

OCP Measurement: A Method to Determine CPVC

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Open Circuit Potential (OCP) is one of the electrochemical methods to evaluate the corrosion performance of organic coatings. Some authors have used OCP measurement data to confirm their results obtained with Electrochemical Impedance Spectroscopy (EIS). In this investigation, there is an attempt to utilize OCP measurements to estimate the CPVC (Critical Pigment Volume Concentration) of two anti-corrosive pigments, i.e., zinc phosphate and zinc chromate. OCP measurements showed two distinct behaviors in the PVCs lower than CPVC and one typical behavior at the PVCs higher than CPVC. The results showed that OCP measurement could be a highly reliable method for the evaluation of CPVC.

INTRODUCTION

Pigment Volume Concentration (PVC) has a great effect on organic coating properties. As PVC increases, a dramatic change occurs at Critical PVC (CPVC), where air-pigment interface is introduced in an organic coating. PVC to CPVC ratios play a most important role in organic coating properties [1-3], so, determination of CPVC is one of the essential laboratory tests. Patton [3] listed 15 properties in relation to PVC in three categories namely: Mechanical, permeability and optical properties. Asbeck [4], in an interesting paper, introduced a method named saline DC conductivity. He showed that, above CPVC, resistance dramatically decreases from 5 to 10 ohms. This method makes it easy to evaluate CPVC in a relatively short time and with high reliability. The other test method for determination of CPVC is impedance measurement [5,6] that produces results with high reliability. The results of impedance measurements are not always easy to fit with the equivalent circuit. In this paper, an effort is made to introduce OCP measurement as a method for determining CPVC. The OCP is Open Circuit Potential. It is the potential of a working electrode when no external current is applied to the

circuit. Although sample preparation is somewhat time consuming, the results are highly reliable.

OCP, as an electrochemical method for estimating corrosion performance, has been used by some authors. Some authors have used OCP measurements data to confirm their results obtained by Electrochemical Impedance Spectroscopy (EIS). Gowri et al. [7] stated that their maximum corrosion resistant specimen showed a rise in potential to a more positive value and other samples showed constant potential or became more negative. Deya et al. [8] showed that the corrosion potential of alkyd paints varied jointly with ionic resistance and that the corrosion potential changed toward less negative values in cases of coatings with high ionic resistance.

Mayne [9] described OCP changes of coated steel by the concept of an iR drop across the coating. Schematically, he showed the potential-current lines of coated and uncoated specimens and suggested an iR drop at the anodic and cathodic areas as a criterion for determination of the corrosion potential of coated specimens. He stated that, in general, anodic areas are, at least in the early stages, much smaller than cathodic areas, so, in the early stages, the corrosion potential is more positive. However, with an increase in anodic sites during immersion, the corrosion potential becomes more negative. Thu et al. [10] evaluated the OCP of aluminum with three different coatings over a period of 400 days. Their results showed a trend toward the OCP of bare aluminum. Also, they evaluated the coating system with an initially stable potential as the worst system. Marchebios et al. [11]

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measured the OCP of specimens coated with zinc rich (50%w) epoxy over 100 days. During the initial 14 days, the potential became gradually positive. After this period, the potential increased rapidly up to 40 days. They concluded that the protection mechanism changes from sacrificial to barrier inhibition during immersion time. Kendig et al. [12] measured the OCP of polybutadien coated steel and concluded that the initial increase of OCP was related to the formation of cathodic areas that it remained unchanged for some time and, subsequently, decreased by activation of the surface. Many other researchers have also used OCP to evaluate the corrosion protection performance [13-18].

Naderi et al. [19] used the Mayne model and suggested that the accumulation of OH⁻ under the coating forms a passive layer, thereby, increasing the cathodic to anodic area ratio, which results in an increase in potential. A higher diffusion of water in the film increases OH⁻ and Cl⁻ permeability, resulting in a breakdown of the passive layer and a higher anodic to cathodic area, which causes OCP to become more negative.

CPVCs of zinc phosphate and zinc chromate are determined using a variation of physical properties and also calculated using an oil absorption method [20]. Oil Absorption (OA) is a method by which the minimum amount of linseed oil to wet 100 g pigment powder is measured (ASTM D281).

CPVC can be calculated from oil absorption [3] using the following equation:

$$\text{CPVC} = \frac{1}{1 + \text{OA}\rho/93.5}, \quad (1)$$

where, ρ is pigment density (g/cm^3). The CPVCs of zinc phosphate and zinc chromate are 52.15% and 54.84%, respectively. In this paper, it is tried to evaluate the electrochemical behavior of organic coatings with OCP measurements at different λ of pigments (λ is PVC to CPVC ratio) to confirm the CPVC calculated using the oil absorption method.

EXPERIMENTAL

Both zinc phosphate and zinc chromate pigments were separately dispersed in epoxy resin (Epikote 1001 Shell) to achieve 10 μm particle size. The fineness of the dispersions was examined with a Sheen Grindometer. The zinc chromate and zinc phosphate were obtained from the SNCZ and NUBIOLA companies, respectively. Mill bases were prepared in seven different concentrations of pigment ($\lambda = 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2$). Polyamide (Crayamid 115) is used as the curing agent.

All coating samples, including the blank sample, contained 1% dispersing agent (EFKA 5244) and rheology modifier (Aerosil). Coating materials were applied

to Q-Panel mild steel to achieve $30 \pm 2 \mu\text{m}$ dry film thickness. Coatings were allowed to be fully cured over 7 days. The exposed area was 4 cm^2 and other areas of the plates were sealed with Beeswax - Colophony. To ensure repeatability, 3 to 5 replications were prepared for each pigment concentration. Specimens were immersed in a 3.5% sodium chloride solution. A silver/silver chloride electrode was used as a reference electrode and a 179/EDA KIT Multimeter was used to measure OCP for up to 28 days of immersion.

RESULTS AND DISCUSSIONS

OCP measurement results are given in Figures 1 and 2 for zinc phosphate and zinc chromate pigmented coatings, respectively. Each data point is an average of 3 to 5 replications.

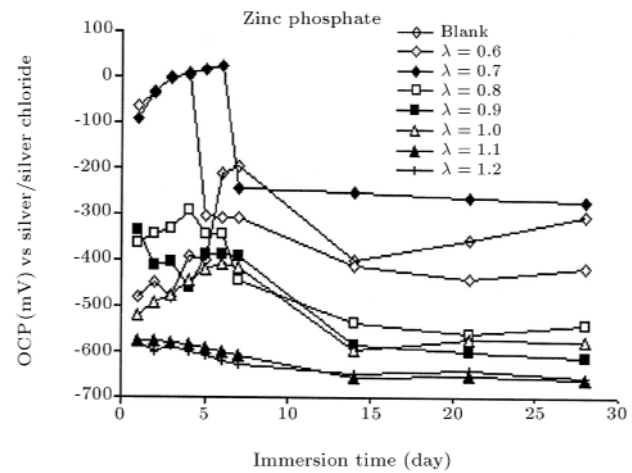


Figure 1. Variations of OCP of coated mild steel containing zinc phosphate at different concentrations during 28 days of immersion in 3.5% NaCl solution.

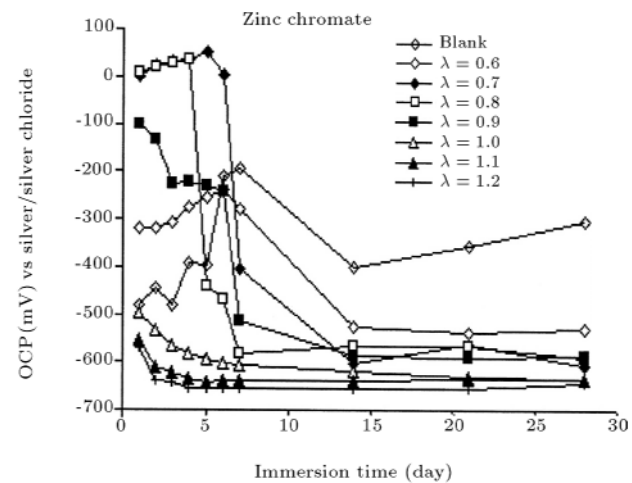


Figure 2. Variations of OCP of coated mild steel containing zinc chromate at different concentrations during 28 days of immersion in 3.5% NaCl solution.

Two general behaviors could be indicated for pigmented samples in Figures 1 and 2 where $\lambda < 1$: First, OCP becomes more positive up to 4-7 days of immersion and second, after this preliminary stage, it becomes more negative.

At the first stage, oxygen and water reach the metal surface and anodic and cathodic reactions take place. This results in the generation of OH^- and Fe^{+2} at the interface. On the other hand, organic coating has a selective permeability [21]. Epoxy coating is more permeable to Fe^{+2} than OH^- [19], so, concentration of OH^- at the interface increases and causes passivation of the surface. Increasing OCP is the result of an increase in the cathodic to anodic area ratio [19].

At the second stage, OCP becomes more negative. Because of selective permeability, the chloride diffusion is slower than that of water [22,23], so, after a while, chloride ions reach the interface and increase the anodic to cathodic area ratio. Therefore, after the preliminary stage, OCP becomes more negative.

The coated specimens formulated at $\lambda > 1$ had OCPs much less than the samples formulated at $\lambda < 1$. For both zinc phosphate and zinc chromate, above CPVC, OCP is negative at the preliminary stages and becomes more negative, gradually, during immersion time (up to 4 days for zinc chromate and 14 days for zinc phosphate). It remains almost stable for up to 28 days. This is because of the large pores in the coating that make it easy for electrolytes to reach the interface, so, organic coating loses selective permeability above CPVC. Therefore, for coating formulated above CPVC, the anodic to cathodic area ratio is maximum. This results in OCPs as low as -600 mV (Ag/AgCl).

There is no unique behavior of OCP for coatings containing zinc chromate and zinc phosphate at the CPVC point ($\lambda = 1$). Specimens containing zinc phosphate showed a somewhat similar behavior to the coatings formulated below CPVC and specimens containing zinc chromate showed a similar behavior to the coating formulated above CPVC. In other words, at the CPVC point, the coatings formulated with zinc phosphate were selectively permeable toward ions, while the coatings formulated with zinc chromate showed no selective permeability. At CPVC ($\lambda = 1$), no large pores exist in the coating and the amount of binder is sufficient to wet the surface of the pigment particles. It is, therefore, expected of the coatings at the CPVC point to show selective permeability toward ions, but zinc chromate does not follow this trend. The reasons behind the zinc chromate causing such behavior is because of its relatively high solubility in water. Because of the high solubility of zinc chromate, leaching occurs readily through the thin layer of binder surrounding it. Therefore, even at CPVC, large pores appear in the coating, which shows a similar behavior to the coating formulated above CPVC.

CONCLUSION

OCP measurement is used to evaluate CPVC. OCP showed different behaviors for formulations below, above and at CPVC.

Below CPVC, the coatings showed an increase in OCP at the initial immersion time, where the cathodic to anodic area ratio increased, due to an accumulation of OH^- at the interface. A subsequent decreasing of OCP occurred, where chloride ions reached the interface and the anodic to cathodic area ratio increased.

Above CPVC, the coatings had no selective permeability and OCPs were as low as -600 mV (Ag/AgCl). The potential got more negative gradually up to 4 days for zinc chromate and 14 days for zinc phosphate and remained almost stable for up to 28 days.

At the CPVC point, the coatings formulated with zinc phosphate were selective permeable toward ions, while the coatings formulated with zinc chromate showed no selective permeability. It is supposed that, because of the relatively high solubility of zinc chromate in water, leaching occurred readily through the thin layer of binder surrounding it. Therefore, even at CPVC, large pores appear in the coating, which showed a behavior similar to the coating formulated above CPVC.

A better criterion for evaluating CPVC is to determine a property, which is changed significantly at this point. OCP shows sharp changes above and below CPVC. Other methods, like a variation of optical properties (e.g. gloss), physical properties (e.g. density) and mechanical properties (e.g. flexibility) can lead to an evaluation of CPVC, but, such properties, because of their different natures, almost never meet each other at an exact point and sometimes their variation is not sharp enough to evaluate CPVC exactly [3]. Hence, there is usually a range for CPVC calculated by different methods. However, CPVC determined by OCP measurement, because of its electrochemical nature, leads anticorrosive primer formulators directly to the point they need. Therefore, OCP measurement could be a method with high reliability for the evaluation of CPVC.

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