Progress in Organic Coatings 77 (2014) 2133–2139

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Study of the effect of corrosion inhibitors on powder coatings applied on steel

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ARTICLE INFO

Article history:
Available online 8 April 2014

Keywords:
Environmentally friendly corrosion inhibitors
Powder coatings
Accelerated tests
Weathering

ABSTRACT

In the search for viable alternatives to produce environmentally friendly organic coatings systems, this work presents the study of several inorganic anticorrosive inhibitors and their further incorporation into a polymeric matrix via powder coating technology. The selected inhibitors are commercially available belonging to the second and third generations of developed replacement alternatives for hazards chromates. Polarization curves, also in the presence of continuous flow of N_2 and air gases, have been used for the characterization of the inhibitors. Succeeding, the inhibitors were embedded in powder coatings and subsequently applied onto mild steel substrate. The coated panels have been investigated by means of accelerated tests (neutral salt spray test, cathodic delamination test), natural weathering alongside electrochemical techniques such as electrochemical impedance spectroscopy. The effectiveness of the different corrosion inhibition pigments in the organic coatings has been evaluated and discussed.

1. Introduction

Chromium containing paints are well-known for their great effectiveness for anticorrosive inhibitive protection of steel alongside toxicity and carcinogenic issues [1]. Hence, in the last decades, a number of strict environmental protection regulations emerged and they have driven scientists and professionals in the field of paints toward the replacement of chromates compounds. More recent, attention has been given to another important environmental concern, the release of volatile organic compounds (VOCs) which motivated the same professionals for the development of solvent free coatings technologies [2,3].

At first, several new compounds have been proposed for substitute chromates, for instance phosphates, molybdates and silicates. Among them, phosphates gained attention as soluble inhibitors and conversion coating materials. Moreover, coating formulations pigmented with zinc phosphate (ZP) became widely used due to relatively good performance and low cost. It has been demonstrated that depending on the exposure media ZP pigments were able to protect steel at the same level or better that the zinc chromate [4]. On the other hand, paints with ZP did not perform well in accelerated tests [5], moreover it is claimed that ZP is classified as not-hazardous for human health but toxic in an aquatic environment [6].

In order to improve the anticorrosive inhibitive properties of zinc phosphate, they were chemically and/or physically modified, therefore, a second and a third generation of pigments have been developed [7,8]. As an example, with the purpose to merge the corrosion inhibition properties of phosphates and molybdates, zinc molybdenum phosphate pigments have been created [5]. In addition, it is possible to mention phosphates modified with aluminum [9] or lithium [10]. Most of them have been successfully tested in solvent-based coatings [4,11] and they are to be found as commercial products, e.g. K-White 105 and Heucophos ZPA®.

Another class of inhibitors that appeared as chromates-free alternative is the ion-exchanged inhibitive pigments. The anion or cation can be selected for specific applications depending on their basic or acidic properties. As an example, the alkaline calcium ion exchanged silica (Ca/silica). Particularly, it has been demonstrated that inhibition starts after the ingress of aggressive cations into the coating layer. Calcium ions are released from the pigments trapping or delaying the movement of aggressive cations toward the metal surface [12,13]. This non-toxic kind of ion-exchanged pigments have been studied inside a solvent-based coating for steel protection [12,14] and they are commercially available under the trade name Shieldex®.

Likewise to the previous scenario, strict directives/regulations has triggered the development and the use of solvent free coatings technologies for minimizing the emissions of VOC's, e.g. radiation

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http://dx.doi.org/10.1016/j.porgcoat.2014.03.014
0300-9440/

curing, water-based and powder coatings [15,16]. Among them, powder coatings appeared as environmentally friendly [17] alternative to the traditional solvent-based coatings, since only dry powder particles are required for the processing. In addition, inside an industrial plant the overspray used for a single application can be re-processed, reducing the waste of materials [18]. Moreover, in the last decades the use of powder coatings is demonstrating continuous acceptance in industry, not only due to economic advantages but also for equivalent protective properties and durability of the final coating when compared to solvent-based paints [19,20].

Considering the context above, the present work aims to investigate the anticorrosive inhibition effectiveness of several compounds incorporated into an organic coating system applied onto steel through powder coating technology. The corrosion mitigation pigments selected for this work are commercially available in the market; they belong to the second and the third generation of chromates-free pigments and are frequently incorporated into a solvent-based organic coating. Initially, the efficiency of the pigments has been verified by means of potentiodynamic polarization curves with the purpose of comprehend their capacity of inhibition. As the materials under investigation are not new, their potential was investigated in particular conditions, such as oxygen depletion or oxygen enrichment, which are likely to occur during the service life of the manufacture to protect. Therefore, polarization curves have also been performed in the presence of continuous nitrogen and air flow, aiming at a comprehensive understanding of their capacity of inhibition under lower and higher levels of oxygen at the metal surface.

Secondly, the pigments were incorporated into an epoxy-polyester paint formulation applied to cold-rolled steel using powder coating technology and the anticorrosive efficiency of the coatings have been studied through both accelerated tests, such as exposure in the salt spray chamber and cathodic delamination and outdoor natural weathering. Electrochemical impedance spectroscopy (EIS) measurements were also carried out in order to investigate the effect of the inhibitors on water uptake and barrier properties of the powder deposited organic coatings. In this sense, the work aims at assessing the potential of commercial available corrosion inhibitors widely used for solvent based paint in the field of powder deposited organic coatings. As these coatings are recognized to show high ohmic resistance of the water saturated coating film and low water solubility [21], the efficiency of the corrosion inhibitors might be affected. In fact, the reduced availability of water and the high ion diffusion resistance of the coating might affect the dissolution kinetic of the inhibitor and the mobility of the ionic compounds in the polymeric matrix, respectively.

2. Experimental

2.1. Characterization of the corrosion inhibition pigments

Commercial available corrosion inhibition pigments were used in this study. Table 1 shows the main features of the inorganic pigments employed.

Table 1
Studied inhibitors.

Pigment label	Chemical composition	Producer/supplier
Sacthoperse	Barium sulfate	Krahn Chemie GmbH (Germany)
Molywhite	Ca phospho-molybdate carbonates derivate	Moly White Pigments Group (USA)
Heucophos	Zinc calcium phosphate silicate derivate	Heubach GmbH (Germany)
Shieldex	Amorphous silicon dioxide calcium-ion exchanged	W.R. Grace & Co.-Conn. (USA)

The inhibition efficiency of the pigments was studied by means of potentiodynamic polarization curves. For that, the saturated solution of each pigment prepared in distilled water containing 0.3 wt% of Na_2SO_4 was used. Sodium sulfate salt was chosen to guarantee sufficient electrical conductivity of the solutions during the tests. After the pigment extraction, the pH of each saturated solution was measured. Potentiodynamic polarization curves were acquired in the inhibitor containing solutions using a traditional three electrodes arrangement. An Ag/AgCl reference electrode (+0.205 V vs SHE), a platinum ring counter electrode and cold rolled steel (supplied by Q-panel, USA) working electrode were employed. Measurements were carried out using Princeton Applied Research PARSTAT 2273 equipment. The surface of the working electrode was grinded with silicon carbide abrasive paper: 150, 400, 800, 1200 and 4000, washed and ultrasonically degreased with acetone. Measurements were performed at room temperature, at 0.166 mV/s scan rate, ranging the potential from the OCP value to −1.2 V for the cathodic polarization and from the OCP value to +1.2 V for the anodic polarization. An Avesta-Cell [22] with an exposed area of the working electrode of 1.0 cm^2 has been employed to perform the experimental measurements.

In addition, cathodic polarization curves were performed in the presence of continuous bubbling of nitrogen (N_2) and air (air) gases. The main purpose of bubbling N_2 was to create an environment near the metal surface with minimized oxygen content. Under these conditions, the measured oxygen level was about 1–2 ppm. On the other hand, air bubbling was used with the purpose to stimulate oxygen diffusion. For that, the gases bubbling time of at least 15 min were respected before running the measurements. All the potentiodynamic polarization curves measurements were performed, at least, for three replicate samples.

2.2. Coated panels characterization

The inhibitors were dispersed in an epoxy-polyester based polymer (supplied by Akzo Nobel, Italy) exploiting a double screw extruder. Barium sulfate was added as inert filler in the polymeric matrix. The polymeric paste was melted by means of the extruder in order to promote a homogeneous dispersion of filler, inhibitor and additives. The air cooled melt was milled to obtain a fine powder. By means of an electrostatic powder coating gun, acetone degreased mild steel Q-panel were coated and subsequently cured in oven at 180 °C for 10 min. The obtained film was considered as a primer layer. Therefore, following a similar procedure, a polyester based polymer (supplied by Akzo Nobel, Italy) was applied on the painted mild steel panels as top-coat. Notice that no inhibitors are contained in the top-coat. Table 2 summarizes the main features of the coated panels as well as their final thickness. Notice that the sum % inhibitor + % filler is maintained constant at 17% for all the primers.

The protective properties of the coating systems were studied by EIS in presence of 5 wt% NaCl medium. The EIS spectra were obtained by using the previously discussed electrodes arrangement using a coated panel as the working electrode. The EIS measurements were carried out on intact coatings at the free corrosion potential. The AC perturbation amplitude was 30 mV, frequency range 10^5–10^{-2} Hz and an analyzed area of about 10 cm^2. The

Table 2
Average thickness of the coated panels.

Pigment label	% Inhibitor	% Filler (barium sulfate)	Thickness (μm)
No inhibitor	–	17	116.4 ± 7.6
Sacthoperse	12	5	174.4 ± 8.1
Molywhite	7	10	102.2 ± 5.7
Heucophos	5	12	99.9 ± 7.6
Shieldex	5	12	115.1 ± 5.4