



## Release of cerium dibutylphosphate corrosion inhibitors from highly filled epoxy coating systems



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### ABSTRACT

Carcinogenic chromates are phased out as corrosion inhibitors in organic coatings, and are replaced by benign alternatives. Cerium-based compounds are excellent corrosion inhibitors in an aqueous environment. However, whether they are effective as corrosion inhibitor in an organic coating also depends on their interaction with the coating matrix, which should result in a sufficient release of inhibitors over a desired period of time. In this work we report on the leaching of cerium dibutylphosphate, Ce(dbp)<sub>3</sub>, from an epoxy coating system as a first step toward a fundamental understanding of the leaching behavior. To this end, coating systems containing various levels of inhibitor loading, ranging from 1 up to 50 wt%, were fabricated. These coatings were characterized using Fourier transform spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). Leaching experiments were performed by exposing the coating films to water, while the concentration of dissolved Ce(dbp)<sub>3</sub> in this water was monitored in situ using ultraviolet–visible (UV–vis) spectroscopy. The leaching of inhibitors showed a clear dependence on the initial inhibitor loading of the coating system. For highly loaded coatings (>25 wt%) all inhibitors leach out, whereas for a low loading level (<10 wt%) no leaching was observed. The difference between the high and low loading levels might be the formation of a porous network in the highly loaded coatings due to the dissolution of large Ce(dbp)<sub>3</sub> clusters. Using Magnetic Resonance Imaging (MRI) we visualized the penetration of a water front into this porous network during the leaching experiments. This water-filled porous network provides an excellent pathway for transport of Ce(dbp)<sub>3</sub>. For low levels of inhibitor loadings such a network is absent, and the transport of Ce(dbp)<sub>3</sub> is blocked. The samples containing moderate levels of inhibitor loading showed an increasing amount of leaching for decreasing values of pH. We believe that this pH dependence is the result of the concurrent leaching of significant amounts of Bisphenol-based coatings residues at low pH since the removal of these residues will also result in an increased porosity of the coating.

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### 1. Introduction

Metallic corrosion is a global problem with a substantial economic impact [1]. In addition, corrosion can lead to catastrophic failures of e.g. airplanes, bridges, or cars. Therefore it is important to protect metals from corroding. Depending on their application, a possible method to do this is by using corrosion inhibitors, e.g., (hexavalent) chromates, which have been used for over a century. However, chromates are believed to be carcinogenic and are therefore banned where possible. In the quest for suitable replacements

cerium-based inhibitors have shown to be a benign alternative [2–6].

Most of the previous research on cerium-based corrosion inhibitors has focused on corrosion tests in aqueous environments containing dissolved inhibitors, whereas their effectiveness in an organic coating has only been sparsely investigated. Experiments performed in such aqueous environments can give a very different outcome than experiments performed on coating systems containing the inhibitors, since in the latter case interactions between coating and inhibitors might play a dominant role. Coating systems in which inhibitors are incorporated should supply sufficient amounts of inhibitors over a desired period of time to spots susceptible to corrosion. This supply requires a dedicated release process, which largely depends on coating–inhibitor interactions. In some cases the coating–inhibitor interactions even provide a triggered release upon an external stimulus, such as pH, which enables

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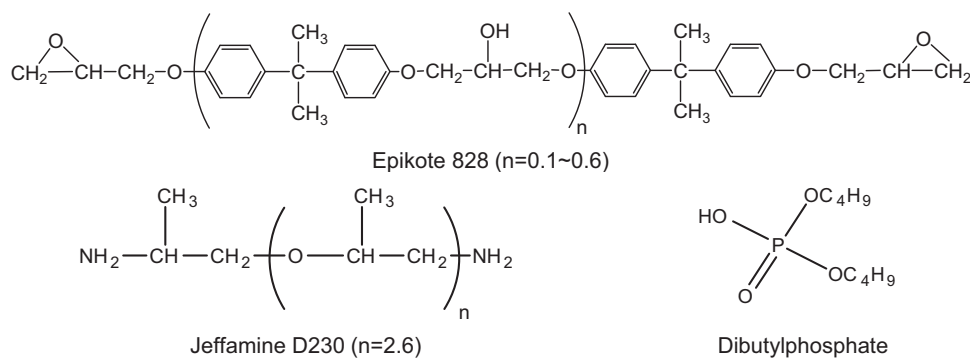


Fig. 1. Chemical structure of the Bisphenol-A epoxy resin (top), the amine hardener (bottom left), and protonated dibutylphosphate (bottom right).

(triggers) the release of inhibitors from the coating system [12,13]. A slow-release mechanism is another option to prevent a rapid loss of inhibitors [14–16].

Coating-inhibitor interactions might also influence the transport mechanism of inhibitors through the coating. Furman et al. [7] found a clear non-Fickian ( $t^{0.25}$ ) time-dependence for the release of chromates from an Anzol primer. Furthermore, they found that the chromate release rate increased with decreasing pH of the leachate, while consistent non-Fickian behavior was observed. They concluded that this behavior could not be explained by changes in the porosity/tortuosity of the coating system, or by pH-dependent chemical reactions. On the other hand, Prosek and Thierry [8] found a logarithmic time behavior for the release of chromate from polyester isocyanate coatings, with also an increasing release rate for decreasing pH of the leachate. Additionally, it has been reported that water can drag along inhibitors as, e.g., found for the anodic inhibitor  $\text{HPO}_4^{2-}$  [9]. However, from permeability cup and diffusion cell experiments Zhang and Jaworowski [10] found that the diffusion coefficient of trivalent praseodymium cations ( $\text{Pr}^{3+}$ ) through an epoxy primer was at least 6 orders of magnitude lower than the diffusion coefficient of water in this primer, which suggest the absence of water dragging. A fundamental understanding of the transport processes of ionic species is important since they play a significant role in the corrosion process [11].

It is generally believed that the high solubility of common cerium-based inhibitors, e.g.  $\text{Ce}(\text{NO}_3)_3$  or  $\text{CeCl}_3$ , results in a release rate that is too high for practical application [16–20]. Consequently, the solubility of cerium-based inhibitors has been reduced by adding a low-soluble anionic component [21,22]. Examples are: cerium acetate,  $\text{Ce}(\text{CH}_3\text{COO})_3$  [23], cerium salicylate,  $\text{Ce}(\text{sal})_3$  [24–26], cerium iodate  $\text{Ce}(\text{IO}_3)_3$  [26], or cerium diphenylphosphate,  $\text{Ce}(\text{dpp})_3$  [27–29]. In this work we will study the low-soluble cerium dibutylphosphate,  $\text{Ce}(\text{dbp})_3$  [30–35]. This inhibitor provides dual protection via the formation of a protective cerium oxide layer on cathodic spots and a dibutylphosphate layer on anodic spots of the corrosion cell, which might be formed locally on the metal surface [30].

The aim of the current work is to study the release rate of  $\text{Ce}(\text{dbp})_3$  corrosion inhibitors from organic coatings with a special focus on the effects of pH and interactions between the inhibitors and the coating matrix. We will study the interaction between the coating and the  $\text{Ce}(\text{dbp})_3$  inhibitors using Fourier transform spectroscopy (FTIR), whereas we will show the distribution of cerium in the coating using electron microscopy. Next, we will present the release of  $\text{Ce}(\text{dbp})_3$  from an organic coating for various levels of inhibitor loading and at different pH. Finally, we will analyze the evolution of the water distribution in the coating systems during this process using Magnetic Resonance Imaging (MRI).

## 2. Experimental

The  $\text{Ce}(\text{dbp})_3$  corrosion inhibitors were synthesized according to the recipe described in ref. [34]. In short; 0.1 mol dbp (96%, Alfa Aesar) was deprotonated with 0.05 mol anhydrous  $\text{Na}_2\text{CO}_3$ , after which 0.033 mol  $\text{CeCl}_3$  heptahydrate was added, and  $\text{Ce}(\text{dbp})_3$  precipitated. The precipitated  $\text{Ce}(\text{dbp})_3$  was subsequently washed with demineralised water. After drying,  $\text{Ce}(\text{dbp})_3$  was dispersed into a Bisphenol-based epoxy resin (Epikote 828, see Fig. 1) using a triple roll mill, which sheared the  $\text{Ce}(\text{dbp})_3$  particles until a homogenous distribution was obtained. Subsequently, the epoxy resin was cured with an amine hardener (Jeffamine D230, Fig. 1) at the stoichiometric ratio of 160/90 (gr. epoxy resin/gr. amine hardener). After mixing with a high speed mixer, the coatings were applied on release paper manually using a square applicator with a 150  $\mu\text{m}$  gap, and were left to cure for 4 days at room temperature. Several coating systems with different inhibitor loadings ranging from 0 up to 50 wt% were fabricated. Even though the highest loadings in this range are unrealistic from a practical point of view, we study them in order to investigate inhibitor release above an intuitive percolation threshold. This study might yield important information for the intermediate loading range. Note that previously it was found that 5–10 wt% of  $\text{Ce}(\text{dbp})_3$  is required to obtain sufficient corrosion protection [21]. After curing, the coating layers were peeled from the release paper and  $\sim 1 \text{ cm}^2$  pieces were cut from the resulting free films.

In order to characterize the epoxy systems we used FTIR (Shimadzu, FTIR-8400S) on maiden samples with an Attenuated Total Reflectance (ATR) insert (Graseby Specac, SPS-130-155X). Furthermore, coating samples were analyzed using Scanning Electron Microscopy (SEM) on a scanning electron microscope (FEI, Quanta 600) under high vacuum. Images were obtained from collected backscattered electrons at a beam voltage of 20 kV, whereas Energy Dispersive X-ray spectroscopy (EDX) was performed at the same voltage.

To monitor the leaching rate, the  $\sim 1 \text{ cm}^2$  pieces of coating were weighed on a balance and transferred into a cuvette for ultraviolet–visible (UV–vis) spectroscopy. These cuvettes were subsequently filled with 3 ml demineralised water at a pH of either 1, 3, or 5 (the acidity of the demineralised water was adjusted using HCl). The cuvettes were covered with a cap to avoid evaporation and were placed in a UV–vis spectrometer (Shimadzu, UV2600). The absorption spectrum from 190 up to 300 nm was recorded at several time intervals. From the recovered spectra the concentration of dissolved cerium ions was determined and leaching curves were obtained. After the leaching experiments a 4-(2-pyridylazo)resorcinol (PAR) indicator, which is sensitive to trivalent cerium ions [34], was added to the solution to independently confirm the presence of dissolved cerium ions.

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