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Corrosion Protection with Ion Barrier Coatings(I) Barrier to Anion Coating

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Abstract: A cation exchange membrane is permeable to cation and impermeable to anions. When the membrane is directly coated on a metal surface, the coating will not provide corrosion protection to the substrate, and it delaminated in salt fog testing. When the barrier to anion membrane coated on the surface of a primer, it inhibits anions to diffuse from the environment through the coating.

Key words: Ion exchanger, ion barrier, corrosion protection, delamination, organic metal finishes, selective permeation.

1. Introduction

Organic coatings were assumed as a barrier to water and oxygen at the coating-environment interface. However, at ~50s last century, Mayne compared the diffusion rate of water, oxygen and salt showing that paint films are so permeable to water and oxygen that they cannot inhibit corrosion by preventing water and oxygen from corrosion reaction at the metal surface. He proposed that organic coatings prevent corrosion by virtue of a high ionic resistance which impedes the movement of ions and thereby, reduces the corrosion current to a low value [1]. However, this concept was called an "old idea" in 80's last century because the relationship between the ion resistance and corrosion protection is not clear in some situation [2].

Organic anticorrosion coatings can be monolithic consisting simply of one layer, or they can be composed of two or more layers. All these systems have two interfaces: the coating-substrate and the coating-environment interfaces. Most studies on the barrier effect, weather barrier to water, oxygen, ions or all of them, focus on the coating-environment interfaces. The present paper briefly reports the effect of barrier to anion coating on the coating-substrate and the coating-environment interfaces.

2. Experiment

Materials: D.E.R.^{TM} 324 Epoxy Resin (Dow Chemical Co.), Ancamide® 2767 Epoxy Curing Agent (Air Products), and Cation exchange resin Ionac C-249 (Na form, 100 -200 mesh, Lanxess Co.) were used, and 10% zinc nitrate solution was used for zinc ion exchange. The Steel (CRS) panels (S-36. Q lab), Aluminum panel (Q Lab.), and Galvanized steel (ACT panel) were used. Panels were degreased with 1:1 mixture of acetone and denatured alcohol before application of the coating.

Ion exchange process: 21.1 g of the Ionac C-249 cation exchange resin (Na form) was placed in a glass Column (r ~ ¾ ', L ~ 12 '), 300 mL of 10% zinc nitrate solution was through the colum over ~24 hrs. The zinc ion exchanged resin is rinsed with distilled water, and dried in an oven at 110 ^{o}C overnight.

The cation exchange resins were mixed with curing agent then mixing with epoxy resins at the weight ratio of cation exchange resin to epoxy resin is 1:4. The mixture was coated onto the surface of test panels with a wire-wound rod applicator. The coatings are dried at RT overnight. The thicknesses of dried film are ~60 µm.

Accelerated corrosion testing of the coated panels was performed according to salt fog test ASTM B117.

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Salt fog was widely used by the paint industry as a quality control. Exposure to salt fog provides information about anticorrosion behavior of the coating. Prior to exposure, the coated panels were all scribed a scribe through the coatings. The painted panels were exposed to neutral salt fog conditions consisting of 95 °F with saturated humid. The salt fog exposure and damage evaluations were all done by a professional testing company.

3. Results & Discussion

3.1 Cation Exchange Resin Pigmented Coatings Directly Coated on the Surface of a Metal

It is well-known that aggressive anions such as chloride ions will accelerate corrosion on the metal surface. Cation exchange membranes have selective permeability; it is not permeable to anions and only permeable to cations [3]. However, a cation exchange membrane coated on the surface of a metal will not provide corrosion protection to the substrate. Fig. 1 shows the coatings on steel substrate after salt fog test (AMST B 117, ~200 h): the control panel without cation exchanger resin is severely corroded along the scribe lines, but only small areas of delamination (Fig. 1a); the coating with cation exchange resin has less corrosion on the scribe lines, but the coating was severely delaminated that is shown by inserting a coin between the substrate and the coating layer (Fig. 1b). The coated aluminum panels also show that the control without cation exchanger resin is small areas of delamination (Fig. 2a), and the coating with cation exchange resin is severely delaminated that is shown by inserting a coin between the substrate and the coating layer (Fig. 2b).

Fig. 3 shows the coated galvanized panels after salt fog test. Fig. 3a shows the control of area delamination. Figs. 3b and 3c are severely delaminated indicating both Na and Zn forms of the cation exchange resin all accelerate the delamination. There are white materials along the scribes and it is much less in Fig. 3b than that in Fig. 3c. If the white material is related to corrosion, there is no advantage of zinc ions for corrosion protection.

Delamination is one of the most common forms of failure in organic coatings. Henry Leidheiser, Jr. [4] concluded that no significant delamination is observed in the absence of metal cation. He also concluded that cation transport through the coatings is the

(a) (b)

Fig. 1 The coating on steel panels after salt fog test (ASTM b 117, ~200 h): (a) without cation exchange resin, and (b) with cation exchange resin,

(a) (b)

Fig. 2 The coatings on aluminum panels after salt fog test (ASTM b 117, ~200 h): (a) without cation exchange resin, and (b) with cation exchange resin.

(a)
(Epoxy + hardener) only

(b)
(Epoxy + hardener)
with cation exchange resin (Na^+)

(c)
(Epoxy + hardener)
with cation exchange resin (Zn^{++})

Fig. 3 The coatings on galvanized panels after salt fog test (ASTM b 117, ~200 h): (a) without cation exchange resin; (b) with cation exchange resin (Na^+); (c) with cation exchange resin (Zn^{++}).

rate-determining step in the cathodic delamination [5]. Greenfield and Scantlebury [6] suggest that delamination only occurs when alkali metal ions from the environment get into the coating-metal interface and act as counter ions to the catholically generated hydroxyl ions. Since a cationic membrane is permeable to cations, alkali metal ions will diffuse from the outside environment through the coating into the coating-metal interface. Therefore, metal ions such as sodium ions and catholically generated hydroxyl ions accumulate in the coating-metal interface. When the concentration of sodium hydroxide increases to make the pH > 10 in the inter face, delamination is expected to occur [6].

3.2 Cation Exchange Membrane Coat on the Surface of a Primer as a Topcoat

A topcoat of a coating system has to resist all the environment impacts. The anticorrosive effect of most topcoats relays on the “tortuous path” barrier of the layer (Fig. 4a). This barrier effect makes the water, dissolved electrolytes, and oxygen take an indirect rout through the resin to the primer. It is a physical barrier and achieved by using lamellar or platy pigments in the coating formulation.

According to Mayne [1], paint films cannot inhibit corrosion by preventing water and oxygen from corrosion reaction at the metal surface. It is well-known that aggressive anions such as chloride ions will accelerate corrosion on the metal surface. A cation exchange membrane is impermeable to anions [3]. This is an electrochemical Donnan exclusion due to the repulsion between the anions and the fixed negative charge of a cation exchanger (Fig. 4b). Experiment results show the electrochemical barrier to anions is more effective than the physical barrier of tortuous path. The measurements of ASTM B117, ASTM D 5894, ASTM D 4541, ASTM D3359, and ISO20340 all show that the topcoat with a primer provides better corrosion protection than current commercial paint systems. The Corrosion Potential Ecorr. (mv) data are listed in Tables 1 and 2 [7]. The topcoats with cation exchange pigments increase corrosion potential indicating better corrosion protection. Other electrochemical data such as EIS will be provided later.

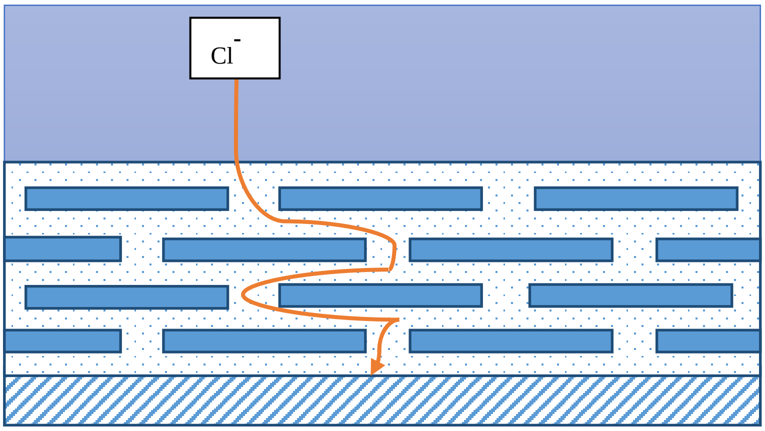

Fig. 4a Barrier to anions by “Tortuous Path”.

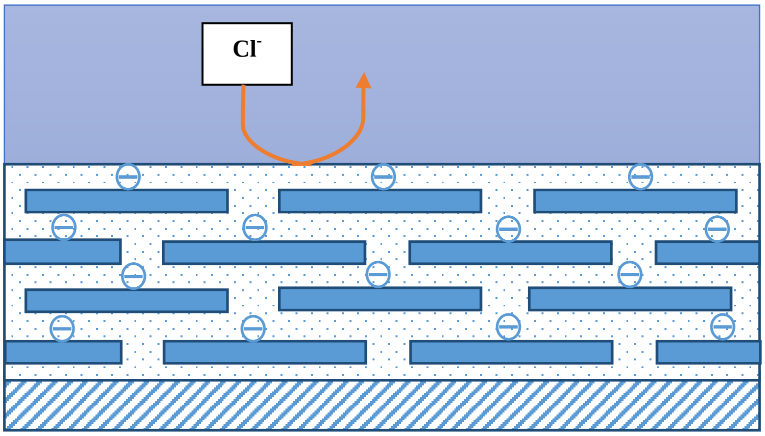

Fig. 4b Barrier to anions by “Donnan exclusion”.

Table 1 Corrosion Potential of the top coat—"Rust-oleum" primer systems, immersed in 3.5 wt. % NaCl aqueous solution for 20 months.

Cation exchange pigment in topcoat	Ecorr. (mV)
None	-480
Shieldex ® AC3	-171
C-249 in solvent topcoat	-43
C-249 in waterborne topcoat	-356

Table 2 Corrosion potential of the top coat—water borne epoxy primer systems immersed in 3.5 wt. % NaCl aqueous solution for 20 months.

Cation exchange pigment in topcoat	Primer	E corr. (mV)
None	Water borne epoxy primer	-223
Shieldex ® AC3	Water borne epoxy primer	-136
C-249 in solvent topcoat	Water borne epoxy primer	-72
C-249 in waterborne topcoat	Water borne epoxy primer	-104

4. Sammary

Because cation exchange membranes are permeable to cations, directly coating it on the metal substrate will result in delamination. The coating with zinc ion exchanged cation exchange resin does not show any improvement on corrosion protection and on delamination.

Because cation exchange membrane are impermeable to anions, as a topcoat it will form a electrochemical barrier to anions, which should be a better barrier than the physically "tortuous" barrier, thereby, provides better corrosion protection to the metal substrate in an environment of aggressive anions.

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