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Performance evaluation of alkyd coatings for corrosion protection in urban and industrial environments

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ABSTRACT

The performance of alkyd based coatings exposed in two different sites in Ecuador, urban and industrial locations, for corrosion protection was evaluated. Atmospheric test sites and corrosion resistance of coatings were examined using mainly ISO and ASTM standards. The alkyd resin degradation was characterized by different methods such as FTIR-ATR, DSC, TGA and SEM.

The studies showed that the corrosion resistance and chemical structural changes were more evident for those samples exposed in the industrial environment although the sun radiation was lower than that measured in the urban location.

1. Introduction

It is well known that atmospheric corrosion is responsible for about 50% of the total economic loss when metal structures and equipment are exposed outdoors.

Organic coatings are the most common, versatile and cost effective mode of corrosion protection for metallic objects and structures [1,2]. Some scientific aspects of corrosion protection by coatings are understood but many are not, for example the exact cause and nature of coating failure is still up for discussion [3–8]. There are many factors that determine the duration of the coating, among which we can mention its nature, composition and thickness as well as the nature and substrate preparation, the method of coating and the environment [9–11].

Outdoor degradation of organic coatings is a complex phenomenon influenced by humidity, solar radiation, temperature, pollution and many other parameters [12,13]. Practical performance of coatings is usually investigated by both laboratory tests or/and outdoor exposure. Although there are significant advances in the development of laboratory tests [14–21], natural weathering is the most reliable exposure method for long-term performance examination of organic coatings [13,19]. However, these types of tests are extremely difficult to establish due to the wide variety of climates and the inherent variability of weather. Therefore, to develop hypotheses linking performance with composition, it is necessary to quantify the "environmental stress" test (meteorological data, pollution and the corrosion categories of the test sites) and detect and analyze the mechanism of formation of defects in the coating. These data are a useful starting point for the design of new coatings and can also be used to evaluate laboratory tests [19].

Advances in nanoscience and technology have led to improved corrosion protection coatings, which is attributed to the small size of the particles and interactions with binders. This provides an important alternative to the employment of toxic anticorrosive pigments [22–35].

This work analyzes the behavior of a pigment-free alkyd resin and a coating formulated with the same resin containing TiO_2 nanoparticles and fillers exposed at two different locations in Ecuador under urban and industrial environments, Quito city (78°29′24″W, 0°10′48″S) and Esmeraldas (79°40′47″W, 0°55′48″N) respectively. The atmospheric test sites and the corrosion resistance of coatings were examined using mainly ISO and ASTM standards (also MEB-EDX). The alkyd resin degradation was characterized by different methods such as FTIR-ATR, DSC, TGA and SEM in order to elucidate its role in the failure of the coating.

An alkyd resin based coating was selected because these resins are still common components in the formulation of paints [26,27] and, particularly, because their own formulations involve the use of natural oils that are relevant for developing countries like Ecuador [2,28–36].

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2. Experimental parts

2.1. Materials

2.1.1. Metallic substrate

Low carbon steel specimens (100 × 150 × 0.9 mm), (ASTM 283, grade C) were cleaned with methyl ethyl ketone (MEK) and stored in a dried atmosphere. A total of 12 samples was used, six of bare metal and the other six to deposit the coatings.

2.1.2. Coatings

Protective coatings were formulated from a commercial long oil soya alkyd resin with pigments (1.5% TiO_2 nanopowder <100 nm particle size, mixture of rutile and anatase) and extenders (8.5% of calcium carbonate and silica). As reference, a coating without pigments was prepared.

The coatings were air-sprayed onto both sides of the metallic substrates following the manufacturer's instructions. After the application, the coatings were allowed to cure for seven days. The edges of the specimens were protected with a thick epoxy resin coat in order to avoid the corrosion process starting at these points. The final thickness was 60 ± 7 μm measured with an Elcometer apparatus (model 345 Elcometers Instruments).

2.2. Field-test procedure

Two different sites in Ecuador were chosen to carry out the field tests. The first one is located in an urban environment of Quito (Metropolitan area 78°29′24″ W, 0°10′48″S at 2835 meters above sea level). The second one was selected on the coast close to the Esmeraldas Petroleum Refinery (an industrial zone) (79°40′47″W, 0°55′48″N).

For the study, three bare and three coated samples were allocated at the stations with a 45° inclination in accordance with ASTM G1 [37], G7 [38] and G50 [39] standards.

2.3. Meteorological and pollution data

The meteorological and pollution data, measured with automatic detection stations, was provided by the "Secretaría de Ambiente del Municipio del Distrito Metropolitano de Quito" and the "Instituto Nacional de Metorología e Hidrología" (INHAMI) from Esmeraldas. The atmospheric chloride deposition rate was measured following the wet candle method ASTM G140 [40], and the atmospheric SO_2 was monitored using the sulfation plate technique ASTM G91 [41].

2.4. Corrosion evaluation techniques for bare samples

Morphological aspects of rusting for bare samples were studied by optical microscopy (Thomas Scientific 1230CM), and the weight loss registered in accordance with ASTM D610 [42] standard.

The corrosion products were analyzed by X-ray powder diffraction (Siemens D-500, with Cu-Ka radiation of k 1/4 0.154 nm).

2.5. Corrosion evaluation techniques for coated samples

The corrosion degree was measured using the ASTM D610 [42] standard and the morphological and chemical aspects of the coatings were studied by optical microscopy (Thomas Scientific 1230 CM) and SEM in an electronic microscope Hitachi, model S3000N.

Table 1
Categorization of test sites according to ISO standards.

Parameter	Quito		Esmeraldas	
	Exp.	ISO st.	Exp.	ISO st.
$[SO_2]$ (μg/m^3)	10.5	P_0	37	P_1
$[Cl^-]$ (mg/m^{2}day)	–	S_0	16.4	S_1
TOW (h)	3500	t_4	6100	t_4
Steel corrosion rate (μm/year)	14.6	C_2	56.5	C_4

Parameter	Quito	Esmeraldas
Temperature (°C)	14	27
Sedimentary particles (g/m^{2}month)	3.75	1.76
Precipitation (mm/year)	2800	700
Radiation (w/m^2)	260	190
$[NO_2]$ (mg/m^3)	32	17

TOW, time of wetness.

2.6. Characterization of the degradation of coatings

Physicochemical characterization and coating degradation studies were carried out by FTIR microspectroscopy (Nicolet 6700 FTIR, Nicolet Continuum microscope) using the ATR technique (Ge crystal). The spectra were collected at a resolution of 4 cm^{-1} with an averaging of 64 scans.

DSC studies were performed with a TA Instruments Q2000 under the following experimental conditions: Temperature range -40 to 200 °C, with a ramp of 10°/min. Two scans were carried out for each sample.

Thermogravimetric data were collected on a thermobalance TA Instruments TGA-Q500 from 50 to 800 °C under nitrogen atmosphere at a flow rate of 80 mL/min. For some samples, air was introduced at 800 °C and an isotherm for 5 min was employed. The heating rate was 10°/min.

3. Results

3.1. Characterization of the test sites

The results of the characterization of the test sites are summarized in Table 1. In accordance with ISO 9223 standard [43], the urban station environment corresponds to category 2 (weak corrosivity, between 1.3 and 25 μm), while the industrial station can be classified as category 4 (high corrosivity between 50 and 80 μm). At Quito station the specimen rusting was more uniform, compact and adherent than in Esmeraldas. In both sites, the X-ray power diffraction results indicated that the specimens showed the presence of lepidocrecite and goethite. However, the concentration of goethite was higher for the sample exposed in Esmeraldas as a consequence of a high corrosion rate in this site.

The higher NO_2 concentration values and sedimentary particles in Quito are due to the fact that the station is located in a very heavy traffic zone. In addition, we must point out that the sun radiation is higher in the city of Quito compared with that of Esmeraldas. Although this factor does not have a direct influence on the corrosion rate, it does on the polymeric coating, as will be described later in the article.

3.2. Corrosion resistance

The alkyd coatings showed decoloration, fissures and rusting, without evidence of any other defects. According to the results (Table 2), the sample upper faces in both sites showed a higher corrosion attack. As in the bare metal corrosion process, Esmeraldas is the station where alkyd coating resistance was more affected.