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The use of emulsion pertraction technology as an eco-innovative membrane process for the galvanic industry

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INTRODUCTION

The final implementation of an eco-innovative process at industrial scale implies the close collaboration between companies and research institutions. The 7^{th} Framework programme theme of the EU "research for the benefit of SMEs" aims at strengthening the 'innovation capacity' of European SMEs and their contribution to the development of new technology based products and markets.

The galvanic industry uses Cr (III) passivation baths to provide Zn electroplated surfaces with an extra protective film against corrosion and a decorative finishing. The lifetime of these baths is considerably limited due to the Zn (II) and Fe (III) impurities released to the formulation while the metallic piece is covered by a protective layer of chromium salts. The galvanic industry of Spain, Sweden and the Netherlands has participated in the EU programme by means of the "Towards an Innovative Galvanic Industry" project (TIGI, 218390-2) during 39 months. The main goal was to enhance the lifetime of the baths and consequently improve the environmental and economical performance of the sector. In order to do so, the project aimed at developing an eco-innovative process able to selectively separate the Zn (II) and Fe (III) impurities during the passivation, allowing chromium and other relevant components to remain in the bath. The selected process was the membrane process Emulsion Pertraction Technology (EPT) (Figure 1), a liquid-liquid extraction technology in which the extraction and back-extraction steps are conducted in a single membrane contactor (Bringas et al. 2011, Bringas et al. 2010, Diban et al. 2011, Klaassen and Jansen 2001, Ho and Poddar 2001, Mediavilla et al., 2010). The EPT uses as extractant and back-extractant an emulsion formed by the dispersion of a stripping acid into an organic extracting phase.

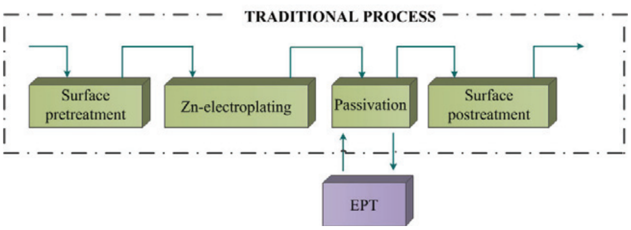

Figure 1. Integration of the EPT to the traditional Cr (III) based passivation process.

The project gathered information about the existing Cr (III) passivation baths and the study the accumulation of Zn and Fe impurities in targeted formulations was conducted.

This work presents a summary of the results obtained in the project. The project gathered information about the existing Cr (III) passivation baths. Further, a survey regarding the accumulation of Zn and Fe impurities in targeted formulations was conducted in close collaboration with the SMEs partners. The project also entailed the investigation of the effect of process variables on the EPT process performance at laboratory scale and the development of a mathematical model. The studied variables were pH, the concentration of impurities in the bath and the selective extractant in the emulsion, temperature and the type of stripping agent.

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Computer aided process engineering tools were applied for the integration of the EPT into the passivation process, alongside the scale-up and design of the large scale EPT units. The recovery of metallic Zn from the effluent generated in the EPT process was evaluated resulting in a significant reduction of the consumption of raw materials and of the generated waste. Further, several EPT units were installed in SMEs in Sweden, the Netherlands and in Spain and are currently running. Finally, the environmental benefits of integrating the EPT to the conventional passivation process were evaluated through the Life Cycle Assessment (LCA).

METHODS

In EPT the bath containing the targeted heavy metals is circulated through the shell side of the membrane module while an emulsion is circulated through the inside of the hollow fibers of the membrane contactor. The membranes are microporous and hydrophobic, and act as the contact interphase. The pores of the fiber are filled with the organic extractant phase because of the hydrophobic character of the membrane material. Zn (II) and Fe (III) are firstly extracted from the aqueous phase to the extractant organic phase in the pores of the hollow fibers. The heavy metals are then, instantaneously back-extracted by the stripping acid on the other side of the membrane.

LCA is a powerful tool for assessing the environmental performance of a product, process or activity from “cradle to grave” that helps in identifying clean and sustainable alternatives in the process design activity (Rebitzer et al., 2004, ISO 2006a and 2006b).

RESULTS AND DISCUSSION

The survey conducted in the project indicated that the accumulation of Fe (III) and Zn (II) in the bath depended on the amount of surface passivated and the correlation was quantified.

The results obtained in the project also demonstrated the feasibility of EPT for selectively remove Zn (II) and Fe (III) from the bath during the passivation process. The fundamental research showed that the working conditions had a considerable effect on the effectiveness of EPT (Urtiaga et al. 2010). The extraction of Zn was enhanced by the pH of the feed solution and by the use of sulphuric acid as back-extractant. Further, the temperature of the system, the concentration of the extractant, and the flow of the emulsion and aqueous phase through the set-up increased the extraction of both heavy metals. On the contrary, high feed concentration of Zn inhibited the extraction of Zn from the bath. Finally the model developed described perfectly the experimental data. Figure 2 and Figure 3 show the typical development of Zn and Fe concentrations in the bath as a function of the EPT treatment time. As it is required chromium concentration, the active metal for the formation of the passivation layer, is maintained constant.

During the project, the recovery of Zn from the effluent generated in the EPT process was successfully achieved using electrodeposition. This fact allows a better use of the resources implied in the galvanization process (Diban et al. 2011). Simultaneously, the corrosion protection properties of the regenerated passivation baths were effectively checked.

Finally, the LCA stated the environmental benefits brought by the integration of the membrane process to the conventional passivation. LCA showed that the main environmental benefit brought by the EPT is the waste avoidance resulting from the purification of the passivation bath. However, the environmental impact may be reduced by decreasing the energy input of the EPT process.

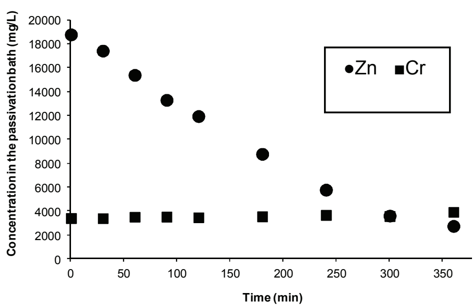

Figure 2. Development of Zn and Cr concentration in the passivation bath during the EPT process

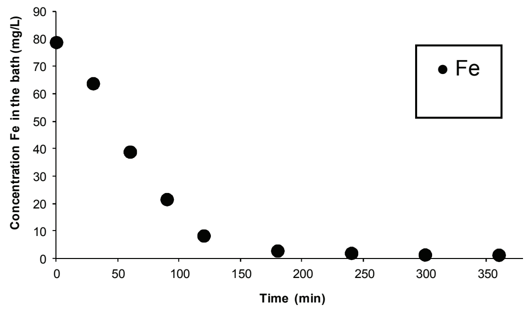

Figure 3. Development of the concentration of Fe in the passivation bath during the EPT process.

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Keywords: Cr (III) passivation bath, Emulsion Pertraction Technology, membrane contactors, Life Cycle Analysis