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Anticorrosion efficiency of organic coatings depending on the pigment volume concentration of polyaniline phosphate

Andrea Kalendová[a,*], David Veselý[a], Irina Sapurina[b], Jaroslav Stejskal[c]

[a] University of Pardubice, Faculty of Chemical Technology, Department of Paints and Organic Coatings, 53210 Pardubice, Czech Republic
[b] Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia
[c] Institute of Macromolecular Chemistry, Academy of Sciences of Czech Republic, Prague, Czech Republic

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ABSTRACT

Polyaniline (PANI) was synthesized by reaction in an aqueous solution of ammonium peroxodisulfate and phosphoric acid. PANI was characterized by means of scanning electron microscopy and its physical–chemical properties were determined. Simultaneously with the synthesized PANI epoxy-ester coatings containing 3, 5, 10, 15, 20 and 24 vol.% of PANI as a corrosion inhibitor were formulated. The coatings were tested for their mechanical properties, film hardness and corrosion resistance. The testing of the anticorrosion efficiency of PANI as corrosion inhibitor was based on accelerated corrosion tests: in condensed water, NaCl mist, and condensing water and SO_2. The prepared PANI displayed inhibition effects in corrosion reactions progressing on a steel base under the organic coating. The synthesized PANI provides good anticorrosion efficiency in an epoxy-ester coating. The studied system does not contain any heavy metals harmful to the environment.

1. Introduction

The last three decades have seen a significant development of materials based on conducting polymers. These substances attract attention not only in the field of sciences but also in the area of practical applications [1]. Electrically conducting polymers can change their structure depending on the reaction of the surrounding environment. One of the conducting polymers is polyaniline. According to currently available studies, this substance displays propitious applications when used as a corrosion-inhibition pigment in organic binders of paints [2–5].

The electrical conductivity of polyaniline, which is comparable to that of common semi-conductors, was known as early as the 1960s. General interest in conducting polymers did not develop until the late 1970s when it was discovered that following the halogenation of *trans*-polyacetylene, the specific conductivity of this polymer increases to the conductivity level of inorganic semiconductors. Despite its high conductivity, the limited stability of polyacetylene directed attention at much more stable polymers, polyaniline (PANI) [6,7] and polypyrrole [8].

1.1. *Chemical structure and forms of polyaniline*

Polyaniline is a macromolecular substance composed of constitutional aniline units. A polyaniline chain can contain hundreds to thousands of these units, thus being a polymeric material (Scheme 1). Polyaniline is synthesized by the oxidative polymerization of aniline. Its emeraldine structure includes oxidized and reduced structural units in equal proportions, $y = 0.5$ [9,6,10].

Polyaniline can be found in five distinctive states mutually differentiated by the degree of oxidation or protonation, or both [6,7]. Every state has a characteristic chemical structure, stability, color and electrical properties. Possible transformations are shown in Scheme 2 [9].

The most common protonated emeraldine (emeraldine salt, Scheme 2) is characterized by a brilliant green hue from which its name was derived. The structure of emeraldine salt contains cation-radicals that establish its conductivity. The positive charge on the chain is balanced with an anion. The anion in the PANI structure is derived from an acid used during protonation. The most frequently used are inorganic acids [11], for instance, hydrochloric acid, sulfuric acid or phosphoric acid [12]. The acids used during polymerization can be replaced by organic acids [13]. The PANI prepared in this way is soluble in certain organic solvents.

When in an alkaline environment, emeraldine salt is transformed into the deprotonated form of emeraldine base (Scheme 2). This form is non-conducting and blue. The re-transformation of emeraldine base into emeraldine salt takes place around neutral pH,

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[*] Corresponding author.
E-mail address: andrea.kalendova@upce.cz (A. Kalendová).

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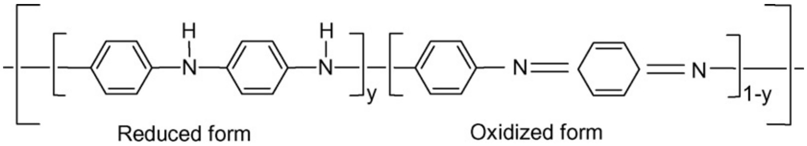


Scheme 1. Polyaniline bases: leucoemeraldine ($y = 0$), emeraldine ($y = 0.5$) and pernigraniline ($y = 1$).

i.e. in a slightly acidic environment. Reduction of emeraldine produces leucoemeraldine (Schemes 1 and 2, $y = 1$). Leucoemeraldine, all of whose units are reduced, is a colorless or yellowish electrically non-conducting substance [14]. Pernigraniline (Schemes 1 and 2, $y = 0$) can be prepared by the oxidation of emeraldine, if strong oxidising agents are employed, for instance, ammonium peroxodisulfate or hydrogen peroxide. If transformation takes place in an acidic environment, protonated pernigraniline is produced. Protonated pernigraniline (pernigraniline salt) exists most easily in a dication-diradical form. It is blue, yet its hue differs from that of emeraldine base. If emeraldine is transformed in a basic environment, the final product is pernigraniline base [15]. This product is non-conducting and purple.

1.2. Preparation and properties of polyaniline

The most frequently employed method of synthesizing electro-active polymers is, in addition to the electrochemical polymerization, chemical oxidative polymerization. The possibilities of oxidation polymerization are somewhat restricted by the solubility of the monomer in aqueous solutions of acids and by their ability to create salts in an acidic environment [16]. The oxidation of aniline is an exothermic reaction.

The efficient polymerization of aniline with oxidation agents is achieved only in an acidic environment in which aniline exists in the form of an anilinium cation. The aniline cation-radical is considered to be the first product of the oxidation reaction of aniline. A doping component used in PANI synthesis can be selected from a broad variety of various concentrations of inorganic and organic acids that predetermine the properties of polyaniline [17]. Depending on the acid used, the final protonated polyaniline is characterized by specific solubility, conductivity and stability. In the course of polymerization, polyaniline has the ability to create thin conducting films with good adhesion on various base materials [18,19]. Its high conductivity and chemical flexibility make polyaniline a conducting polymer suitable for applications in special paints [20].

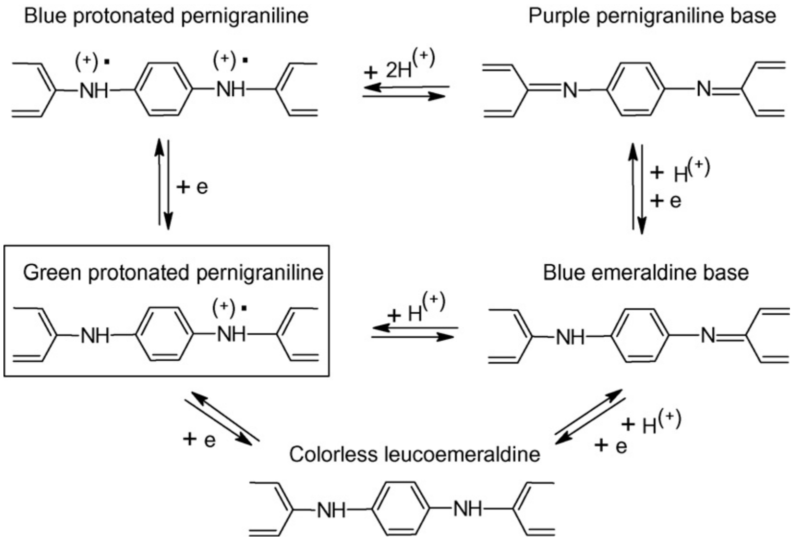
1.3. Tests of PANI properties

Thanks to its high electrical conductivity, PANI phosphate (hereinafter referred to as ‘polyaniline’ or ‘PANI’), a conducting polymer, appears to be a possible inhibitor of corrosion reactions. If its inhibition properties and efficiency were proven in a paint film, it would suggest its prospective applications in organic binders where it would function as an organic corrosion inhibitor or in the form of an anticorrosion pigment. Therefore, it is important to prove its corrosion-inhibition properties in organic coatings applied onto metal-based materials, and to identify the pigment volume concentration (PVC) at which pronounced inhibition of corrosion reactions takes place. Furthermore, it has to be found out how this substance affects the other qualities of paints, especially the adhesion-barrier ones. These are the objects of the present study.

2. Experimental

2.1. Synthesis of polyaniline

Polyaniline was prepared at laboratory temperature in an aqueous solution of 0.25 M ammonium peroxodisulfate (Lachema), an oxidizing agent, and 0.2 M aniline (Merck) in 1 M phosphoric acid [21]. A weighed amount of aniline was dissolved in dilute phosphoric acid while agitated continuously. Once perfectly dissolved, potassium peroxodisulfate solution in water was added. The mixture was stirred by an electric agitator for 60 min until precipitation of the product was complete. The individual stages of this process were accompanied by the color changes of the reaction compound. Polyaniline was created in the form of both a precipitate and a film that covered the walls of the reaction container. The precipitated



Scheme 2. Forms of polyaniline and their conversions (Stejskal et al. [9]).