 g dm^{-3} Cr_2O_3). As the baths are used, their chromium concentration has to be rectified so that they do not lose their effectiveness. Nevertheless, with time the bath gets impurities due to electrochemical reactions and the oil and particles on the parts surface. Finally, after a long time the bath gets exhausted and has to be changed. The problem with the rinsing waters is even more important, because great volumes of such waste are generated, which contains chromium at low concentration that it cannot be totally be reused, but with an important environmental concern.

Chromium from exhausted baths and rinsing waters could be recovered and used in a profitable way using a process after which chromium was found as a suitable species and with the right concentration. Tanning is an appropriate process in order to reuse chromium that the galvanic industry is not able to use. Tanning with chromium implies using 10-12 % of impure chromium salt [2], with a purity of 25 % of chromium oxide (III), which means 2.5-3 % of chromium oxide (III).

In Spain, the priorities of waste minimization follow the sequence: Reduction, Reuse, Recycling and Treatment prior to Landfilling. Treatments for preventing and / or reducing the generation of waste at source are preferable; hazard reduction has priority against quantity reduction and re-use, recycling and recovery are a priority [3]. There exist different options in order to minimize the impact of chromium wastes, used either by the surface treatment industry [4, 5] or by the tanning industry [6, 7]. Although the different techniques used show a high degree of effectiveness, in many cases it would be necessary to do economic studies before their industrial application.

The present work shows a method to recover chromium from exhausted chromate baths and their further use at the tanning industry. This combination may be highly favorable for the global economy of the process, given that the exhausted baths show a high chromium concentration (11 % approx.) that, after the appropriate treatments, will lead to a chromium (III) solution with a concentration equal or higher than the one that is necessary for the tanning process (2 % approx.). This will allow having a solution with the correct chromium concentration without the need of a concentration process.

2. MATERIALS AND METHODS

2.1. Materials

The chromate exhausted baths were provided by a surface treatment company in St. Fruitós de Bages (Barcelona-Spain), where metallic parts are subjected to hard chromium plating.

The reagents used in this work are: NaOH, Na₂SO₃ and H₂SO₄ (95-97 %) of Scharlau (for analysis). Deionized water has conductivity below 18.2 MΩ.cm.

2.2. Experimental methods

First of all, an analysis was performed to the chromate exhausted bath in order to determine the Cr, Ni, Cd, Pb, Cu and Zn concentration, using ICP-MS (plasma inductively coupled mass spectrometer).

Secondly, 7.027 g of NaOH were added to 50 ml of the exhausted bath, so that pH of 6.6 was reached. A precipitate formed, that was then filtered. The concentration of the heavy metals in the solution was determined using the same technique.

Figure 1 shows the titration curve of the chromate exhausted bath using NaOH 2N as titration agent.

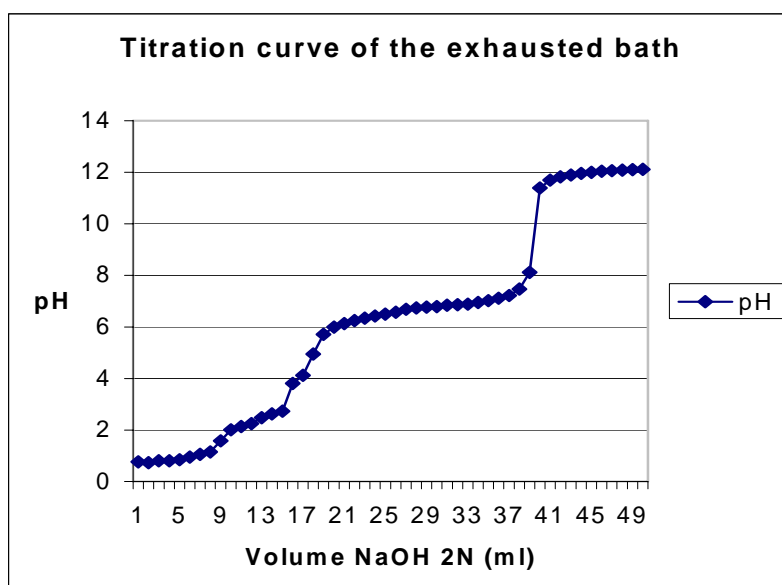
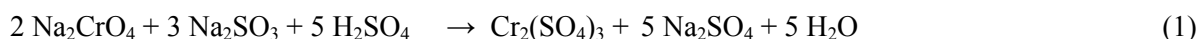


Figure 1. Titration curve of the chromate exhausted bath with NaOH 2N.

Taking into account the curve, a quantity of NaOH was added to the bath so that the pH of the solution was almost neutral (central part of the curve), which would allow the precipitation of most of the heavy metals as hydroxides. It is not recommended to use a basic pH because the Cr (VI) reduction reaction that will come next needs acidic conditions, and also to avoid the solubilization of heavy metals (amphoteric behavior).

The subsequent reduction reaction is as follows:



When performing the reaction using stoichiometric amounts of reactants, 9 % of hexavalent chromium was detected using UV-VIS spectrometry, which had not been reduced. For this reason, an excess of Na₂SO₃ was used and no hexavalent chromium was detected after the redox reaction.

In this case, 30 ml of the solution (approx. 0.07 mol Cr) were mixed with 0.17 mol H₂SO₄ (16.56 g) and 0.17 mol Na₂SO₃ (21.00 g), which had been previously diluted with deionized water. The pH of the solution needs to be near 2 so that the reaction takes place. All the chromate ions were reduced after 30 minutes. The final solution was then filtered and the concentration of heavy metals was determined.

It is important to notice that the chromium sulfate solution may be basified with sodium hydrogen carbonate, so that the product can be reused for leather tanning [7].

OBSERVATIONS: For the reduction of Cr (VI) other reduction agents may be also used as glucose, ethilenglycol, Fe²⁺, metallic Fe...Some of the a.m. reagents are wastes from other processes. It must be taken into account, nevertheless, that wastes may add not desirable impurities to the solution.

3. RESULTS

At table 1 there are the obtained concentrations of Cr, Ni, Cd, Pb, Cu and Zn, as well as the pH for the exhausted bath, the neutralized solution and the final solution after reducing Cr(VI) to Cr(III):

Table 1. pH and concentration of Cr, Ni, Cd, Pb, Cu and Zn for the exhausted bath, the neutralized solution and the final solution.

| | EXHAUSTED BATH | BATH AFTER NEUTRALIZATON WITH NaOH | BATH AFTER REDUCTION WITH Na ₂ SO ₃ (approx. dilution ¼) |
|------------|----------------|------------------------------------|--|
| [Cr] (ppm) | 113079 | 140423 | 32250 |
| [Ni] (ppm) | 85.2 | 3.3 | < 1 |
| [Cd] (ppm) | 5.0 | 0.4 | 0.3 |
| [Pb] (ppm) | 51.6 | < 0.05 | < 0.05 |
| [Cu] (ppm) | 2449 | 52.2 | 4.7 |
| [Zn] (ppm) | 1633 | 44.1 | 11.3 |
| pH | 0.87 | 6.64 | 2.33 |

At table 1 it can be seen that the exhausted bath presents a very high Cr concentration, as well as other metals like Ni, Cd, Pb, Cu and Zn at lower concentrations. After neutralizing bath with NaOH, the concentration of divalent metals is reduced as expected, because pH is in the neutral zone, near to the minimum solubility area for most of the metal hydroxides. Nevertheless, the Cr concentration (oxoanion) does not decrease (a light increase is appreciated, which could be due to the evaporation of the solvent during exothermic neutralization process and subsequent filtration). After the redox

reaction, and having into account that it has implied a dilution of 1 to 4.3, it may be considered that the amounts of all the metals studied remain almost constant. No hexavalent chromium was detected after the redox reaction. The final Cr concentration of 32250 ppm is even higher than the requested concentration by the tanning industry (about 20000 ppm).

4. CONCLUSIONS

Sodium sulfite in acidic conditions is an effective reagent for the reduction of the hexavalent chromium contained in an exhausted bath from chromium plating. The final chromium concentration (32250 ppm) allows using it at the tanning industry. Previously, a neutralization of the bath is required, for example with NaOH, in order to precipitate the divalent cations of heavy metals contained in the bath. It is important to notice that, with this procedure, it is not necessary to concentrate the bath, avoiding an operation which would increase the process.

5. ACKNOWLEDGEMENTS

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