Chemical Engineering Science 111 (2014) 402–409

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Improvement of the electrochemical behaviour of Zn-electroplated steel using regenerated Cr (III) passivation baths

J. García-Antón [a,*], R.M. Fernández-Domene [a], R. Sánchez-Tovar [a], C. Escrivà-Cerdán [a,c], R. Leiva-García [a,c], V. García [b], A. Urtiaga [b]

[a] IEC, Dpto. Ingeniería Química y Nuclear, Universitat Politècnica de València, C/ Camino de Vera s/n, 46022, Valencia, Spain
[b] Departamento de Ingenierías Química y Biomolecular, Universidad de Cantabria, Av de los Castros s/n, 39005 Santander, Cantabria, Spain
[c] School of Materials, University of Manchester, Manchester M13 9PL, UK

HIGHLIGHTS

- Emulsion Pertraction Technology (EPT) separates Zn and Fe from Cr (III) baths.
- EPT step coupled to the passivation bath reduces the Zn and Fe impurities.
- After using EPT the samples presented higher values of polarization resistance.
- The EPT step improves the protective properties of the electroplated steels layers.

ARTICLE INFO

Article history:
Received 4 December 2013
Received in revised form
3 March 2014
Accepted 7 March 2014
Available online 14 March 2014

Keywords:
Trivalent chromium
Passivation baths
Emulsion Pertraction Technology
Zn-electroplated steel

ABSTRACT

Conversion coatings based on trivalent chromium are more sensitive to the presence of zinc and iron impurities than the chromate formulations. This fact contributes to a decrease in the quality of passivation and to the generation of a significant amount of hazardous liquid waste. Recently, a new eco-innovative process based on Emulsion Pertraction Technology (EPT) is being implemented at industrial scale for selectively removing Zn and Fe from spent passivation baths in order to enhance the lifetime of the Cr (III) baths. In this study, the effect of Zn and Fe removal on the electrochemical behaviour of Zn-electroplated steel samples was evaluated by means of polarisation curves and electrochemical impedance spectroscopy measurements at open circuit potential conditions in 3.5 g/L NaCl solutions. The main objective was to assess the benefits brought by EPT using electrochemical methods. Cr (III) passivation baths regenerated using the EPT process have been compared to the bath used in a local industry as well as to fresh and spent baths. According to the results, the samples passivated in the EPT regenerated bath showed a significant improvement in their electrochemical behaviour compared to the samples passivated in the spent baths. This study concluded the suitability of EPT for regenerating Cr (III) passivation baths.

1. Introduction

Chromate conversion coatings based on Cr (VI) chemicals have been widely used for many years to protect metals and alloys from corrosion (Zhang et al., 2005; Mekhalif et al., 2005), in particular, to provide an extra protective film against corrosion and decorative finishing to electroplated zinc surfaces (Cho et al., 2007; Campestrini et al., 2001). The chemical passivation mechanism consists of the formation of a physical barrier between the metal/alloy substrate and the corrosive medium during immersion (Bellezze et al., 2002). As a result of this, a passivation layer containing zinc oxides and hydroxides, zinc chromate and mixed Cr (III) and Cr (VI) oxides and hydroxides is formed.

However, the use of Cr (VI) compounds is considered carcinogenic for human health (Tomachuk et al., 2010; Jeffcoate et al., 2000) and causes serious environmental pollution; this is the reason why several research studies have focused on finding substitutes to Cr (VI) chemicals (Zhang et al., 2004, 2005; Rosalbino et al., 2011; Deflorian et al., 2005; Saravanan and Mohan, 2009).

Cr (III) passivation baths are used as an alternative to chromate conversion coatings. Although the substitutes reduce the toxicity of the used raw materials and of the produced wastes, they have several negative effects from the environmental and economic perspective (Garcia et al., 2013). The formulations based on Cr (III)

* Corresponding author.
E-mail address: jgarciaa@iqn.upv.es (J. García-Antón).

http://dx.doi.org/10.1016/j.ces.2014.03.005
0009-2509/

need higher chromium concentrations and the presence of cobalt to provide equivalent properties to chromate-based passivation coatings. This fact implies a higher consumption of raw materials for the baths formulation. In addition, the Cr (III) baths are sensitive to the presence of Zn and Fe impurities, causing a decrease in the quality of passivation (Zaki, 2007), formation of off-specification products and the generation of a significant amount of hazardous liquid waste when the passivation bath is replaced.

In order to enhance the lifetime of the baths and to improve the environmental and economical sustainability of Cr (III) passivation, a new eco-innovative process, is being developed based on Emulsion Pertraction Technology (EPT). EPT is able to separate Zn and Fe from the bath allowing Cr (III) and other relevant components such as cobalt to remain in the bath, i.e., preventing the loss of passivation properties. EPT combines liquid–liquid extraction with hollow fibre membrane contactors to extract and back-extract targeted compounds from an aqueous solution in one separation step. The fundamentals of EPT are explained in detail by Ho and Poddar (2001) and Urtiaga et al. (2005). The main benefit of the process is that Cr (III) regeneration is conducted during passivation. This process for the regeneration of Cr (III) baths is being studied in detail at laboratory scale (Diban et al., 2011, 2012; Urtiaga et al., 2010; Garcia et al., 2012) and it has already been implemented at industrial scale (Garcia et al., 2013). Its environmental benefits were already assessed in a previous work (Garcia et al., 2013). However, the evaluation of the effectiveness of the EPT process from the corrosion protection perspective was lacked.

The main objective of this work is to evaluate the effectiveness of EPT on the electrochemical behaviour of Zn-electroplated steel samples by means of polarization curves and EIS measurements. Cr (III) passivation baths regenerated using EPT are compared to freshly-made formulations, in-use baths and spent baths.

2. Experimental procedure

2.1. Material

Test specimens of $3.9 \times 7.9\ cm^2$ were cut from a Zn-electroplated steel sheet 0.1 cm thick. The sheet previously underwent the following surface treatments conducted at a local plating industry: chemical degreasing, rinsing in water, pickling, rinsing in water, electrochemical degreasing, rinsing in water, Zn electroplating, rinsing with water, neutralizing, passivation, rinsing in water and drying. Zn electroplating was conducted using $2.6\ A\ dm^{-2}$ in alkaline media. The passivation step lasted 1 min at pH$\sim$1.8. Four passivating baths were tested for comparison: a fresh bath, the bath used at the company (in-use bath), spent bath and a bath regenerated using EPT. The fresh bath corresponded to a readily prepared formulation. The in use and spent baths were of the same chemical formulation as the fresh one and represented different degrees of usage. The bath regenerated using EPT resulted from the regeneration of the spent bath using the EPT process. The content of impurities was decreased until the Fe and Zn concentration levels were similar to the ones presented in the in use formulation. Table 1 indicates the composition of the baths in terms of Zn (II), Fe (total) and Cr (III) concentrations.

2.2. Raman spectroscopy

Prior to the electrochemical tests, the samples were examined by Raman spectroscopy ("*Witec 300R$^+$ Raman microscope*") in order to determine the presence of chromium oxides in the surface film. The samples were illuminated by a 632 nm neon laser with a magnification factor of 500 $\times$, the intensity of the laser being fixed. Several areas of the different samples were examined and the spectra were averaged.

Table 1
Concentration of Cr (III), Zn (II) and Fe (total) in the baths used to passivate the Zn electroplated specimens.

	Cr (III) (mg/L)	Zn (II) (mg/L)	Fe (total) (mg/L)
Fresh bath	6729	<0.3	0.72
EPT regenerated bath	6363	5824	11
In use bath	5400	7410	10
Spent bath	6402	13,088	63.4

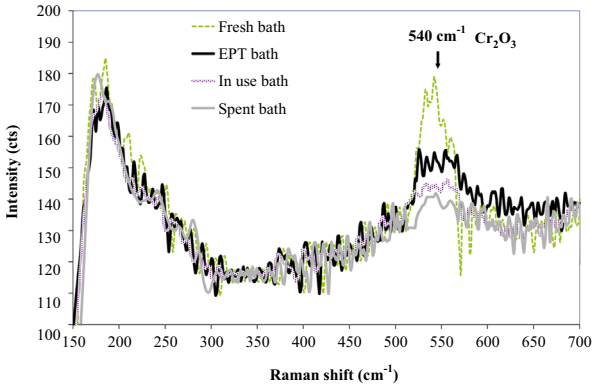

Fig. 1. Raman spectra obtained for the samples treated in the following baths: fresh bath, EPT regenerated bath, in-use bath and spent bath.

2.3. Potentiodynamic polarization curves

The potentiodynamic polarization curves were determined using a potentiostat "AUTOLAB PGSTAT302N". The tests were carried out in a three-electrode cell. The potential of the working electrode was measured against a silver–silver chloride with 3 M KCl reference electrode. The auxiliary electrode was a platinum electrode. The polarization curves were obtained in a naturally aerated 3.5 g/l NaCl aqueous solution, starting from a cathodic potential of $-1100\ mV_{Ag/AgCl}$ to $500\ mV_{Ag/AgCl}$ at 0.5 mV/s sweep rate.

During the electrochemical test, the surface area in contact with the NaCl solution was $0.626\ cm^2$.

2.4. Electrochemical impedance spectroscopy (EIS) measurements

The EIS measurements were conducted at open circuit potential (OCP) in the 3.5 g/L NaCl solution after 1, 24, 48 and 144 h of immersion in order to study the evolution of the film with time. The voltage perturbation amplitude was 10 mV in the frequency range of 100 kHz to 10 mHz. The temperature of the solution was 25 °C.

3. Results and discussion

3.1. Raman spectra

Fig. 1 shows the Raman spectra obtained by spotting a laser beam on the different samples. The peak of chromium oxide ($540\ cm^{-1}$) (Thierry, 1988) can be clearly observed in the specimen immersed in the fresh bath. In the other samples there is a decrease in the intensity of this peak with the following order: EPT-regenerated bath, in-use bath and spent bath. According to Rosalbino et al. Rosalbino et al. (2011), about 40% of the chromium