Journal of Hazardous Materials 209–210 (2012) 343–347

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Chromium recovery from exhausted baths generated in plating processes and its reuse in the tanning industry

Josep Torras[a], Irene Buj[b,*], Miquel Rovira[c,d], Joan de Pablo[c,d]

[a] Department of Mining Engineering and Natural Resources, Universitat Politècnica de Catalunya, Av. Bases de Manresa, 61-73, 08240, Manresa, Barcelona, Spain
[b] Department of Mechanical Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain
[c] CTM Technological Centre, Universitat Politècnica de Catalunya, Av. Diagonal, 647, 08028, Manresa, Barcelona, Spain
[d] Department of Chemical Engineering, Universitat Politècnica de Catalunya, Av. Diagonal, 647, 08028, Barcelona, Spain

ARTICLE INFO

Article history:
Received 18 July 2011
Received in revised form
14 November 2011
Accepted 10 January 2012
Available online 21 January 2012

Keywords:
Chromium recovery
Exhausted baths
Surface treatment
Tanning
Chromium reduction

ABSTRACT

Chromium plating used for functional purposes provides an extremely hard, wear and corrosion resistant layer by means of electrolytic deposition. Typical layer thicknesses range between 2.5 and 500 μm. Chromium electroplating baths contain high concentrations of Cr(VI) with chromium trioxide (CrO_3) as the chromium source. When because of technical or economic reasons a bath gets exhausted, a waste containing mainly chromium as dichromate as well as other heavy metals is generated. Chromium may then be purified for use in other industrial processes with different requirements. In this work, a sustainable system for using galvanic wastes as reagents in the leather tanning industry, thus reducing quantity of wastes to be treated, is presented. Metal cations present in the chromium exhausted bath were precipitated with NaOH. Then, the solution containing mainly soluble Cr(VI) was separated. By means of sodium sulphite in acidic conditions, Cr(VI) was reduced to Cr(III) as chromium (III) sulphate. From chromium (III) sulphate a basic Cr(III) sulphate may be obtained, which is one of most used compounds in the tanning industry. Cr(III) concentration in the final solution allows its reuse without concentration, but with a slight dilution.

1. Introduction

Hard or functional chromium plating of metallic parts provides an extremely hard and corrosion resistant layer with low friction coefficient and exceptional wear resistance. It may also be used for rebuilding worn parts like rolls, dies or tools. Usual thicknesses of the chromium layer ranges between 2.5 and 500 μm [1].

Electrolytic chromium plating baths have a high concentration of Cr(VI) as dichromate owing to the high acidity of the system because of chromic acid and sulphuric acid. Usual chromium concentration ranges between 110 and 130 g/l of chromium, which is equivalent to about 150 g/l Cr_2O_3 [1]. During bath operation it is necessary to increase chromium concentration so that the bath does not lose effectiveness. Nevertheless, with time impurities accumulate in the bath due to electrochemical reactions as well as oil and particles on the workpieces' surface. Finally, after a long time the bath gets exhausted and needs to be changed. The problem with rinsing waters is even more important than that of exhausted baths. Great volumes of water are generated containing chromium at such a low concentration that it is difficult to completely reuse it.

The tanning process transforms skins into leather by incorporation of chromium in its structure. Basic chromium sulphate, $CrSO_4(OH)$ is a common salt employed in the tanning industry. In order to obtain it, chromium dichromate, $K_2Cr_2O_7$, is used. Hexavalent chromium is reduced to trivalent chromium in acidic conditions. Later, in order to increase the tanning properties of chromium salts and to improve its fixation on leather, it is usual to basify them. To do so, anhydrous sodium carbonate is added to the solution. Usual initial chromium concentration is 20 g/l [2]. Typical spent tanning baths Cr(III) concentrations range between 3.5 and 4 g/l, with neutral salts such as NaCl between 50 and 60 g/l and Na_2SO_4 between 10 and 12 g/l [3].

For chromium reduction in origin in the surface treatment industry, for instance cleaning process of racks, use of pure metal anodes and filtration of the bath solution are recommended [4]. For chromium recovery, hydrometallurgical techniques such as liquid–liquid extraction, ion exchange and/or electrochemical separation [5] or precipitation, acid leaching and subsequent precipitation [6,7] are recommended.

In the tanning industry, although some authors describe application of biosurfactants [8] and also recycling of spent tanning liquors after membrane separation, usual recovery method consists of Cr(III) is precipitation as chromic hydroxide by means of an alkali. Later, Cr(III) in the concentrated sludge is dissolved with sulphuric acid and basic chromic sulphate is regenerated for reuse.

---

* Corresponding author. Tel.: +34 93 4054016; fax: +34 93 4016693.
E-mail address: irene.buj@upc.edu (I. Buj).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2012.01.036

However, the method does not solve the problem of dissolved neutral salts in the liquor [9]. In addition, evaporation of the solution is necessary in this case so as to achieve desired Cr(III) concentration of 20 g/l.

Other authors obtained basic chromium sulphate from wastes from the tanning industry different than exhausted tanning liquors. Erdem studied the reduction of chromate ions from chrome shaving generated in tanning processes, by adjustment of pH with H_2SO_4. Contact time was 30 min and at the end of the process a solution of chromium sulphate was obtained [10]. On the other hand, Dettmer et al. employed H_2SO_4 to obtain $Na_2Cr_2O_7$ from Na_2CrO_4 from heat ashes of thermally treated leather. Later, they reduced dichromate with Na_2SO_3 and obtained chromium (III) sulphate, $Cr_2(SO_4)_3$. From that compound, by adjustment of pH with sodium hydroxide or sodium bicarbonate, they obtained basic chromium sulphate [11].

Basic chromium sulphate could alternatively be obtained from galvanic exhausted baths containing Cr(VI), provided that after the reduction process chromium is found as an appropriate compound and at the right concentration. Thus, tanning industry can reuse chromium that the surface treatment industry is not able to use. Many processes employed for reducing Cr(VI) concentrations in solution are based on reduction of Cr(VI) to Cr(III) and precipitation of Cr(III) [12,13]. Different reducing agents are known for chromium. They are classified into four main groups: sulphur compounds, Fe^0 or Fe^{2+} compounds, organic compounds and other. Amongst sulphur compounds, hydrogen sulphide (H_2S) [14], iron (II) sulphide (FeS_2) [15], sodium metabisulphite ($Na_2S_2O_5$) [16] and sodium sulphite (Na_2SO_3) have been reported. Regarding iron compounds, metallic Fe [17,18], ammonium iron (II) sulphate ($Fe(NH_4)_2(SO_4)_2$) [19], sodium hydrosulphide (NaHS) and iron (II) sulphate ($FeSO_4$) [20] and siderite ($FeCO_3$) [21] amongst other are known. Concerning organic compounds, common ones are ethylene glycol [22], ascorbate [23], citrate [24], organic acids with TiO_2 [25] or soil organic matter [26]. Other reagents such as H_2O_2 have been also employed [8].

The present work shows a sustainable method for recovering chromium from exhausted chromium plating baths generated by the surface treatment industry and their further use in the tanning industry. Exhausted baths show a high chromium concentration (about 110 g/l Cr) [1]. After appropriate treatments, it will lead to a Cr(III) solution with a higher concentration than that of tanning liquors (about 20 g/l Cr) [2]. Thus, an evaporation process to concentrate the solution is not necessary in this case.

Cost of basic chromium (III) sulphate is relatively low (about 1 € per kg of powder material) [27]. However, the strategy of reusing wastes from a certain industry as raw material for another productive process falls squarely within the field of industrial ecology [28]. By means of such strategy quantities of hazardous wastes generated in the surface treatment industry will be reduced. That is the recommended option by the United Nations Environment Programme's (UNEP's) International Panel for Sustainable Resource Management (Resource Panel) on metal recycling rates [29]. Although the present method requires a reduction reaction of Cr(VI) to Cr(III), such reduction would also be necessary if exhausted chromium plating baths were treated by stabilization with Portland cement [30], since chromium is in anionic form.

2. Materials and methods

2.1. Materials

A sample from an exhausted bath from hard chromium plating was provided by a surface treatment company in the area of Barcelona. Reagents used in this work, NaOH, Na_2SO_3 and H_2SO_4 (95–97%), were purchased from Scharlau (analytical grade). Deionized water was obtained by means of Milli-Q system. Water resistivity was 18.2 MΩ cm at 25 °C. It was filtered with a 0.22 μm pore diameter filter. Ultra-trace quality nitric acid was used for preparing standard solutions. ICP-MS (inductively coupled plasma mass spectrometer) calibration standards for quantitative analysis of Cr, Cd, Cu, Ni, Pb and Zn, as well as for semi quantitative analysis of Mg, Rh and Pb were provided by Scharlau. Metal concentration of all standards was 1000 mg/l.

Table 1
Molarity, mass (g) and volume (ml) of the different compounds employed in the reduction reaction: a) stoichiometric quantities; b) excess of Na_2SO_3.

	Molarity	Mass (g)	Volume (ml)
a) Stoichiometric quantities			
Cr neutralized bath	0.065		30.000
H_2SO_4	0.163	15.974	8.870
Na_2SO_3	0.098	12.348	
b) Excess of Na_2SO_3			
Cr neutralized bath	0.065		30.000
H_2SO_4	0.170	16.660	9.260
Na_2SO_3	0.170	21.420	

2.2. Experimental procedure

A process for recovery of chromium from surface treatment exhausted baths and subsequent reuse in the tanning industry was developed. The process consists of following steps: bath characterization, bath neutralization with NaOH and Cr(VI) reduction to Cr(III) with Na_2SO_3 in acidic conditions.

After characterization of the bath, neutralization was performed. To that end, 7.027 g of NaOH was added to 50 ml of the exhausted bath. A precipitate containing metal hydroxides was formed. The neutralized bath was filtered in order to remove the precipitate.

For the reduction reaction, 30 ml of the neutralized bath containing Na_2CrO_4 were mixed with Na_2SO_3 in solution. The reduction reaction of sodium chromate in solution is as follows (Eq. (1)):

$$2Na_2CrO_4 + 3Na_2SO_3 + 5H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 5Na_2SO_4 + 5H_2O \quad (1)$$

Two different conditions were considered: stoichiometric quantities (molar ratio of 3 to 2 with respect to Na_2CrO_4 according to Eq. (1)) and excess of Na_2SO_3 (molar ratio of 5.2 to 2 with respect to Na_2CrO_4) (Table 1).

Reaction was considered to be finished after 30 min.

2.3. Methods of analysis

The exhausted bath was characterized by means of elemental semiquantitative analysis, elemental quantitative analysis of Cd, Cr, Cu, Ni, Pb and Zn, pH measurement and titration. Elemental analyses were performed in a Perkin Elmer ELAN 6000 ICP-MS. Samples were diluted with HNO_3 (Scharlau, trace analysis) at 1%. pH was measured by means of a CRISON GLP 22 pH-meter with temperature compensation. Titration was performed with NaOH 2 N.

Both the neutralized bath and the final solution were characterized by means of elemental quantitative analysis and pH measurement.

Hexavalent chromium in the final solution was determined by diphenylcarbazide method [31] using a UV–vis spectrometer (Shimadzu model UV-1603).