



Corrosion inhibition of aluminum by coatings formulated with Al–Zn–vanadate hydrotalcite

J.M. Vega, N. Granizo, D. de la Fuente*, J. Simancas, M. Morcillo

Department of Materials Engineering, Degradation and Durability, National Centre for Metallurgical Research (CENIM/CSIC), Av. Gregorio del Amo 8, 28040 Madrid, Spain

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ABSTRACT

The hydrotalcite structure is an ionic lamellar solid with positively charged layers incorporating two kinds of metallic cations and hydrated gallery anions. The ability of these compounds to retain aggressive ions and simultaneously release a corrosion inhibitor is the main reason for the development of hydrotalcite compounds to replace hexavalent chromium compounds (chromates) as inhibitive pigments.

In this study, alkyd coatings formulated with Al–Zn–vanadate hydrotalcite, at different pigment concentrations were applied on aluminum specimens. The painted panels were subjected to different accelerated tests (condensing humidity, salt spray and Kesternich) and atmospheric exposure in atmospheres of different aggressiveness. Corrosion performance was evaluated by electrochemical impedance spectroscopy (EIS). A traditional zinc chromate pigment was also tested for comparative purposes.

The obtained results confirm that hydrotalcite compounds achieve corrosion inhibition of the underlying aluminum substrate. It has been shown that an increase of anticorrosive pigment content (for a constant pigment volume concentration) does not always improve the primer behavior, but a larger amount of vanadates released from Al–Zn–vanadate hydrotalcite particles does improve anticorrosive behavior.

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1. Introduction

It is known that the combination of a physical barrier, a chemical inhibitor and an electrical resistor improves the performance of coating systems [1]. The role of pigments as anticorrosive inhibitors depends on how they influence the above parameters.

Nowadays there is a special interest to study and develop new anticorrosive pigments to replace chromates (one of the most effective inhibitive pigments) due to their toxicity and carcinogenic effects. The use of ion-exchangeable pigments (IEP) is one alternative that is being studied. Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds (HTlc), are one example of IEPs with the following general equation: $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(A_{x/n}^{n-}) \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are the divalent and trivalent metals. Their structure consists of brucite-like layers comprised of edge-sharing $\text{Mg}(\text{OH})_6$ octahedra. The isomorphous substitution of Mg^{2+} by M^{3+} generates a positive charge in the hydroxyl sheet. This net positive charge is compensated by anions (usually CO_3^{2-}) and water. In general these compounds consist of a host structure with a fixed charge and within the host there are 'galleries' that can accommodate anions and solvent molecules.

This intrinsic feature allows hydrotalcites (HTs) to be described as anion-exchange compounds. HTs are thus being studied in corrosion research as anticorrosive inhibitors loaded with different anions [2,3] and also in relation with coating application [4–8]. These pigments are commonly used in the form of solid particulate materials dispersed throughout the paint film. In this case the cathodic, anodic or both reactions are suppressed for as long as the inhibitor is present. The proposed mechanism makes the use of these pigments in coating formulation more attractive, since they can retain aggressive anions (e.g. Cl^-) during their permeation through the paint and at the same time can release a corrosion inhibitor (e.g. vanadate) during the leaching process.

Several studies have been carried out to assess the anticorrosive behavior of different types of coatings (conversion coating, sol-gels, model coatings, commercial primers, etc.) formulated with different HTs [9–23]. Williams and McMurray showed that HT can provide effective inhibition against filiform corrosion propagation on organic-coated AA2024-T3 alloy [9–11]. Álvarez et al. observed by EIS that the addition of HT to sol-gel films improved the corrosion resistance of coated AA2024-T3 alloy in salt spray [12]. Anticorrosive improvements were studied by the application of a HT conversion coating on AZ91D alloy, AA2024-T3 alloy and galvanized steel. Different corrosion resistance levels and an improvement in the adhesion properties were found [13,16–21]. On the other hand, Yu et al. observed by EIS some inhibition by adding HT to an epoxy resin applied on AZ31 alloy [14].

* Corresponding author. Tel.: +34 91 5544506; fax: +34 91 5345108.
E-mail address: delafuente@cenim.csic.es (D. de la Fuente).

Table 1
Formulation of the studied alkyd paints, showing composition as %wt. of components between brackets.

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
HT-V (5%)		HT-V (5)	TiO ₂ (20), CaCO ₃ (20)	39.4
HT-V (10%)		HT-V (10)	TiO ₂ (20), CaCO ₃ (15)	39.3
HT-V (15%)		HT-V (15)	TiO ₂ (20), CaCO ₃ (10)	39.3

Among the different HTs, attention has particularly been paid to Al–Zn–vanadate hydrotalcite (HT-V) [21,24–27]. With regard to HT-V, Buchheit et al. studied inhibition on AA2024-T3 alloy coated with an epoxy binder formulated with HT-V pigment in salt spray. They found that HT-V affords protection by a combination of barrier protection and active inhibition. Corrosion protection was also observed at scribes, where the underlying bare metal is exposed [24,27]. On the other hand, Chico et al. observed an irregular behavior of primers formulated with HT-V and applied on low carbon steel [25]. Zheludkevich et al. studied a commercial water-borne epoxy primer formulated with HT-V on AA2024 alloy. These samples displayed good behavior during immersion in sodium chloride but showed significantly higher blistering in the humidity condensation test compared to chromates [26].

Therefore, the few studies conducted with coatings formulated with HT-V are not conclusive about their anticorrosive efficiency and controversy surrounds their functioning mechanisms in a real commercial primer.

The present work focuses on the study of anticorrosive protection of aluminum by alkyd paint coatings formulated with HT-V, assessing performance in environments with different aggressiveness, both natural and accelerated.

2. Experimental

HT-V pigment was prepared in the laboratory following the coprecipitation method developed by Kooli and Jones [28] and described by Buchheit et al. [27], wherein the HT-V compound is synthesized using decavanadate anions to compensate the positive charge in the HT structure $[\text{Zn}_x^2+\text{Al}_y^3+(\text{OH})_2(x+y)]^{y+}$, with an x:y ratio of 2:1.

Table 1 shows the composition of the five alkyd paints used in this study. The different paints were formulated maintaining the same pigment volume concentration (PVC). In order to know the PVC, the HT-V density (ρ) was determined experimentally according to ISO 787-10 by the method of Gay-Lussac [29].

As can be seen in Table 1, a TiO₂ (25%) coating, formulated without anticorrosive pigment, and a ZnCrO₄ (10%) coating, with 10% zinc chromate, were also considered as references. HT-V (5%), HT-V (10%) and HT-V (15%) coatings (containing 5%, 10% and 15% HT-V, respectively) were prepared and applied in order to study the effect

of the pigment content on anticorrosive behavior. The paints were applied by air-spraying to a dry film thickness of $60 \pm 10 \mu\text{m}$ on degreased $15 \text{ cm} \times 10 \text{ cm}$ panels prepared from 1 mm aluminum 1050 plate. A scribe of 0.3 mm width and 6 cm length was made in the lower part of the panels to evaluate the inhibitive properties of the different pigments in natural and accelerated tests.

Adhesion measurements were carried out on painted panels according to the cross cut test described in ISO 2409:1991 (E) [30].

2.1. Corrosion tests

The paints were subjected to the following accelerated corrosion tests: resistance to condensing humidity (ISO 6270-1) [31], salt spray (ISO 9227) [32] and Kesternich (ISO 3231, 0.2 L SO₂) [33]. An atmospheric corrosion exposure test was also conducted at two test sites: one located on the roof of the CENIM laboratory in Madrid (Spain), in an urban atmosphere of corrosivity category C2-C3, and the other in Avilés (Spain), in an urban-mild industrial atmosphere of corrosivity category C3, according to ISO 9223[34].

2.2. Electrochemical impedance spectroscopy (EIS)

The anticorrosive performance of the coatings was investigated by EIS in a classic three-electrode cell consisting of a silver/silver chloride reference electrode, a stainless steel counter electrode and the coated aluminum 1050 specimens as a working electrode in the horizontal position, with a working area of 9.62 cm². EIS measurements were carried out at room temperature using a potentiostat/galvanostat (AutoLab EcoChemie PGSTAT30) equipped with a FRA2 frequency response analyzer module. Frequency scans were carried out by applying a $\pm 5 \text{ mV}$ amplitude sinusoidal wave perturbation, close to the corrosion potential. Five impedance sampling points were registered per decade of frequency. The analyzed frequency range was from 100 kHz to 1 mHz and the electrolyte used was 0.1 M sodium sulphate solution. The impedance data was analyzed using the electrochemical impedance software ZView® (Version 3.1c, Scribner Associates, Inc., USA).

Different measurements were carried out. On one hand, the samples exposed to the accelerated tests were evaluated after dif-

Table 2
Summary of results obtained in the accelerated corrosion tests.

Designation	Condensing humidity		Salt spray		Kesternich (0.2 L)	
	Delamination at the scribe (mm) 816 h	Blistering of the painted surface 300 h	Delamination at the scribe (mm) 576 h	Blistering of the painted surface 780 h	Delamination at the scribe (mm) 318 h	Blistering of the painted surface 318 h
TiO ₂ (25%)	0	7	0	9	0	9
ZnCrO ₄ (10%)	0	5	0	9	0	9
HT-V (5%)	0	3	0	10	0	8
HT-V (10%)	0	7	0	9	4	9
HT-V (15%)	0	3	0	10	a	a

^a Significant paint failure was observed at 120 h (Fig. 8).

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