# Withdraw Study for Hybrid Coating on Tinplate

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### Introduction

The utilization of inorganic-organic hybrids against corrosion, obtained by sol-gel process, was introduced in 1985<sup>1</sup>. Nowadays, these films have been extensively employed onto different substrates such as tin coated steel<sup>2</sup>, aluminum<sup>3</sup>, zinc<sup>4</sup>, among others<sup>5</sup>. In order to improve the anticorrosion properties of these materials, once the presence of micropores allows the diffusion of corrosive species, the use of corrosion inhibitors is indicated<sup>6</sup>. Nowadays, lanthanides ions have been used as alternative corrosion inhibitors<sup>7,8</sup> to chromate<sup>9,10</sup>. In recent work using 29Si NMR, Suegama et al.<sup>2</sup> demonstrated that Ce(IV) increases the reticulation of the siloxane chains. The authors suggested that in the presence of Ce(IV) ions, alcohol molecules of the hydrolysis solution can be incorporated in the siloxane chains, increasing their length. All the evidences indicate that the addition of Ce(IV) ions to the initial solution leads to the formation of free radicals, improving the reticulation of the silane films. The corrosion resistance of the hybrid sol-gel coatings is based on their physical barrier properties. Therefore, a homogenous crack-free material is required. Other factor important is the control of thickness. This control is possible only if the parameters involved in the process and their relationships are sufficiently known. Starting from Schroeder in 1969<sup>11</sup>, many papers have been published with indications about the influence of different parameters on the thickness of coatings. One of the most important and practical parameter is the relationship between thickness and withdrawal rate<sup>12</sup>. Therefore, the aim of this work is to study how the deposition step affects the corrosion behavior of thin films doped with Ce(IV) deposited onto Sn coated steel.

#### **Experimental**

The substrate used in all experiments was Sn coated steel (Incoflandres LTDA), cleaned with 3% Extran<sup>®</sup> at 80 °C for 10 min. The presence of Sn on the steel was not uniform and it was observed the formation of rows of tin on the entire steel plated surface. The polysiloxane films were prepared using MPTS (3-methacryloxypropyltrimethoxysilane , Fluka, 98 % purity) and TEOS (tetraethyl orthosilicate, Aldrich, 98 % purity) with a ½ molar ratio, respectively, MMA (methyl methacrylate, Aldrich, 98 % purity) with MMA/Si molar ratio of 2/1, mixed with 8 mg/mL Benzoyl peroxide (BPO) and 900ppm Ceric ammonium nitrate ((NH<sub>4</sub>)<sub>2</sub>Ce( NO<sub>3</sub>)<sub>6</sub>, Aldrich). The films were deposited by dipping onto Sn coated steel. One and three layers systems were prepared with withdrawal rates of 100 and 500 mm/min at room temperature. In three-layers systems, the second and the third layers were deposited 5 minutes after the deposition of the previous one. Finally, the samples were heat treated at 55 °C for 24 h with a subsequent curing at 160 °C for 3 h. The abbreviations for extreme composition are show in the Table 1.

**Table I**. The abbreviations for extreme film with rate deposition and layer number.

v (mm/min)	LAYERS	
	1	3
100	1L1	3L1
500	1L5	3L5

The coating homogeneity was evaluated by scanning electron microscopy (Carl Zeiss EVO 40) equipped with energy dispersive X-ray spectroscopy. Horiba JY Glow discharge optical emission spectroscopy (GDOES) analyses were performed to determine the films thickness. The corrosion resistance of the films was evaluated using 50 mL of 0.05M NaCl solution. Ag|AgCl|KCl<sub>sat</sub> electrode and rhodium network were used as reference and counter electrodes, respectively. The working electrode was mounted in a three electrode cell, exposing an area of 1 cm<sup>2</sup>. Electrochemical impedance spectroscopy (EIS) experiments were carried out using AUTOLAB PG-STAT 12 potentiostat equipped with a frequency response analyzer module. The EIS plots were acquired for immersion times up to 144 h, and were performed applying a 10 mV (rms) sinusoidal perturbation signal to the OCP, from 1 x  $10^{5}$  down to 1 x  $10^{-2}$  Hz with 8 points per frequency decade.

# **Results and Discussion**

Figure 1 shows the surface morphology of films with one (a) and three layers (b). In Figure 1(a) is possible to observe that the film formed by one layer and deposited with the slowest withdrawal rate (sample 1L1) does not cover completely the surface as indicated in the small box. On the other hand, the film with three layers (Figure 1(b)) and withdrawal rate of 500 mm/min (sample 3L5) appears defect-free providing a good covering of the surface.



Figure 1 Scanning electron microscopy (SEM) micrograph of a) sample 1L1 and b) sample 3L5.

The GDOES profiles depicted in Figure 2 show that samples produced with higher withdrawal rates (3L1 and 3L5) are thicker than those deposited with lower withdrawal rates (1L1 and 1L5). The deposition of multi-layers generally increased the total thickness of hybrid sol-gel systems even if, for withdrawal rates up to 300 mm/min, it was found this influence was less marked.



Figure 2. Quantitative GDOES profiles for samples with different layers number and withdraw rate.

EIS diagrams were acquired for the polysiloxane films described in Table 1. In Figure 3 are reported the Bode phase and angle plots for mono and three-layers systems deposited with withdrawal rates of 100 and 500 mm/min. Electrochemical impedance measurements show that the protection provided by the thicker systems is better than that given by the thinner solgel layers. Therefore, multi-layers systems and/or systems produced with higher withdrawal rate are able to produce a better physical barrier against corrosion attacks.

By evaluating the impedance behavior at high frequency, it is possible to have information about the insulating properties of coatings. By applying this approach as a function of immersion time, it is possible to follow the electrochemical behavior strictly correlated to the coating properties. In this work, the frequency chosen for calculating the coating capacitance was  $10^4$  Hz. Figure 4 shows the paint capacitance normalized versus the initial capacitance as a function of immersion time.

It is well known that the initial water adsorption can be associated to the not reversible diffusion of water through the coating. The coating capacitance increases due to the contribution of the water amount filling the voids within the organic material. By considering the trends shown in Figure 4a, the first water uptake is very limited for all the coatings. Nevertheless, the coating 3L5 capacitance shows a more limited increase (Figure 4 (b)) with respect to that exhibited by other coatings probably due to its higher thickness.



Figure 3. Impedance samples with one and three layers.



Figure 4. Coating capacitance, normalized vs. the initial capacitance C<sub>0</sub>, as a function of immersion time a) first 54h, b) until 144h.

### Conclusions

All studied coatings initially protected the tinplate steel substrate but the 3L5 system presented the better barrier properties. The best protection is related to the presence of a thicker coating covering the sample surface.

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