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Anticorrosion properties of polyaniline-coated pigments in organic coatings

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ABSTRACT

Four pigments of various morphology – specularite, α-Fe_2O_3; goethite, α-FeO(OH); talc, $(Mg_3(OH)_2$-(Si_4O_{10}); and graphite, C – without and with polyaniline phosphate coating, were tested for the anticorrosion performance in coatings produced by epoxy binders on iron plates. The corrosion tests were carried out in a condenser chamber with continuous water condensation or humidity with sulfur dioxide, and in a salt mist cabinet. Polyaniline coating of pigments in all cases improved the anticorrosion properties. Graphite coated with polyaniline performed the best among eight systems under investigation. The role of graphite and polyaniline conductivity in the electron transfers associated with corrosion of iron has been proposed.

1. Introduction

Conducting polymers have recently been studied as a new class of materials for the corrosion protection of metals [1–7]. These polymers are non-toxic and it is anticipated that they could replace harmful anticorrosion additives based on transition metal oxides [8,9]. In contrast to other macromolecular compounds used in the corrosion protection due to their barrier properties, conducting polymers have a porous structure and are highly permeable to liquids and gases. For that reason, they are used in the combination with barrier coatings, either as a primer [10,11], or as a component of the barrier layer [12,13]. The highest number of papers on the anticorrosion application of conducting polymers is associated with polyaniline (PANI) [4,8,9,11,14], due to its high environmental stability and the easy and economic preparation [15].

Polyaniline can serve in various forms differing in the degree of oxidation or protonation [16]. The most important form of PANI, protonated emeraldine [16] (Scheme 1), is green, electrically conducting. Its conductivity is close to that of common semiconductors [17], within the order of the units of $S\,cm^{-1}$. This value markedly exceeds the values exhibited by common polymers, $<10^{-12}\,S\,cm^{-1}$, yet it is lower than the values for typical metals, $>10^{4}\,S\,cm^{-1}$. Emeraldine salt is obtained as a direct product of the polymerization of aniline in a suitable acid solution [15,18]. Inorganic acids are most often used [19], the protonation with organic acids improves the processibility of PANI [20].

While the oxidized form of PANI, pernigraniline, and reduced form, leucoemeraldine, have a limited stability, the intermediate oxidation form, emeraldine, has a good thermal stability [21] compared with ordinary polymers, and excellent stability in the concentrated solutions of acids and alkalies [22,23]. The salt–base transition in emeraldine (Scheme 1) takes place at pH 4–6 and is fully reversible. Both the protonated and base emeraldine forms may be reduced to leucoemeraldine. The transition takes place at potential region 0–0.2 V *vs.* SCE [24]. These redox processes are responsible for the corrosion inhibition activity. It has to be stressed that the conductivity of conducting polymers less is important factor than their electrochemical participation in redox processes.

The mechanism of the corrosion protection by PANI, based on the electrochemical activity of PANI [25], is not completely understood. Polyaniline obviously passivates the metal surface [26,27] and/or reduces the cathodic reactions by transferring them from metal–electrolyte interface to electrolyte–polymer interface [28]. In accord with the mechanism of anodic passivation [29], emeraldine form of PANI oxidizes the surface of the metal to more stable oxidation products. At the same time emeraldine reduces to leucoemeraldine [30]. Leucoemeraldine is oxidized by the aerial oxygen back to emeraldine which is regenerated. It was experimentally shown that emeraldine is reduced to leucoemeraldine in air in contact with iron [31]. The electrochemical potential of the surface increases to positive values, *ca* 0.1–0.3 V [32]. Iron oxide is produced at the surface [32] as a film of a few nanometre thickness, composed most likely of Fe_3O_4 [33]. This results in ennoblement of the metal and in reduction of the rate of subsequent anodic reaction.

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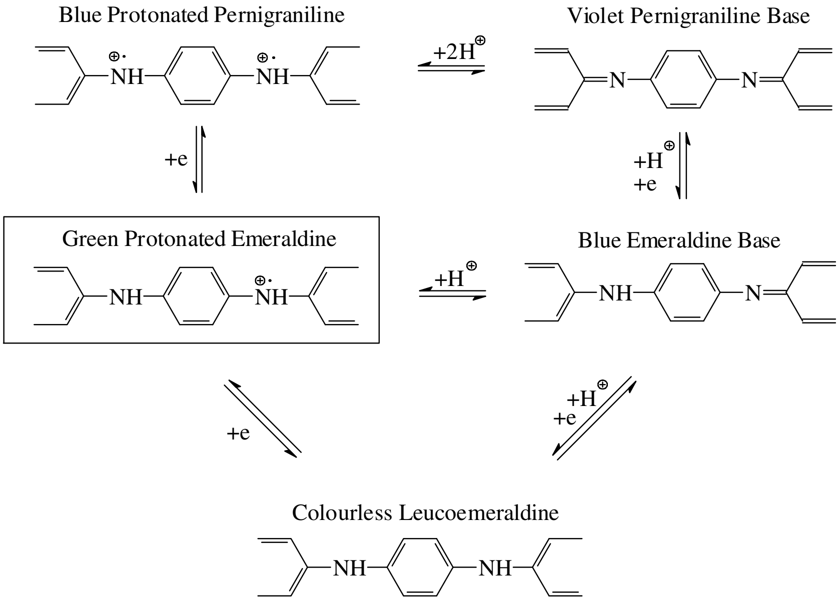

Scheme 1. Polyaniline forms (modified from Ref. [16]).

Experimental evidence confirming the participation of PANI in cathodic processes is demonstrated by its ability to reduce the oxygen in air [34]. It has been demonstrated that not only leucoemeraldine, but also emeraldine, reacts with oxygen. It is assumed that both mechanisms of corrosion protection can be operative simultaneously, and PANI, in various oxidation states, participates both in the cathodic and anodic processes [30,35]. In this way, emeraldine form seems to be the most effective in the design of corrosion protection.

The ability of simultaneous participation in various reduction and oxidation processes is obviously achieved by the redox heterogeneity of the polymer. It was reported that, at common conditions, PANI in emeraldine form is composed of local areas having the different oxidation degree, including pernigraniline, emeraldine, and leucoemeraldine [36] (Scheme 1). The concept of local heterogeneity introduces the dynamic structural character in polymer film and when exposed to external stimuli, the oxidation degree of local areas may change. The various degree of oxidation thus may coexist in PANI and participate in both the anodic passivation of metal and cathodic processes of its protection. Such mechanism is applicable especially to a non-conducting PANI base. In a protonated conducting form, the local leucoemeraldine and pernigraniline inhomogenities would efficiently be converted to emeraldine by simply exchanging electrons between such inhomogenities through the conducting PANI phase.

For an efficient corrosion protection, PANI has to be uniformly distributed in a close vicinity of protected metal. For anodic passivation, the electrical contact with metal is necessary. For that reason, the use of PANI as a primer corresponds the best to these concepts. Polyaniline, however, has a bad adhesion and, moreover, during the redox processes changes its density, and thus also its volume; the delamination of PANI-containing layers may be a serious consequent problem [24,37].

Because all redox processes involving PANI are based on a transfer of electrons, the concentration of PANI is likely to be also important. At sufficiently high volume fraction of PANI above the percolation limit ($\sim$16 vol% for spherical particles), infinite conducting pathways are produced in the system. Such system will behave in a different manner than at lower PANI loading, below the percolation limit, where the individual PANI particles are isolated, and their electrical communication is not possible.

The delamination problems may be prevented, if the PANI is introduced into the whole volume of the coating. As a rule, for the pronounced corrosion inhibition effect, low concentrations of PANI, not exceeding 10–15 vol%, are sufficient [38,39]. The dispersion of PANI is also an important factor to be considered. The uniform dispersion of PANI to small particles will increase the efficiency of corrosion inhibition. The use of colloidal dispersions of PANI [40] may be the feasible route. The macroscopic PANI particles and their high volume fraction, on the other hand, are likely to damage the mechanical properties of coating and increase the permeability to small molecules. Polyaniline has also been introduced into the paint formulations in a form of an organic dispersion [41].

In this study, PANI has been introduced into the protective coatings in a form of inorganic pigments surface-modified with a PANI overlayer. The coating of particles takes place *in situ* during the polymerization of aniline [42]. The deposition of PANI on suitable carrier particles can solve the problems caused by the changes in PANI density and/or volume during the conversion of individual forms. The amount of PANI can be therefore considerably reduced because PANI-coated objects manifest themselves in many respects as PANI particles. Four inorganic pigment currently used in the paint compositions have been used for this purpose. When non-isometric high-density carrier particles are used, it can be anticipated that they will sediment in the deposited paints to produce a barrier layer during drying. At the same time, the deposited PANI is brought in contact with the metal, thus fulfilling its role of a primer. The permeability of PANI to liquids, however, may have a negative effect on barrier properties. It should be noted that the hydrophobicity of PANI and, thus, permeability to water, can be controlled by a suitable protonation of PANI [43]. Pigments alone and after coating with PANI phosphate have been investigated with respect to corrosion protection and compared with the properties of neat PANI powder and with commercial corrosion protection filler.

1.1. Carrier pigments for polyaniline deposition

Pigments constituted by non-isometric particles of flaky, lamellar, or needle-like shape increase the resistance to permeability of organic coatings to water and corrosive gases. They improve mechanical properties of films, prevent the direct penetration of