“Release-on-demand” ion-exchange anticorrosive pigments

Ion-Exchange anticorrosive Pigments (IEPs) are advanced, eco-friendly additives for coatings on metals. These pigments act as smart, non-toxic replacements for chromates by trapping corrosive ions such as H^+ and Cl^- and releasing inhibitive ions. The loading of these pigments in coatings would help offer superior metal protection in harsh environments.

IEPs use a "smart release" mechanism triggered by the onset of corrosion: 1) **Uptake:** As aggressive ions (such as Cl^- and H^+) permeate the coating, the pigment traps them within its structure; 2) **Release:** In exchange for the aggressive ions, the pigment releases corrosion-inhibiting ions (such as Ca^{2+}, Ce^{3+} , or vanadates); 3) **Protection:** The released ions migrate to the metal surface to form a passive protective layer (e.g., calcium oxide or hydroxide), which inhibits further electrochemical reactions [1].

Common types of IEPs include:

1) **Calcium-Exchanged Silica (Si/Ca)**: One of the most common commercial types, often used in coil coatings and industrial primers. It exchanges calcium ions for hydrogen or sodium ions from the medium.
2) **Bentonite/Calcium (BT/Ca)**: A cation-exchange pigment based on modified clays. It has high specific surface area but may show higher water absorption, leading to blistering.
3) **Hydrotalcite/Vanadate (HT/V)**: An anionic exchanger that releases vanadate ions (anodic inhibitors) in exchange for aggressive anions like chlorides.

IEPs are primarily used in primer coatings for various metal substrates in industries such as automotive and marine coatings, general industrial and construction machinery, metal coils (galvanized steel, zinc alloys, galvalume) and radiation-cured (UV/EB) systems and powder coatings.

This NSF SBIR-funded research developed a series of environmentally friendly IEPs for use in anticorrosive coatings. Among them, Phosphate-Exchanged Silica (also called “SA-PO” internally) IEP has successfully demonstrated its enhanced corrosion inhibitive effect in an epoxy coating on metal surfaces. Figure 1 illustrates the SA-PO anion-exchange anticorrosive pigment.

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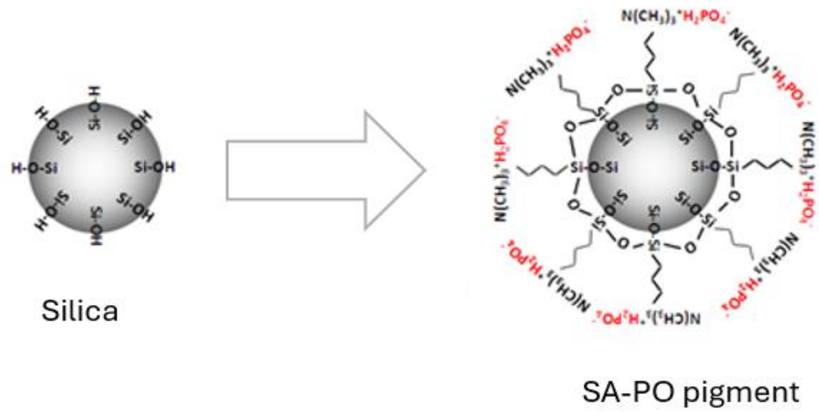

Figure 1. illustration of SA-PO anion-exchange anticorrosive pigment

The SA-PO pigment synthesis process includes: 1) coating silica particles with a special silane aqueous solution to add exchangeable anions; 2) exposing the coated silica to a phosphate solution, allowing phosphate ions to replace the above anions on the silica surface; 3) water rinsing to remove excess phosphates.

The SA-PO pigment was incorporated in an epoxy coating and was tested on AA 2024-T3 Al alloy substrate in a 500-hr salt spray test according to ASTM B117. Figure 2 compares test panels with various pigments after SST. The $BaSO_4$-filled epoxy coating (Figure 2a) shows massive paint loss; the chromate ($SrCrO_4$)-loaded coating (Figure 2c) performs the best, showing no paint loss in either scribes or intact areas. The SA-PO-added coating (Figure 2d) performs similarly to the one with zinc phosphate (Figure 2b). Both coatings show no paint loss in the scribes, but some blisters appear in intact areas. These results indicate that SA-PO pigment in epoxy coatings offers a strong self-healing effect by trapping corrosive chloride ions to release phosphate ions, and then quickly re-passivates exposed metal to stop corrosion.

Remarks:

1) SA-PO is an effective anticorrosive IEP with a strong "self-healing" effect.
2) SA-PO is compatible with various resins and can be used in anticorrosive coatings for protecting metals.
3) Like other IEPs, SA-PO is susceptible to osmotic blistering in humid conditions because of its water solubility and ion-exchange properties.

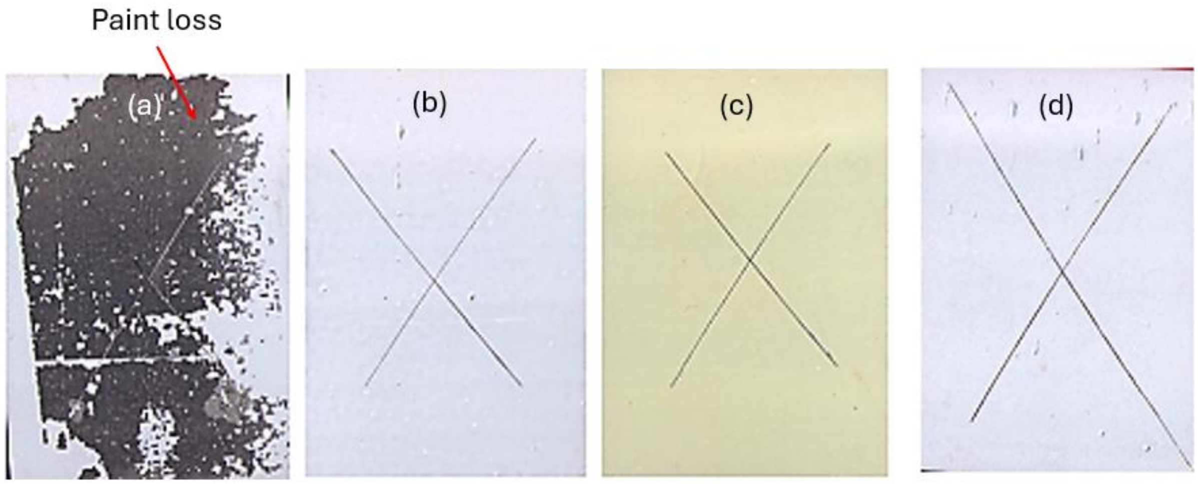

Figure 2. A 500-hr SST result for the epoxy painted AA 2024-T3 panels; (a) epoxy coating without anticorrosive pigment, (b) epoxy-zinc phosphate coating, (c) epoxy-chromate coating and (d) epoxy-SA-PO coating

Reference

N. Granizo, J.M. Vega, D. de la Fuente, et al, "Ion-exchange pigments in primer paints for anticorrosive protection of steel in atmospheric service: Cation-exchange pigments", Progress in Organic Coatings, 75(3), 2012, 147-161