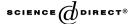


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Corrosion inhibition by chromate and phosphate extracts for iron substrates studied by EIS and SVET

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Abstract

The anticorrosive performance of zinc chromate and zinc phosphate, used as extracts in 0.1 M NaCl, was studied using electrochemical impedance spectroscopy (EIS), the scanning vibrating electrode technique (SVET) and open circuit potential (OCP) measurements. Neither of the pigments managed to totally prevent corrosion. Phosphate had a much lower inhibiting efficiency and acted at a very low rate, whereas chromate acted immediately after immersion, but lost some of its action after a few hours of continuous immersion. Iron corroded uniformly in the phosphate extract, whereas in the chromate extract nucleation of metastable pits occurred. Evolution of the chromate layer with time was revealed in the EIS spectra in the form of a relaxation constant that developed during immersion, which was interpreted as being due to the formation of a porous healing layer formed on repassivated pits. The joint use of open circuit potential measurements, EIS and SVET is illustrated as a means of assessing different phenomena on the metal surface.

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1. Introduction

Zinc chromate has for many years been used as inhibiting pigment for steel. Its toxicity, however, is leading to great restrictions to its use and has caused intensive research on alternative pigments with better human compatibility. The inhibitive action of chromate seems to be based upon the oxidizing power of Cr(VI), which becomes reduced to Cr(III) in a reaction that neutral pH occurs as

$$2CrO_4^{2-} + 5H_2O + 6e^- \rightarrow Cr_2O_3 + 10OH^-$$

forming a layer of chromium oxide. The healing properties of chromate arise from the fact that this reduction occurs at sites where oxidation of iron initiates, as:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

Although chromate ions participating in the cathodic reaction come essentially from the solution, it seems that conversion coatings formed on the surface of steel can have a high content of Cr(VI), which acts as a source of oxidising agent whenever corrosion starts [1,2]. Chromium oxides, namely Cr_2O_3 , are thermodynamically stable above pH 5, but reports have been given that for acidic solutions the oxidising power of Cr(VI) ions can enhance corrosion of steel [3]. Chromate pigments are frequently used in the form called *zinc yellow*, a classical pigment consisting of a mixed salt of zinc chromate, potassium chromate and zinc hydroxide. The mode of action of this pigment, although essentially based upon the chromate, is reinforced by the hydroxyl ion from the zinc hydroxide, which raises the pH, enhancing the stability of Cr(III) salts, whereas Zn^{2+} precipitates as $Zn(OH)_2$ at cathodic sites, creating also a protective layer [4].

Zinc phosphate, which is probably the most important alternative to chromate, has been used either as soluble inhibitor, in the formulation of conversion coatings and also as anticorrosive pigment in paints [5–7]. Solubility of zinc phosphate is higher in acidic media [8] and therefore phosphate pigments are usually considered to be more effective at low pH.

In a previous work [9], on the action of zinc chromate and zinc phosphate pigments on zinc substrates it was concluded that both pigments were effective in 0.1 M NaCl, although the phosphate did not quite match the high efficiency of chromate. It was also observed that the inhibiting action of chromate was practically instantaneous, whereas phosphate took several hours to achieve total protection of the surface. In the present paper, which corresponds to the second part of that study, the action of the same pigments is studied for pure iron.

2. Experimental

2.1. Samples

The substrate consisted of iron foil (from Goodfellow, Ltd, UK, 99.5% pure). For the EIS study, 1 cm² samples were electrically connected via a copper wire with silver

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