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# Anticorrosion efficiency of zinc-filled epoxy coatings containing conducting polymers and pigments

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ABSTRACT

The dependence of the corrosion-inhibiting properties of zinc-filled organic coatings on the nature of the conducting polymers and conducting pigments added and on the pigment particles' surface coating with conducting polymer layers were investigated. The following materials were selected to examine the corrosion-inhibiting properties of the conducting polymers: polyaniline phosphate (PANI), polypyrrole (PPy), natural graphite, and carbon nanotubes. Conducting pigment combinations for application in coating materials were formulated by applying pigment volume concentrations (PVC) of 0.3%, 0.5% and 1%, which were completed with Zn dust to obtain pigment volume concentrations/critical pigment volume concentrations (PVC/CPVC) = 0.64. Such conducting pigment/zinc dust combinations represented corrosion inhibitors to be used as ingredients in protective coatings. Solvent-based 2K epoxy resin based coating materials containing the corrosion inhibitors so formulated were prepared to examine their anticorrosion properties. The pigmented coatings were subjected to laboratory corrosion tests in simulated corrosion atmospheres and to standardized mechanical resistance tests. The protective coatings so obtained exhibited a higher efficiency than coating materials containing zinc dust alone. The coating material containing carbon nanotubes at PVC = 1% and the coating material containing graphite coated with polypyrrole (C/PPy) at PVC = 0.5% emerged as the best zinc-filled coating materials with respect to their corrosion-inhibiting efficiency. Treatment with the conducting polymers had a beneficial effect on the coating materials' mechanical properties.

## 1. Introduction

Zinc metal particles have been used for many years as ingredients in anticorrosion coating materials. The first use of zinc in coating materials dates back to 1840, when zinc-containing coating materials were used with a view to making use of the zinc particles' high covering power rather than their electrochemical properties to improve the coating's anticorrosion properties [1]. Zinc is used in the form of spherical or lamellar particles [2,3]. Since zinc metal powder in contact with an iron-containing metallic substrate initiates electrochemical reactions, it is often added to coating materials designed for metal protection to serve as a "sacrificial anode". The mechanism of action of the zinc is explained by electrochemical theory in terms of cathodic protection of the ferrous substrates [4].

Zinc metal reacts with oxygen, water and carbon dioxide present in air to give rise to corrosion products such as zinc oxide, zinc hydroxide and zinc carbonate. Such reaction products are able to perfectly seal all pores in the coating material (Fig. 1). A very compact and perfectly adhering barrier layer that is highly resistant to normal atmospheric effects emerges. This represents active protection because the function of electrochemical cathodic protection is renewed after each instance of mechanical damage to the film [1,5]. Zinc oxide and zinc hydroxide also possess some anticorrosion properties [6]. Metal substrate protection against corrosion by the mechanism described is limited so far to the use of zinc and, to a lesser extent, magnesium [7].

Coating materials containing zinc powder particles at concentrations just near the CPVC provide substrate protection through electrochemical reaction in the cathodic region. A high pigment concentration is necessary to provide electric conductivity between adjacent particles as well as between the pigment particles and the substrate metal. The film so obtained is very porous, capable of absorbing the penetrating solutions [8].

Hence, the first phase of protection consists of the electrochemical reaction alone, as shown in Fig. 2. After some time, zinc in the coating material is coated with a layer of oxide (ZnO), whereby the conductivity of the zinc particles is reduced (Fig. 3a and b). The corrosion product prevents zinc corrosion and also hinders the

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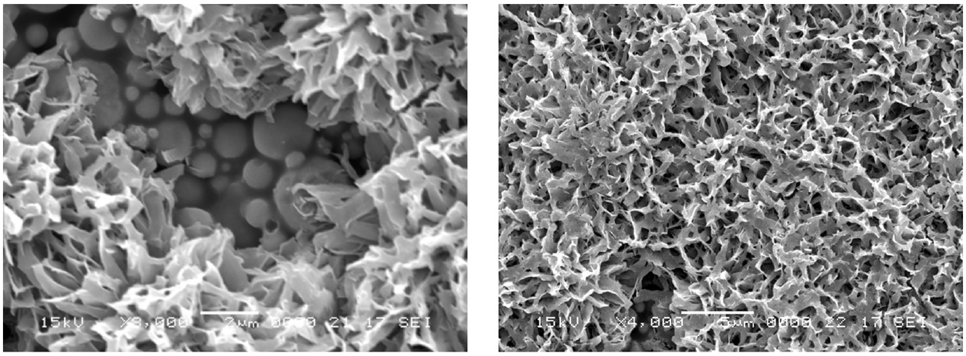

a) Magnification 8000× b) Magnification 4000×

**Fig. 1.** Corrosion changes on the surface of a coating material pigmented with zinc (spherical particles), caused by exposure to a humid/moist environment [1].

electrochemical role of zinc in the zinc-steel cells. The zinc oxide content of the film can be up to 20% without degrading its protection efficiency, owing to a certain conductivity of the zinc oxide [1,5].

The electrochemical-action of coatings containing zinc particles cannot be fully compared to the action of zinc metal layers formed on steel substrates by spraying molten zinc. In organic coatings obtained by applying the coating material to the substrate, where a highly crosslinked polymeric film is formed by crosslinking (curing) reactions, a binder which of necessity must coat the zinc particles is also present (Fig. 4). The resistivity of the coating is thereby increased to the point where its electrical conductivity decreases below the critical level beneath which the coating material does not provide electrochemical protection any longer [9]. Hence, the electric conductivity of the pigmented film is related to the zinc particle concentration (PVC) in the coating material binder. The highest electric conductivity is achieved at zinc particle concentrations of 92–95% (w/w), the binder content then being a mere 5–8%. Such low binder content, however, is insufficient for the coating material to attain the required physico-mechanical properties – adhesion, impact resistance and cupping resistance are reduced substantially [10].

Efforts to substitute zinc in coating materials with other pigments exist, mainly for financial as well as environmental reasons [11]. Research aimed at replacing zinc with more suitable materials focuses mainly on combinations of conducting polymers, inorganic pigments, fillers and zinc with different particle shapes [11,12]. Carbon and graphite-based pigments represent another solution [13]. Of particular interest are conducting polymers, whose applicability in coating materials for anticorrosion protection of metals has been studied extensively during recent years. Among conducting polymers that have attracted attention in this respect is polyaniline. The properties of pigments coated with polyaniline layers as potential anticorrosion pigments are being investigated [14].

If any inorganic supports preserving the properties of PANI (especially its conducting nature) and ultimately exhibiting anticorrosion properties are found, they might be promising materials for anticorrosion protection of metals. Carbon nanotubes are also interesting materials whose applicability to anticorrosion protection deserves investigation [14,15].

### 1.1. Conducting polymers

Polyacetylene (PA), polypyrrole (PPy), polythiophene (PTH), polyaniline (PANI), polyphenylene and poly(p-phenylene vinylene) (PPP) are among polymers with the capacity to conduct electric current. This conductivity is due to the system of alternating single and double bonds (conjugated system) in the polymers' molecular structure. In addition to such a system of conjugated bonds, the presence of movable charge carriers providing transport along the conjugate chain is a prerequisite for conductivity [16,17]. Such charge carriers are created by a process that is referred to, by analogy to classical semiconductors, as doping [18]. Polyaniline is one of these electrically conducting polymers; its macromolecule consists of constitutional aniline units. A single polyaniline chain can contain hundreds to thousands of such units, which constitute the polymeric material [19]. Polyaniline can be prepared in 5 basic forms differing in their degree of oxidation or protonation. Each species has its own characteristic chemical structure, stability, colour and electrical properties [20]. Polyaniline exists in its

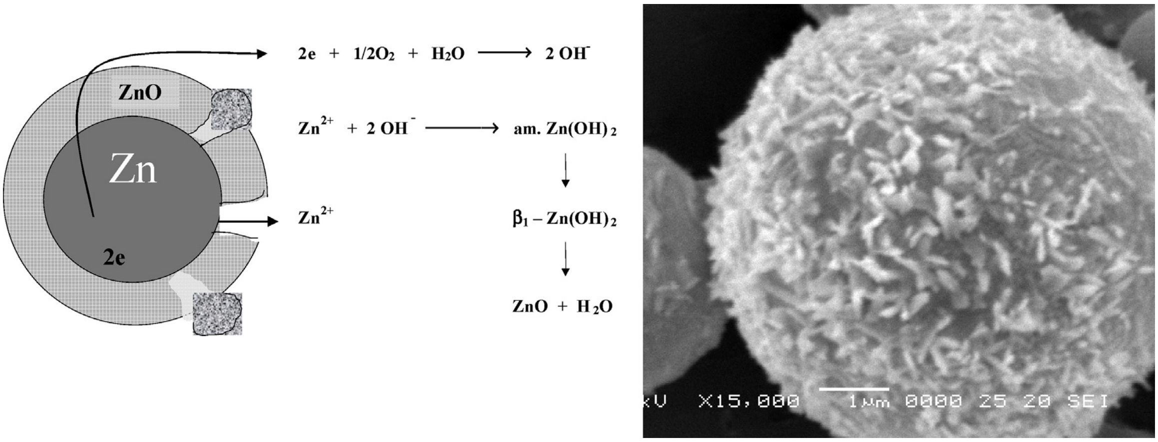

**Fig. 2.** Behaviour and properties of Zn-pigmented coatings under laboratory corrosion conditions: electrochemical phase of Zn action in a coating.