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Ammonium molybdate added in hybrid films applied on tinplate: Effect of the concentration in the corrosion inhibition action

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ABSTRACT

One of the ways to improve the anticorrosive properties of the hybrid films is with the addition of corrosion inhibitors based on inorganic salts. The protection mechanism involves the release of molybdate ions inserted in coatings by sol–gel during the immersion in the electrolyte, thereby minimizing the corrosion process. Siloxane–PMMA hybrid films are constituted by a silica network, to which the chains of poly (methyl methacrylate) (PMMA) are connected by covalent bonds (Class II) or by physical interactions (Class I). The stability and transparency enable the application of these materials in the coating of tinplate packagings in order to enhance corrosion resistance and reduce the brittleness of these products. In this context, the objective of this study is to coat the tinplate with a hybrid siloxane–PMMA (Class II) film obtained from a sol constituted of the alkoxide precursors: 3-(trimethoxysilylpropyl) methacrylate (TMSM), poly(methyl methacrylate) PMMA and tetraethoxysilane (TEOS), by varying the added corrosion inhibitor concentration from 0.01 to 0.02 M. The films were obtained by a dip-coating process and characterized according to their morphological and electrochemical behavior. The results showed that hybrid films doped with corrosion inhibitors showed an increase in the layer thickness in comparison to the inhibitor-free film. Furthermore, the addition of a higher concentration of ammonium molybdate resulted in an increase of the corrosion performance of the hybrid films.

1. Introduction

In order to minimize the corrosion impact and extend the life of metal structures, protective coatings are applied on the metal. The typical protection system is composed of several layers, such as pre-treatment, primer and finishing. The pre-treatments play a major role in a protection system, increasing the adhesion between the metal and the organic coating and often providing an active protective barrier [1].

The tinplate, used in the packaging industry, is formed from a metal substrate comprised by a steel base which has undergone a surface treatment, producing a thin $FeSn_2$ layer, a tin layer and a tin oxide layer [2]. Currently, industrial packaging made from this substrate is produced with chromate-based conversion treatments, to provide an increase in the corrosion resistance [3]. However, due to the toxicity present in these hybrid film pretreatments, they have been the subject of many studies, which offer promising environmentally friendly alternatives [4].

Among the possible alternatives, the pre-treatments based on siloxane–PMMA (poly(methyl methacrylate)) have been showing promising results also attracting the attention of industries in recent years, as these hybrid coatings improve the protection features against the substrate corrosion and the adhesion properties of organic coatings, in addition to causing reduced environmental impact when compared to the chromatization [5]. Furthermore, the siloxane–PMMA hybrid coatings promote an excellent anchoring on metals of difficult adhesion such as tinplate [6–7] for the subsequent paint coating on the silane film. This can be done by releasing the silicone with ultraviolet curing by the functional siloxane components [8].

Although the hybrid films have some advantages over other protective coatings, when they are applied individually they do not offer the same resistance to corrosion when compared to a chromium-based protective coating [1,9–10]. Besides, the protection is provided for a limited time, which is due to the probable presence of defects in the conversion layer. This favors the spread of aggressive species to the coating–substrate interface acting as preferred sites of corrosion initiation. For this

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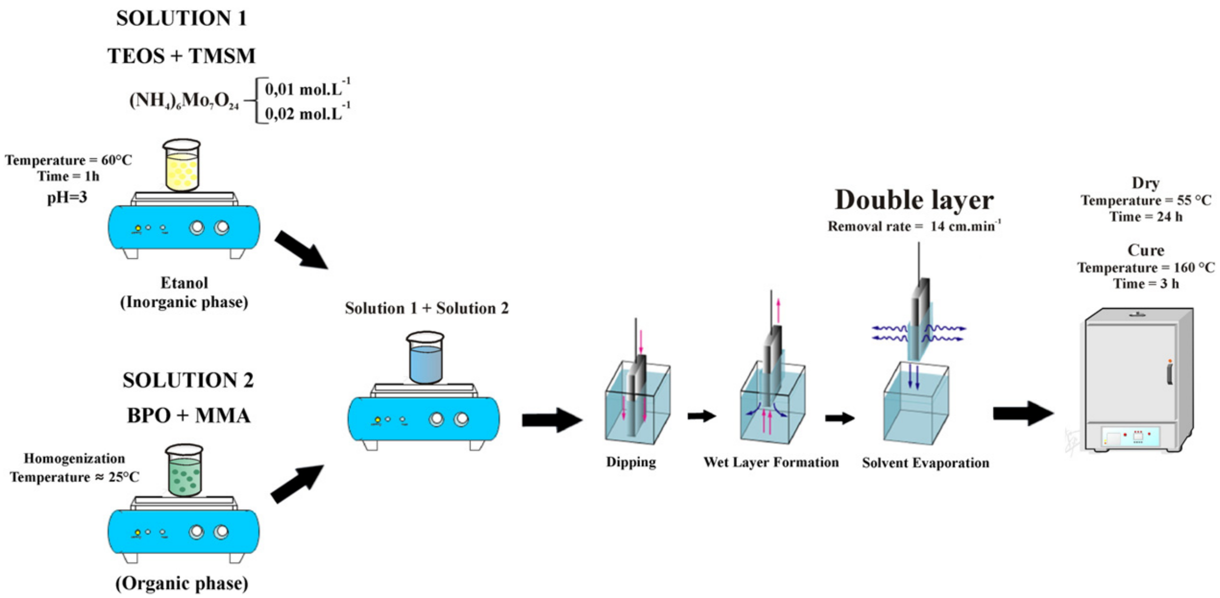

Fig. 1. Scheme illustrating the stages of the hybrid films development.

reason, and in general to improve the corrosive properties, corrosion inhibitors are being incorporated into these sol–gel films [9]. When a defect arises in the coating, the inhibiting compound can be released from the sol–gel layer suppressing the attack to the localized corrosion.

The combination of the hybrid film stability and the inhibitor solubility enables an increased long-term corrosion protection [9]. In this context, in order to obtain more efficient hybrid coatings for metal surface treatment, the combination of hybrid coatings with the addition of corrosion inhibitors has been extensively studied [9–11].

The literature reports the modification of hybrid films with rare earth salts [12–13], which provide good anti-corrosion properties when used as single layers in aluminum and galvanized steel alloys [14]. Amongst the potential alternatives of inhibitors being developed, molybdate has been showing certain advantages such as competitive prices, a low environmental impact and compatibility with a wide range of inorganic and organic substances [10]. In addition, studies have shown the use of molybdate as an inhibitor as a significant action in the corrosion process for zinc substrates, galvanized steel, and aluminum alloys and other metals [9,15].

Thus, the goal of this paper was to investigate the role of ammonium molybdate (Mo) on the eletrochemical, physico-chemical and morphological behavior of siloxane–PMMA hybrid coatings prepared from hydrolysis and condensation of the silicon alkoxides ontetraethyl orthosilicate (TEOS) and trimethoxysilyl propyl methacrylate (TMSM) and covalently bonded with polymeric chains of the poly (methylmethacrylate) (PMMA), deposited on tinplate substrates. The covalent bonds between phases (Class II) provide the chemical stability and crosslinked structure to hybrid coatings limiting access to the electrolyte substrate.

2. Experimental

2.1. Surface preparation

The tinplate was washed with acetone and dried. Then, the samples were immersed in Extran® neutral detergent (pH = 7) at 60 °C for 5 min and washed with deionized water and dried and again washed with ethanol and dried in an oven at 80 °C for 1 min.

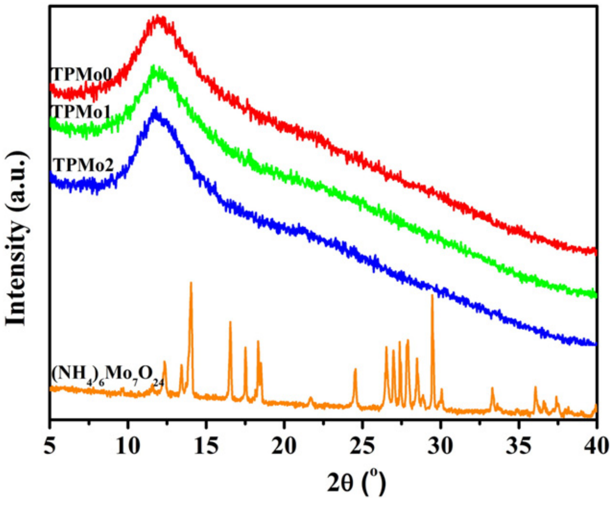

Fig. 2. XRD diffractogram of the hybrid films: TPMo0, TPMo1, TPMo2 and $(NH4)_6Mo_7O_{24}$.

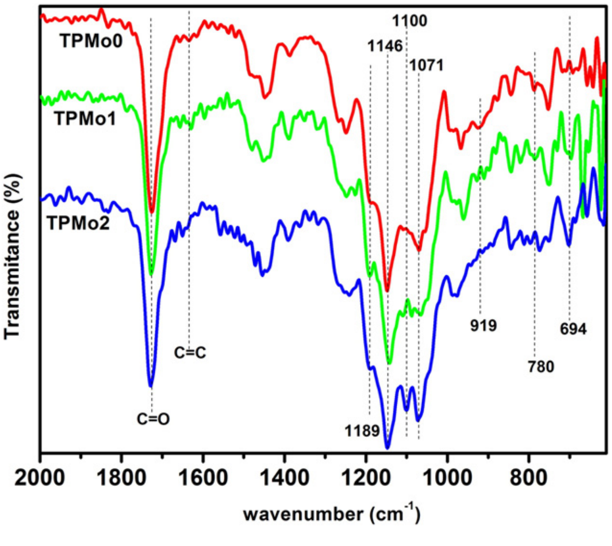

Fig. 3. FT-IR spectra of the hybrid films: TPMo0, TPMo1 and TPMo2.