



Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Effect of surface treatment of pigment particles with polypyrrole and polyaniline phosphate on their corrosion inhibiting properties in organic coatings

Andrea Kalendová^{a,*}, David Veselý^a, Miroslav Kohl^a, Jaroslav Stejskal^b^a Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic^b Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

ARTICLE INFO

Article history:

Received 14 January 2014

Accepted 8 April 2014

Available online xxx

Keywords:

Conductive polymer

Polypyrrole

Polyaniline phosphate

Coating

Anti-corrosion efficiency

ABSTRACT

The effect of pigment particle surface treatment with conductive polymers on the corrosion inhibiting properties of organic paints was investigated. Mixed oxides possessing the spinel and perovskite structures were synthesised for the study. Natural graphite and pigments based on ferric oxide and silicate were studied. Coating materials based on a water-based epoxy resin were prepared for the investigation of the corrosion protection properties of the pigments, the surfaces of which had been provided with a conductive polymer layer. Laboratory corrosion tests were applied to the paint films. A commercial corrosion protection pigment, based on modified zinc phosphate, served as the corrosion protection efficiency standard. Polyaniline phosphate was found preferable to polypyrrole as the modifying agent of the pigment surface regarding the pigment's corrosion inhibiting efficiency. Surface treatment with the conductive polymers is also beneficial to the mechanical properties of the paint.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Conductive polymers are promising materials that are beneficial in protective anti-corrosion paints [1–4]. It is hoped that conductive polymers may replace corrosion inhibitors containing heavy metals. They are classed as electrochemically active corrosion inhibitors [5–8]. Examples of conductive polymers include polyacetylene, polypyrrole, polythiophene, polyaniline, polyphenylene and poly(*p*-phenylenvinylene), which are all systems containing conjugated double bonds with charge carriers providing charge transfer along the chain [9,10]. Polyaniline is probably the oldest synthetic conductive polymer [11]. The green protonated emeraldine is a conductive form of polyaniline [12]. Polypyrrole is appealing owing to its simple preparation in the form of a powder, film or composite [13–15]. Organic–inorganic composites containing inorganic nanoparticle fillers exhibit both improved electrical and mechanical properties. Inorganic nanoparticles in the composites are coated with a conductive polymer layer, which improves the physical properties of the material [16].

The potential of using polyaniline in inorganic paints as an anti-corrosion agent is the subject of extensive studies. In powder form,

in which it is used most frequently as a pigment, polyaniline is prepared by chemical polymerisation by the oxidation of aniline [17]. Pigments that are coated deliberately with a thin layer of polyaniline have also been used in many studies aimed at creating a new anti-corrosion pigment that could provide the highest level of protection to metallic surfaces coated with it [18,19]. In a number of applications into organic paints, it is convenient to apply composite particles formed by a layer of a conductive polymer on an inorganic particle, as a corrosion protection element. Hence, the systems comprise pigment or filler particles, which are provided with a layer of an active compound; a conductive polymer and a suitable substance (pigment substrate) that provides an additional active effect [20–22]. The inner core should determine the paint's physical properties at the substrate metal/paint film interface, such as its adhesion to the substrate [23]. However, the polymer's conductive property must be preserved. With polyaniline phosphate (PANI), such a particle must not be appreciably alkaline in order to preserve its conductive form for polymerisation on the particle surface. Also, the particle structure must not undergo change during the conductive polymer preparation process. In view of the specific properties of paint fillers and of the different corrosion conditions, it is necessary to find pigment particles with morphological and physicochemical properties that would not affect adversely the stability of the film-forming component of the paint binder or the physical properties of the cross-linked polymeric paint [24].

* Corresponding author.

E-mail address: andrea.kalendova@upce.cz (A. Kalendová).

2. Experimental

2.1. Laboratory preparation of pigments for conductive polymer testing

The effect of pigment surface treatment with polypyrrole (PPy) and polyaniline phosphate, on the anti-corrosion properties of organic coatings, was tested on pigment particles that differ in their structure, chemical composition and morphology. Pigments that are well suited for treatment with conductive PANI and PPy were selected based on previous work [20,22,25]. Three pigments based on mixed oxides possessing the spinel and perovskite structure: calcium titanate, strontium titanate and spinel type ferrite, were synthesised in the laboratory for testing and for investigating their anti-corrosion properties in coating materials (paints). Two iron oxide types (specularite and magnetite), two silicate-based pigment types (calcined kaolin and talc) and graphite of natural origin were also tested.

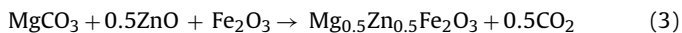
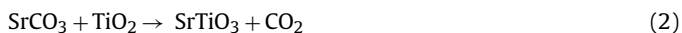
2.1.1. Synthesis of mixed-metal-oxide-based pigments possessing the spinel or perovskite structure

Spinel structure constitutes an extensive class of crystalline substances whose elementary cell contains 32 oxygen ions with suitable interstitial cations in two types of gaps [26]. Ferrospinels, i.e., ferrites (MeFe_2O_4) possessing the spinel structure, contain combinations of divalent and trivalent cations [27,28]. Perovskites can be described generally by the formula ABO_3 where atom A is in the oxidation state 2+ and atom B is in the oxidation state 4+ [29,30].

Starting substances for the synthesis of the pigments: $\alpha\text{-Fe}_2\text{O}_3$ (ferric oxide, hematite structure, manufactured by Lanxess-Bayer Leverkusen, Germany, red colour, density 5.05 g/cm^3 , M_r 159.6882 g/mol); TiO_2 (titanium oxide, anatase structure, manufactured by Precheza a.s., Czech Republic, density 4.25 g/cm^3 , M_r 79.88 g/mol); CaCO_3 (calcium carbonate, calcite structure, manufactured by Omya, GmbH, Austria, density 2.75 g/cm^3 , M_r 100.0869); SrCO_3 (strontium carbonate, strontianite structure, manufactured by Sigma-Aldrich Chemie, Germany, density 37 g/cm^3); MgCO_3 (magnesium carbonate, basic, heavy, magnesite structure, manufactured by Lach-Ner, s.r.o., Czech Republic, density 298 g/cm^3 , M_r 84.3139 g/mol).

2.1.2. Laboratory synthesis of the pigments:

The weights of the starting materials for the synthesis of CaTiO_3 , SrTiO_3 and $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ were calculated based on the stoichiometry of Eqs. (1)–(3) with respect to the total amount of pigment.



The weighing precision for the starting materials was $\pm 0.01\text{ g}$. A Dyna-10-therm (Germany) planetary mixing device was used for the dry homogenisation. Homogeneity of the emerging product was enhanced because the process programme conducts the vessel rotation procedure as a quasi-stochastic process [31]. The homogenised mixtures of the starting materials, accommodated in corundum crucibles, were calcined in an electric furnace (manufactured by Clasic, Czech Republic).

The first calcination phase was conducted at 1000°C and the second phase, at 1180°C . In each phase, the holdup time at the respective temperature was 2 h, ramp $5^\circ\text{C}/\text{min}$. The temperatures were chosen based on experience from previous studies [32,33] and were confirmed by X-ray analysis. After cooling, the calcined products were removed from the furnace and subjected to the subsequent operation, i.e., grinding to particle size within the range of $10^0\text{--}10^1\ \mu\text{m}$. The wet grinding process was conducted in ethanol

in a Pulverisette 6 (Netzsch, Germany) planet ball mill at 400 rpm for 4 h with a reverse mode after 2 h. The milling container was made of zirconium oxide, 500 mL volume. The 10-mm-diameter milling balls were made of zirconium silicate. The milling procedure was followed by pigment rinsing with a multiply larger volume of distilled water followed by drying at 110°C in a hot-air dryer for 10 h.

2.2. Other pigment types for testing the process of surface treatment with conductive polymers

2.2.1. Calcined kaolin

Kaolin contains kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, quartz SiO_2 and impurities. While calcined, kaolin loses crystal water at approximately 600°C to be transformed to the amorphous metakaolin [34,35]. Calcined kaolins, which are silicates with a non-isometric particle shape, are also intended for use in anti-corrosion coating materials [32].

2.2.2. Talc

Talc, $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$, is added to coating materials to improve adhesion and bending strength. Selected talc types are used in primers with anti-corrosion properties. They are silicates with a non-isometric particle shape [36].

2.2.3. Natural graphite

Graphite can be used in top coats as a pigment possessing high chemical and colour stability. This pigment also possesses the ability to form stratified barrier structures [37].

2.2.4. Oxidic compounds of iron

Oxides or hydroxy-oxides are usable as pigments in coating materials [37]. Important are black magnetite $\gamma\text{-Fe}_3\text{O}_4$ with regular particles and specularite $\alpha\text{-Fe}_2\text{O}_3$, known as foliated hematite (micaceous iron ore) with lamellar particles.

2.3. Preparation of pigments with conductive polymer surface layers

The surface of the pigments was modified by treatment with polyaniline phosphate and polypyrrole. The anti-corrosion efficiency was evaluated both for the untreated pigments and for the pigments with surfaces modified with polyaniline or PPy. The following pigments prepared in the laboratory were coated with a layer of PPy or polyaniline. Mixed-oxide-based pigments: $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (ferrite with the spinel structure), CaTiO_3 (perovskite structure) SrTiO_3 (perovskite structure); Fe_3O_4 (magnetite, Lanxess-Bayer Leverkusen, Germany) and lam- $\alpha\text{-Fe}_2\text{O}_3$ (specularite, MINKO, Kutná Hora, Czech Republic); silicates for polyaniline treatment: calcined kaolin ($\text{Al}_6\text{Si}_2\text{O}_{13}$, containing the amorphous metakaolinite phase, the crystalline fraction is a mixture of quartz and a small fraction of corundum) and talc $\text{Mg}_3(\text{OH})_2(\text{Si}_4\text{O}_{10})$. Particles based on graphitic carbon (natural graphite) were also subjected to the treatment.

2.3.1. Laboratory preparation of pigments modified with a surface layer of polyaniline phosphate (PANI)

The pigment (100 g) was suspended in 250 mL of 0.2 M aniline ($\text{C}_6\text{H}_7\text{N}$, Fluka, Switzerland) solution in 0.4 M *ortho*-phosphoric acid (Lachema, Czech Republic) and 250 mL of 0.5 M ammonium peroxydisulfate (Lach-Ner, Czech Republic), also in 0.2 M *ortho*-phosphoric acid, was added to initiate the aniline polymerisation process at room temperature. The suspension was stirred for 1 h during which the aniline polymerised on the surface of the pigment particles [38]. The following day, the solids were filtered out and rinsed with 0.2 M phosphoric acid followed by acetone. The pigment particles coated

Download English Version:

<https://daneshyari.com/en/article/692630>

Download Persian Version:

<https://daneshyari.com/article/692630>

[Daneshyari.com](https://daneshyari.com)