



Exploring the corrosion inhibition of aluminium by coatings formulated with calcium exchange bentonite



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ABSTRACT

Environmentally friendly calcium-exchange derived from naturally occurring sodium-bentonite clays (Wyoming) are shown to significantly enhance resistance to corrosion protection in organic coatings applied on aluminium under aggressive environment typical from industrial areas. Two pigments classified as ion-exchange were also studied for comparison (Shieldex® and Al-Zn-vanadate hydrotalcite) together with zinc chromate as reference corrosion protection pigment. Electrochemical impedance spectroscopy (EIS) is used to study the corrosion protection in the metal/coating interface of pigmented alkyd coatings and a blank coating (without corrosion inhibitor pigment) in combination with visual inspection. The protection performance of these specimens was studied using outdoor exposure (two atmospheres with different aggressiveness) and accelerated tests (condensing humidity, salt spray and Kesternich tests, respectively). Results have shown strong dependence of the coating performance with the aggressive environment (e.g. Cl⁻, H⁺, SO₂) for all coatings formulated with ion-exchange pigments. The corrosion protection of the underlying aluminium substrate provided by calcium-exchange bentonite coating was shown under the presence of cationic aggressive agents in accelerated corrosion tests (specifically in Kesternich test). However, poor performance was observed for this coating using chlorides as an aggressive agent. Therefore, the presence of bentonite pigment improves the corrosion protection due to the cation-exchange mechanism.

1. Introduction

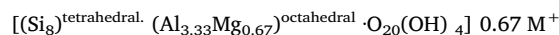
The formulation of organic coatings using anticorrosive pigments will enhance the protection of the metal substrate. Different protection mechanisms are observed depending on the type of pigment and their properties [1]. Hexavalent chromium pigments are known as one of the most effective corrosion inhibitors. Unfortunately, their replacement is necessary due to their toxicity and carcinogenic effects [2,3] despite their good efficiency [4].

Nowadays, ion-exchange pigments (e.g. Shieldex®, bentonites, zeolites, layered double hydroxides (LDH), etc.) are being widely explored as an environmentally friendly alternative [5–16]. According to their mechanism, the aggressive ions are trapped into the pigment and its counter-ions are simultaneously released due to an ion-exchange process in order to protect the metal (e.g. reach the metal/coating interface in order to protect/passivate the substrate).

Most of those compounds are natural clays. Bentonites can be found as sodium (Wyoming) and calcium in nature. Their chemical composition (e.g. the type of cation) determines the properties and classifies them within smectites compounds: $(Si_{4-x}Al_x)O_{10}(Al_{2-y}Mg_y)(OH)_2M_{(x+y)}$ [17].

Bentonites, which contain interlaminar water, are aggregates of lamellar platelets (trilaminar phyllosilicates or 2:1), packed together because of the electrochemical forces. Taking into account this 2:1 structure, each platelet consists of three sandwich-arranged layers: a central octahedral layer (Al₂O₃) and two tetrahedral layers (SiO₂). The aluminium cation (Al³⁺) often undergoes isomorphic substitution by lower valence metal, such as magnesium and iron. This substitution leads to a negative charge imbalance (e.g. 0.67 units per cell unit), compensated by exchangeable cations (M⁺/M²⁺/M³⁺), in particular Na⁺, K⁺, Mg²⁺ and Ca²⁺ as the most common ones. This feature provides the ion-exchange capability independently of the pH as intrinsic feature.

Therefore, the ideal chemical composition per cell unit of a bentonite could be defined as [18–21]:



where M⁺ cation provides the electrostatic interactions.

Bentonites are also known as *Montmorillonites* [17,22]. Epoxy coatings formulated with modified montmorillonites (using organic compounds intercalated within the structure) were created in order to improve adhesion, water absorption [23,24] and corrosion protection [25–27]. Initially, the

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main use of bentonites in the field of corrosion was focused on galvanized steel as substrate. The performance of organic coatings, formulated with bentonite as a pigment, has been evaluated in terms of cathodic disbondment (a) and corrosion protection under exposure to salt spray chamber (b).

In case (a), poly-vinyl butyral (PVB) model coatings formulated with cerium modified bentonites (high pigment volume concentration) has reduced the cathodic disbondment compared with a reference system (a coating formulated with SrCrO_4 pigment) [28–30]. This improvement was assigned to the low mass transport rate. It was justified because of the precipitation of cerium oxide/hydroxide on the zinc substrate rather than the cation-exchange capacity of Na^+ by Ce^{3+} [30].

Recently, new PVB model coatings have been formulated with synthesized bentonites using different alkaline earth cation ($\text{Me} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$), and Ca^{2+} bentonites have shown the lowest delamination rate. The protection mechanism for cathodic disbondment is also based on the precipitation of $\text{Me}(\text{OH})_2$ on the metallic substrate [10,31]. Under similar cathodic disbondment mechanism, organic coatings formulated with Y^{3+} and Ce^{3+} bentonites showed worse performance than Ca^{2+} bentonite [32]. However, Zn^{2+} bentonite improved the performance of Ca^{2+} bentonite, showing a different protection mechanism against cathodic disbondment [10].

In case (b), accelerated corrosion tests were carried out to compare Ce^{3+} and Ca^{2+} bentonites. Polyester coatings formulated with both types of bentonites were applied to galvanized steel. The delamination and substrate mass loss was reduced after 1000 h of exposure into the salt spray chamber [33]. Similar studies showed better behaviour in terms of delamination compared with Shieldex[®] and SrCrO_4 (the efficiency increase in the following order: Shieldex[®] < $\text{SrCrO}_4 \approx \text{Ca}^{2+}$ bentonite < Ce^{3+} bentonite), but the corrosion protection in solution by the different cations was $\text{Ca}^{2+} \ll \text{Ce}^{3+} < \text{SrCrO}_4$ [9].

Despite bentonites have shown good performance against cathodic disbondment on pretreated galvanized steel, there are uncertainties related to the corrosion protection provided by these pigments (e.g. Ca^{2+} bentonite has improved the resistance to cathodic disbondment but Ca^{2+} cation has provide poor corrosion protection). Moreover, corrosion studies have mainly focused on salt spray chamber (i), and there is a lack of studies on passive metals (ii). All these uncertainties bring the interest of this research to use coatings formulated with Ben/Ca pigment, applied to aluminium substrate and exposed to environments with different aggressive agents.

The goal of this study is to provide a first insight about the protection of aluminium by alkyd coatings formulated with Ca^{2+} bentonite (Ben/Ca) pigment and to assess their behaviour under different environment (both outdoor natural exposure and several accelerated corrosion tests). Well known ion-exchange pigments will be used for comparison. Moreover, the presence of different aggressive ions along the test will provide information about how important the ion-exchange process is in the protection mechanism.

2. Material and methods

2.1. Synthesis and samples preparation

Ben/Ca was synthesized from a commercial sodium bentonite

Table 1

Alkyd coatings formulation (composition of components (% wt.) between brackets). Xylene as solvent (17.2%) and other components (2.3%) were used for each coating formulation.

Designation	Binder	Anticorrosive Pigment	Others	Pigment Volume Concentration (PVC)
TiO ₂ (25%)	Linseed-soybean oil modified alkyd resin (35.5)	None	TiO ₂ (25), CaCO ₃ (20)	38.3
ZnCrO ₄ (10%)		ZnCrO ₄ (10)	TiO ₂ (20), CaCO ₃ (15)	38.0
Si/Ca (10%)		Si/Ca (10)	TiO ₂ (20), CaCO ₃ (15)	42.4
HT-V (10%)		HT-V (10)	TiO ₂ (20), CaCO ₃ (15)	39.3
Ben/Ca (5%)		Ben/Ca (5)	TiO ₂ (20), CaCO ₃ (20)	39.7
Ben/Ca (10%)		Ben/Ca (10)	TiO ₂ (20), CaCO ₃ (15)	39.9
Ben/Ca (15%)		Ben/Ca (15)	TiO ₂ (20), CaCO ₃ (10)	40.2

(Wyoming). The experimental procedure indicated by Bohm et al. [9] was followed to incorporate the Ca^{2+} cations into the structure. The ion exchange of Na^+ by Ca^{2+} was confirmed experimentally by X-ray diffraction [34]. Al-Zn vanadate hydroxalcalcite pigment was synthesized in the laboratory following the precipitation method developed by Kooli and Jones [35] and described by Buchheit et al. [12].

In order to evaluate the corrosion protection of coatings formulated with Ben/Ca as anticorrosive inhibitor, seven alkyd primers were obtained (see Table 1). Five alkyd coatings were formulated using different amounts of ion-exchange pigments: 10 wt.% of Shieldex[®] (Si/Ca (10%)), 10 wt.% of Al-Zn vanadate hydroxalcalcite (HT-V (10%)), and 5, 10 and 15 wt.% of bentonite-calcium (Ben/Ca (5%), (10%) and (15%)). These coatings were formulated maintaining approximately similar total pigment volume concentration (PVC). Ion exchange pigment density was determined experimentally according to ISO 787-10 by the method of Gay-Lussac in order to settle on PVC [36]. Additionally, two alkyd coatings were formulated for comparative purposes: TiO₂ (25%) coating without anticorrosive pigment and ZnCrO₄ (10%) with 10 wt.% of zinc chromate. Coatings were applied by air-spraying to a dry film thickness of $60 \pm 10 \mu\text{m}$ on degreased $15 \times 10 \text{ cm}$ panels prepared from 1 mm aluminium 1050 plate. A scribe of 0.3 mm width and 60 mm length was made in the lower part of the panels to evaluate the inhibitive properties of the different pigments and delamination of the coatings in natural and accelerated tests. Delamination was averaged measuring the maximum value from both sides of the scribe.

2.2. Corrosion tests

Accelerated corrosion tests were carried out in order to study the anticorrosive behaviour under environments with different aggressive conditions (saturated humidity, Cl^- , SO_2). Three different tests were used in order to obtain different experimental conditions: condensing humidity (ISO 6270-1) [37], salt spray (ISO 9227) [38] and Kesternich (ISO 3231, 0.2L SO_2) [39].

On the other hand, weathering exposure was carried out to provide complementary information about the performance of the coating exposed in a real aggressive environment. Thanks to this exposure, we are able to know about the performance in terms of corrosion protection without affecting the degradation mechanism of the coating. However, the main drawback is the long time of exposure. This test was conducted at two different sites: an urban atmosphere with corrosivity C2-C3 (roof of CENIM laboratory in Madrid, Spain) and urban-mild industrial atmosphere with corrosivity C3 (Avilés, Spain), according to the classification indicated by ISO 9223 [40]. Information after one year of exposure was obtained for all the coatings.

Coating degradation under accelerated and weathering exposure (delamination and blistering) was periodically evaluated according to the standard ASTM D714 [41].

2.3. Electrochemical impedance spectroscopy (EIS)

Visual evaluation of the coating degradation on aluminium substrate provides insufficient information to discriminate the corrosion protection

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