



# Influence of polyaniline and cerium oxide nanoparticles on the corrosion protection properties of alkyd coating



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## ABSTRACT

A study of the anticorrosive properties of an alkyd coating loaded with polyaniline and cerium oxide (CeO<sub>2</sub>) nanoparticles is presented in this paper. Investigated by means of Electrochemical Impedance Spectroscopy and accelerated salt spray test, the blank alkyd coating has been loaded with PAni, ceria nanoparticles and the combination of both with 1.0 wt.% content. Through the monitoring of open circuit potential, an ennoblement effect was detected for the systems in the presence of a mild solution. Moreover, EIS evolution of the alkyd containing polyaniline revealed a stable performance of the system in the presence of sulphate solution, whereas for those containing ceria nanoparticles a considerable raise in the  $|Z|_{0.015\text{ Hz}}$ , from 10<sup>7</sup> to 10<sup>8</sup> Ω cm<sup>2</sup> in the course of 24 h of immersion, an increasing trend of the charge transfer resistance during the equivalent period of exposure was observed. Furthermore, the anticorrosive contribution given by the ceria nanoparticles is supported by the accelerated salt spray test which revealed lower delamination rates. In the case of the alkyd loaded with polyaniline and ceria nanoparticles simultaneously the evidences are less perceived by means of electrochemical analysis, however, from salt spray tests it can be seen that the influence of the mixture is promising at a certain extent.

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## 1. Introduction

Driven by regulations, scientists are encouraged to create and develop new coatings chemistries that, simultaneously, are able to protect metals and respect environmental aspects [1]. For instance, the traditional alkyd coatings containing hexavalent chromium pigments are well-known to provide efficient corrosion protection. However, these are considered to have hazardous consequences for the environment and human health [2]. The use of intrinsic conductive polymers, such as polyaniline, and rare earth compounds is among new strategies for replace the chromium (VI). They have been identified as promising inhibitors candidates, in addition are considered environmentally acceptable due to their non-toxic behavior and a little content concentration inside coating resin is necessary [3]. Moreover, considering the features of the alkyd coatings, such as good adhesion and low cost of application [4], the possibility to add PAni and rare earths into an alkyd coating would come as promising.

In the middle of 80s, the reports of DeBerry have propelled the use of Polyaniline (PAni) as a promising anticorrosive candidate for

steel protection [5]. At first, several researches have demonstrated the corrosion protection effectiveness of a uniform film obtained via electrodeposition of PAni onto steel [6,7]. Consequently, a number of mechanisms were suggested with the purpose of explaining the protection given by the PAni film. Amongst these, it is most believed that the electrodeposited PAni ennobles the surface of steel and promotes the formation of a thin but dense passive oxide layer on the surface [8]. On the other hand, once PAni is synthesized via the chemical oxidative polymerization, particles are obtained. When the particles are added into an organic coating, the distribution at the interface is considered a critical parameter in order to obtain satisfactory anticorrosive properties [9].

Pioneer use of coatings containing polyaniline particles is attributed to Wessling et al. [10,11]. According to the authors, the presence of polyaniline particles into paints has led to the formation of Fe<sub>2</sub>O<sub>3</sub> film above a very thin Fe<sub>3</sub>O<sub>4</sub> layer over the iron surface, as demonstrated through SEM and XPS, thus, an ennoblement of the metal surface is proposed.

Similar mechanisms have been proposed by Sathiyarayanan et al. [12,13]. The anticorrosive properties of steel coated with epoxy containing the doped PAni under saline and acidic media were investigated. In both studies it has been demonstrated that PAni is able to protect the surface of the metal by shifting the open circuit potential in the direction of more noble values.

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Adhikari et al. [14], prepared PANi particles via chemical oxidative polymerization in the presence of methane sulfonic acid (MeSA) before addition into poly (vinyl acetate) coating. It was found via open circuit potential (OCP) observations and EIS investigations that the presence of PANi-MeSA formed a protective oxide layer at the steel surface. Besides, supported by an increase in the charge transfer resistance ( $R_{ct}$ ) observation, the reduction reaction of the conductive polyaniline after exposure to oxygen, have started the formation of the passive layer.

Cerium oxide nanoparticles have been used in many industrial applications [15], such as catalysts [16,17], semiconductor polishing agents and full additives, and being studied for many other applications such as electrode [18], electrolytes [19], anti-oxidant [20], UV absorbers [21,22], as well as functional pigments [23]. Recently, there is an increased interest in potential application of cerium oxide in corrosion protection of metals [24,25]. Considering cerium oxide, apart from few works that have demonstrated the effectiveness of those, until now the corrosion inhibition mechanism has not been completely comprehended.

R. Sharmila et al. demonstrated that cerium oxide shows good performance as a corrosion inhibitor for steel in HCl and  $H_2SO_4$  solution mediums [26]. The evaluation of inhibition properties of cerium oxide nanoparticles submitted to a cerium nitrate treatment was studied by M.F. Montemor et al. [27].  $CeO_2$  nanoparticles and  $Ce^{3+}$  ions were added as filler on silane films on galvanized steel. It was evidenced that  $CeO_2$  nanoparticles promote the stabilization of a passive film on galvanized steel.

Fedel et al. [28] studied the potential effectiveness of a mixture of  $CeO_2$  and  $SiO_2$  nanoparticles in an urethane coating coating, top coated with a polyester/epoxy blend for the protection of galvanized steel. Superior salt spray chamber performance was observed for systems containing the  $SiO_2/CeO_2$  pigments, in which a good protection with a little delamination was observed.

Considering the above, this present work reports the anticorrosive potential behavior of mild steel substrates coated with an alkyd solventborne polymer containing both, ceria and polyaniline nanoparticles. The study has been entirely carried out using steel coated panels with a single layer based on alkyd chemistry holding near  $10\ \mu\text{m}$  of thicknesses. Electrochemical Impedance Spectroscopy has been chosen in order to get understanding into the fundamental mechanisms through which cerium oxides and polyaniline nanoparticles themselves as well as in combination promote corrosion protection of steel when inside the alkyd coating. Complementary characterization of the coated panels has been done by means of the accelerated salt spray chamber test.

## 2. Experimental

### 2.1. Materials

The studied samples were formulated with a solventborne alkyd polymeric binder. The alkyd polymeric resin was supplied by Arkema Coating Resins (Verneuil en Halatte, France). In order to verify the individual contribution of each of the components, the binders were loaded with polyaniline and cerium oxide nanoparticles separately as well as in combination. For a proper comparison, the panels were compared with steel panel coated with the blank alkyd binder.

Polyaniline nanoparticles were produced by Enthone Nano Science Center (Amersbach, Germany) via the chemical oxidative polymerization of aniline in the presence of sulfonic acid. The average particle size is around 50 nm and electrical conductivity in the order of  $10^{-5}$  S/cm obtained from a spincoated film on ITO/glass substrate.

**Table 1**

Coatings labels, contents of each component and dry film thickness.

	Label	Polyaniline	Cerium oxide	dft ( $\mu\text{m}$ )
Solventborne Alkyd	S.Blank	–	–	$13.0 \pm 0.4$
	S.PAni	1.0 wt.%	–	$11.5 \pm 0.4$
	S.Ceria	–	1.0 wt.%	$13.0 \pm 0.5$
	S.Mixture	1.0 wt.%	1.0 wt.%	$7.25 \pm 2.1$

Cerium oxide nanoparticles used in this study, are synthesized by the precipitation of cerium  $Ce(NO_3)_3 \cdot 6H_2O$  with  $NH_4OH$  in the presence of  $H_2O_2$  and acetic acid at elevated temperature. Due to the stabilization of nanoparticles with acetic acid, initially prepared particles have a positive potential of +20 mV and particle size of 20 nm. However, as synthesized cerium oxide particles are stable only in acidic medium pH less than 3. Thus, surface of nanoparticles was modified with polycarboxylate to further stabilize the particles at neutral pH. After surface modification, 10 wt.% stable solvent dispersion (butyl-acetate) of ceria was obtained and dispersion remained stable for more than a year. A dynamic light scattering study showed that average size of ceria particles in the dispersion is around 70 nm and zeta potential is  $-22$  mV. TEM study indicated that primary particle size of cerium oxides nanoparticles is around 15–20 nm [29].

After the dispersion of the particles, the coatings were applied onto cold rolled mild steel from Q-Panel, with a Bar Coater instrument, with a dry film thickness (dft) average of  $10\ \mu\text{m}$  measured with a PHYNIX instrument, model Surfix<sup>®</sup> FN. With the purpose to obtain the optimal film formation, panels were kept a drying period of 3 weeks at  $23\ ^\circ\text{C}$  – 50% RH plus another week inside a desiccator with dry atmosphere before the beginning of the tests. Table 1 summarizes the main features of the studied coatings systems. One can notice from Table 1 the lower thickness measured to the S.Mixture system. Even though the deposition process were strictly the same for these panels, authors believed that the barrier properties are to be affected because of the lower thickness, however, the active inhibition effect of ceria and polyaniline nanoparticles at the metal/polymer interface are not.

### 2.2. Methods

The protective properties of the coatings were studied by Electrochemical Impedance Spectroscopy (EIS) measurements obtained in aqueous 0.3%  $Na_2SO_4$  solutions which simulate a mild corrosive environment. The choice of a mild electrolyte is mainly justified by the relatively low thicknesses of the coatings, moreover, the authors were expected to observe any inhibition effect of the nanoparticles taking part at the initial period of exposure. The EIS measurements were obtained on intact coatings at the open circuit potential (OCP) using a potentiostat and frequency response analyzer (FRA) equipment (AutoLab model: PG STAT 302N), signal amplitude 20 mV, frequency range  $10^5$ – $10^{-2}$  Hz and testing area about  $10\ \text{cm}^2$ . A classical three electrodes arrangement was used. An Ag/AgCl (+0.205 V vs SHE) electrode and a platinum wire were used as reference and counter electrode respectively. Before the acquisition of any impedance spectra the OCP (with respect to the Ag/AgCl reference electrode) of the coated steel has been measured. All the measurements were duplicated in order to confirm the results and the presented results are considered comparable. Quantitative analysis, i.e., spectra fitting using an equivalent electrical circuit was made using the software ZSimpWin 3.22.

The accelerated salt spray tests have been performed following the standard ISO 9227 in both situations: intact coatings and with the presence of a 2 cm long scratch.

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