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Painting rusted steel: The role of aluminum phosphosilicate

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ABSTRACT

Surface preparation is a key factor for the adequate performance of a paint system. The aim of this investigation is to employ a wash-primer to accomplish the chemical conversion of rusted surface when current cleaning operations are difficult to carry out. The active component of the wash-primer was aluminum phosphosilicate whose electrochemical behavior and the composition of the generated protective layer, both, were studied by electrochemical techniques and scanning electron microscopy (SEM), respectively. Primed rusted steel panels were coated with an alkyd system to perform accelerated tests in the salt spray chamber and electrochemical impedance measurements (EIS). These tests were conducted in parallel with a chromate wash primer and the same alkyd system. Results showed that the wash-primer containing aluminum phosphosilicate could be used satisfactorily to paint rusted steel exhibiting a similar performance to the chromate primer.

1. Introduction

Surface preparation is a key factor prior to painting and the success of the protective paint system depends on its correct execution. Poor surface preparation followed by a good paint system usually brings worse results than the use of low quality products on a well prepared surface.

One of the major factors affecting the paint system performance is the presence of soluble salts at the paint metal interface. It is known that the presence of water soluble species, mainly chlorides and sulfates, at the metal/paint interface, promotes osmotic blistering of the coating and underfilm metallic corrosion when the concentration exceeds a critical level. Both processes can lead to the deterioration of the paint system in a very short period of time. However, it is difficult to set acceptable unique levels since each type of coating varies in susceptibility to soluble salt degradation which also depends on both coating thickness and the exposure conditions [1].

The other factor that may influence negatively the behavior of a paint system is the presence of oxides on the metal surface. Manual cleaning to prepare surfaces for coating may be accomplished by brushing, scraping or abrading the metal surface to remove rust, mill scale or slightly adhering old paint. It is slow and laborious but often used when it is not possible to employ other methods such as sand or grit blasting. It is recommended in the case of difficulties to access certain region of the pieces, complicated configuration or very high cost cleaning operations. Blasting operations may be risky to the operator and, at the same time, contaminate the environment. Mechanical cleaning requires of devices such as wire brushes, air guns, impact grinders, and abrading discs. Both manual and mechanical cleaning do not completely eliminate rust or scale and subsequent painting brings serious problems such as lack of adherence of the coating system to the base metal.

The effect of remaining oxides and different degrees of surface preparation on the performance of the coating system was studied by different authors through outdoor exposure tests and electrochemical essays [2,3]. They found that the most corrosion resistant surfaces were those primed with inorganic zinc rich paints. The same conclusion was obtained with epoxy paints and paints pigmented with red lead which was banned [3]. In many cases it was found that the influence of the presence of surface oxides on the performance of the coating system was negligible.

When it is not possible to eliminate oxides or the mill scale by blasting, the chemical conversion of the surface is the recommended method. A conversion coating may be defined as one formed by a chemical reaction which converts the surface of a metal substrate into a compound which became part of the coating. The primer designed in this research is aimed to generate conversion films [4–6].

The formation of a stable conversion layer is mandatory to ensure the adequate performance of the paint system; particularly during wetting and drying of steel surfaces exposed to the atmosphere. In these cases corrosion potential also changes periodically with time and rust formed on the steel modifies its nature by phase transformations [7–11]. In addition, several cations coming from the paint components can migrate into the oxide layer to be incorporated in the iron oxide lattice [12,13]. As a consequence, strong

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changes in the corrosion behavior are to be expected [14]. These cations may act either on the dry or on the wet cycle. For instance, chromium may decrease the corrosion rate during drying, presumably by inhibiting the cathodic reaction [15].

Tannins were normally used to convert the steel surfaces because they react with the remaining iron oxides, in the presence of phosphoric acid, to form iron “tannates” [16–20]. Several types of tannins, from different trees, were employed. The most widespread ones were extracted from the following plants: mimosa [21–24], chestnut [25,26], pine [27], “quebracho” [28], mangrove [29,30], etc. Results obtained with the use of tannins are controversial although, as a general rule, when applied on corroded substrates they improve the corrosion behavior of the coating system [26,31,32].

More recently, self-priming and surface-tolerant paints were developed. These paints incorporate phosphoric acid in their formulation to react with one of its components, polyvinyl alcohol, to form an ester. The ester diffuses into the oxide layer when moisture penetrates the paint film and transforms the different phases of iron oxide in a stable one constituted by maghemite. The transformed oxide layer strongly adheres to the binder through O–P–O bond to form, in this way, a passivating layer which improves the corrosion resistance of the paint [33,34].

The objective of this research was to modify a chromate based wash primer and study its performance on rusted SAE 1010 steel substrates. Zinc tetroxychromate was replaced by aluminum phosphosilicate, synthesized in the laboratory. Aluminum phosphosilicate combines two inhibitive species, the phosphate anion and the silica particle. The anti-corrosion behavior of aluminum phosphosilicate was studied by electrochemical techniques, particularly linear polarization experiments. The corrosion behavior of steel primed and painted with an alkyd system was evaluated in the salt spray chamber and by electrochemical impedance measurements (EIS). In both cases, electrochemical measurements were supplemented with observations by scanning electron microscopy (SEM).

2. Experimental section

2.1. Precipitation curves

Different solutions were prepared so that it was possible to study the acid–base and precipitation equilibria in systems consisting of the reagents used in the synthesis of aluminum phosphosilicate: SiO_2, H_3PO_4 and Al^{3+}. The composition of the titrated solutions may be found in the caption of Fig. 1. The acid–base equilibrium of each reagent was studied firstly. Then, the same study was carried out employing the aforementioned reagents but combined in pairs and, finally, all three together. Except for the sodium silicate solution, the remainder systems were acidified with hydrochloric acid to bring the pH below 1.20 to observe changes occurring with increasing pH, which finally, should lead to the precipitation of aluminum phosphosilicate. The titrant was 0.5000 M sodium hydroxide. Due to its alkaline nature, the sodium silicate solution was titrated with hydrochloric acid of the same concentration as the sodium hydroxide employed as titrant. The titrations were made following the procedures described in the literature [35,36].

2.2. The synthesis of aluminum phosphosilicate

In the first instance, a sodium silicate solution was prepared employing Aerosil 200®, a nanometric silica, whose particle size ranged between 12 and 16 nm and its specific surface area was 200 m^2 g^{-1}. The solution was obtained by dissolving 0.6000 g of this silica in 100 mL of distilled water containing 0.800 g of sodium hydroxide. Then, the pH was lowered to 1.2 with phosphoric acid. Finally, 3.75 g of aluminum nitrate nonahydrate we added to the colloidal dispersion to precipitate the aluminum phosphosilicate. The addition of the reagents was performed with constant stirring of 300 rpm. The resulting system was allowed to stand for 24 h and the pH was adjusted to 3.5 using a glass electrode and 0.50 M NaOH.

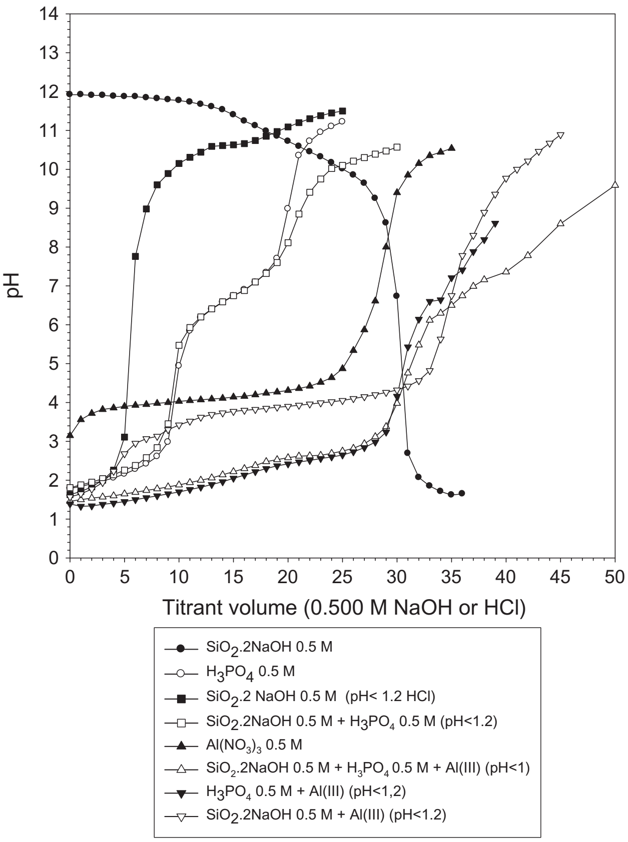

Fig. 1. Study of acid–base and precipitation equilibria of the reactants employed to synthesize aluminum phosphosilicate.

Once the precipitate was obtained, it was vacuum filtered through a Büchner funnel with medium pore filter paper (Whatman 40 or similar), air dried and milled to pass through the sieve No. 20. Finally, the precipitate was dried at 50 °C until constant weight.

The solid obtained as described before was characterized by conventional analytical techniques and by FTIR spectroscopy, preparing a potassium bromide pellet, with a Perkin Elmer SPECTRUM ONE spectrometer.

2.3. Study of reaction products between aluminum phosphosilicate and iron oxides

The nature of the reaction products between the aluminum phosphosilicate and the oxides naturally grown on a SAE 1010 steel panel was studied employing a mixture containing the oxides and the pigment in a molar ratio: 2:1. The oxides were scraped up from steel panels rusted in the laboratory atmosphere (20 ± 2 °C, RH 70%) during 2 years and they were characterized by FTIR spectroscopy. The mixture was left in the laboratory environment during 15 days, wetting it periodically with distilled water. After this period, it was dried at 100 ± 5 °C to constant weight just to eliminate free water to obtain the FTIR spectrum employing a potassium