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ANTI-CORROSION COATINGS BASED ON MODIFIED EPOXY COMPOSITIONS

<https://doi.org/10.23939/ctas2023.01.144>

The influence of surface-modified titanium dioxide on the electrochemical features of epoxy compositions was researched. The raise of epoxy primer protective properties by the presence of surface-modified fillers in its composition was determined. It is shown that the mechanism of the modified filler protective effect in epoxy coating applied on the steel is similar to the effect of solid zinc phosphate which effectiveness corresponds to the level of the known inhibitory pigment.

Key words: epoxy primer; surface-modified fillers; inhibitory pigments; corrosion resistance.

Introduction

The development of new organic coatings containing inhibitory components and capable to work in through-through damage places of the main coating and additionally protect the metal from the corrosion is extremely relevant. Currently, zinc phosphates inhibitory pigments are widely applied for this purpose. Mentioned pigments slowly release zinc ions and phosphate ions which are effective in inhibiting electrochemical corrosion into the corrosion medium contacting with the metal surface in the places of through-defects of the paint coating [1, 2]. However, zinc phosphate is relatively expensive and therefore the search for more affordable inhibitory pigments is topical.

Modern anti-corrosion pigments are finely dispersed inorganic particles of spherical or needle shape of 1 to 10 μm diameter [3]. However, only the upper layers of pigments work effectively. Unused inhibitors remain in the mass of the paint coating and there are later removed together with it during periodic repairs of anti-corrosion protection. Thus, an inefficient application of expensive inhibitory components of paint and varnish materials is taking place.

Applying of inhibitory pigments based on inert fillers and oxides surface-modified with phosphate compounds, in particular, titanium dioxide in paint coatings might be pretty perspective. The last one while having inhibitory properties should give the organic coating a white color. However, the phosphatized titanium dioxide application is impos-

sible without checking of its anti-corrosion efficiency and determining the features of the protective action mechanism in the paint coating. Therefore, the purpose of this work was corrosion-electrochemical studies of priming epoxy coatings filled with surface-modified titanium dioxide.

A number of scientific teams in Ukraine and abroad are working on the problem of degradation of polymer coatings. It should be noted the works of the corrosion center of the University of Manchester (England), University of Stuttgart (Germany), Lehigh University (USA), Delft Technical University (Holland), Kharkiv Technical University and many others. Modern methods of physical and electrochemical research, methods of non-destructive testing and accelerated corrosion tests are used to solve this problem. However, in the vast majority of cases, researchers study the protective properties of multilayer coatings in various environments, without highlighting certain aspects of their degradation (for example, loss of barrier properties, destruction of adhesive bonds at the metal-polymer interface, localization of electrode processes under the coating layer). At the same time, the creation of new coatings with increased protective properties and high resistance to degradation requires the use of new scientific approaches, including taking into account the influence of the mechanical factor on the properties of polymer coatings.

The purpose of the work is to study the production and properties of anti-corrosion coatings based on modified epoxy compositions.

Materials and research methods

The most effective method of accelerated anti-corrosion research of organic coatings is the method of electrochemical impedance spectroscopy [4]. Epoxy coatings containing inhibited fillers in the first layer and with through defects were studied applying mentioned method. The FRA frequency response analyzer connected to IPC – Pro potentiostat and a calomel comparison electrode as well as an additional platinum one has been used. Measurements were carried out at a corrosion potential in the frequency range from 10 kHz to 5 mHz with a signal amplitude of 20 mV. Coatings with defects were studied, since the protective effect of inhibitory pigments or fillers should be appeared at the moment of medium penetration through the coating to the metal.

On the defatted low-carbon St3 steel a two-layer epoxy coating with a general thickness of 100 μm was applied. The first primer layer of mentioned coating contained 6 vol. % of rutile type titanium dioxide (composition 1), 6 vol. % of zinc phosphate modified with 1 wt. % of molybdate (composition 2) and 6 vol. % of titanium dioxide superficially modified with zinc alkyl phosphate (composition 3). The latter is produced by the Sachtleben company Chemistry GmbH (Germany) under the “Hombicor” trademark. The organic basis of the coating consisted of ED-20 epoxy resin, plasticizer – carboxyl-containing rubber, polyamide hardener and a mixture of organic solvents. A through defect of 1 cm long and 100 μm wide was made in the coatings with a scalpel. A synthetic rain solution was used as the working medium which simulates atmospheric precipitation in industrial areas of European countries (Table 1).

Table 1

Composition of synthetic rain solution

Name of the components	Concentration, mg/l
	Single solution (pH 4.4) *
Sulfate acid	3.185
Ammonium sulfate	4.620
Sodium sulfate	3.195
Nitric acid	1.575
Sodium nitrate	2.125
Sodium chloride	8.484

* pH was adjusted to 4.4 by adding sodium carbonate.

Results and discussion

During the exposure in the environment of acid rain, it can be seen that the impedance spectra of samples containing epoxy polyamide coatings consist of two compressed semi circles overlapping each other (Fig. 1). As the exposure time increases, the impedance spectra change their shape and after seven days, mostly transform into one strongly deformed and elongated semicircle. According to the conclusions of the authors studying paint coatings with defects [5, 6], the first (high-frequency) semicircle can mainly be attributed to the dielectric properties of the polymer film. The second one – to the properties of the electric double layer on the metal surface in places of through defects. The shape of the latter is affected by diffusion limitations in the supply of oxygen for the cathodic reaction which are caused by the formation of a layer of corrosion products at the cut site. However, a clearly defined diffusion branch of the impedance spectrum in the form of a straight line at an angle of 45° to the abscissa axis at low frequencies is not observed here.

The equivalent circle R_s (C_{coat} (R_{coat} (CPE_{dl} (R_{ct}))) and the ZView2 program [7] were applied to approximate the experimental data and calculate the electrochemical parameters of the coated samples which were kept in an aggressive environment. In this case, R_s is the resistance of the solution; C_{coat} – electrical capacity of epoxy coating; R_{coat} is the resistance of the electrolyte in the pores of the coating; the constant phase element CPE_{dl} refers to the frequency-dependent electrochemical and diffusion processes occurring in the double layer on the metal and R_{ct} characterizes the resistance of the metal charge transfer. Kinetic dependences of the calculated parameters R_{ct} , T (conductivity of the element of the constant phase CPE_{dl}), P (the element degree index of the constant phase CPE_{dl}), C_{coat} and R_{coat} are shown in Fig. 4.

The application of mentioned equivalent circle (Fig. 2) gives a good coordination with the experimental data. The divergence between the experimental impedance spectrum and the theoretical one does not exceed 6 %.

Coatings containing phosphate pigment and surface-modified talc possess the highest resistance to charge transfer in described corrosive environment (Fig. 3).

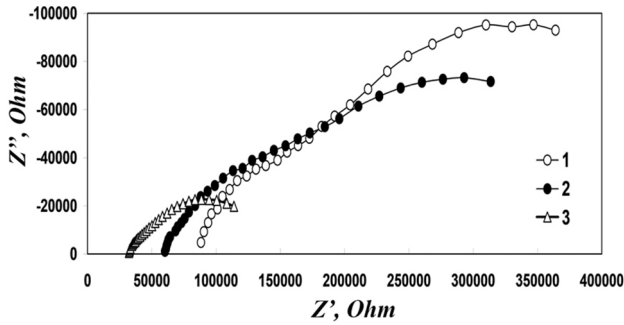


Fig. 1. The shape of the impedance spectra of low-carbon steel with inhibited epoxy coatings after two days of exposure in an acid rain solution (1, 2, 3 – composition number)

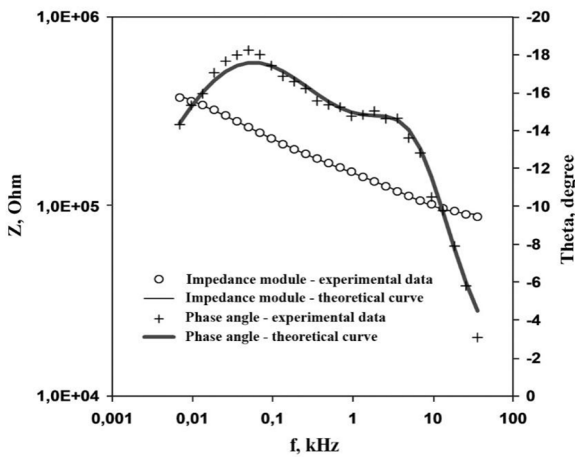


Fig. 2. The results of theoretical approximation of impedance spectrum of the sample with a defective epoxy coating (composition 3) after two days of exposure in the environment

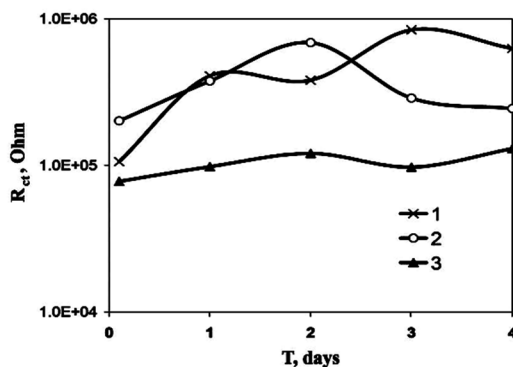


Fig. 3. Kinetic dependences of charge transfer resistance of low-carbon steel samples with epoxy coatings in acid rain environment (1, 2, 3 – composition number)

The uninhibited coating resistance during the tests corresponds to the level of $9.0 \cdot 10^6 - 1.1 \cdot 10^6$ Ohm, while for the inhibited coatings (compositions 2 and 3) its values are 5 to 10 times higher. The charge transfer

resistance of the coating with the surface-modified inert filler continuously increases during the tests, while in the presence of phosphate pigment it passes through a maximum after two days of exposure. The resistance growth in time for the coating containing a surface-modified filler occurs due to the formation of a complex blend of corrosion products and phosphate compounds on the metal under the coating at the point of the through defect. By the visual observations was established that the area of distribution of steel corrosion products under the paint layer in the place of the cut is much smaller than in other coatings.

The component T of the element of the CPE_{dl} constant phase during the testing within 4 days is the lowest in coating 3 containing surface-modified talc (Fig. 4). The appropriate T value is within $7.0 \cdot 10^6 \dots 9.0 \cdot 10^6$ 1/Ohm. The T parameter in the coating with zinc phosphate is also low and grows monotonically reaching a value of $1.5 \cdot 10^5$ 1/Ohm after 4 days. Described behavior may indicate some corrosion of the steel substrate and slight delamination of the coating. As a result of coating peeling, the contact area between electrolyte and metal enlarges as well as the T index characterizing in some way the capacity of the double layer, increases. The T value for the uninhibited control epoxy coating first slowly decreases and then, after 2 days of exposure, it increases more sharply. Perhaps, in that case the corrosion process is initially localized on the exposed metal at the location of the coating defect and the corrosion products cover the defect and exhibit certain barrier properties. Thereafter, corrosion spreads under the coating film farther from the defect and the T characteristic increases. Peeling of the coating can be caused by a cathodic reaction on the metal. The T_0 parameter is directly proportional to the surface area of the metal contacting with the environment and actively corrodes. Grounded on the data of electrochemical impedance spectroscopy, it can be concluded that application of talc modified with zinc alkyl phosphate significantly improves the protective properties of the epoxy coating on low-carbon steel in an atmospheric environment.

The n coefficient of the constant phase element CPE_{dl} characterizes the dispersion of the electrode capacity in the electrolytic solution. This frequency-dependent dispersion can be caused by surface roughness, local deviations in the thickness of the coating or high resistance of the surface layer [8, 9]. Kerner and Paikossi in their work [10] refer the capacitance dispersion on a polycrystalline solid to surface heterogeneity on an atomic scale. The kinetic dependences of n for the studied coatings indicate a

significant influence of diffusion limitations on the corrosion processes. For an uninhibited coating, mentioned effect is evident after two days of exposure.

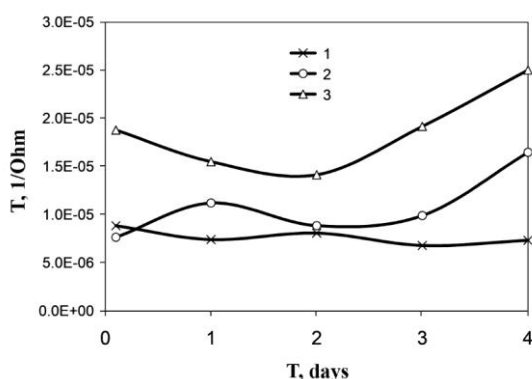


Fig. 4. Kinetic dependences of T conductivity of constant phase element for low-carbon steel with epoxy coatings in the environment of acid rain (1, 2, 3 – composition number)

Conclusions

Epoxy coatings containing inhibited fillers in the first layer and with through defects were studied. It was found that coatings containing phosphate pigment and surface-modified talc possess the highest resistance to charge transfer in described corrosive environment. By the visual observations was established that the area of distribution of steel corrosion products under the paint layer in the place of the cut is much smaller than in other coatings.

Conducted on the carried out research, it can be concluded that the mechanism of the protective effect of inert surface-modified titanium dioxide as a filler for epoxy polymer compositions is similar to that observed in molybdate-modified zinc. Such a filler better inhibits subfilm corrosion of low-carbon steel in mentioned above environment than the phosphate pigment.

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АНТИКОРОЗИЙНІ ПОКРИТТЯ НА ОСНОВІ МОДИФІКОВАНИХ ЕПОКСИДНИХ КОМПОЗИЦІЙ

Досліджено вплив поверхнево модифікованого діоксиду титану на електрохімічні характеристики епоксидних композицій. Встановлено підвищення захисних властивостей епоксидної ґрунтовки за присутності у її складі поверхнево модифікованих наповнювачів. Показано, що механізм захисної дії модифікованого наповнювача у епоксидному покритті на сталі подібний до впливу суцільного фосфату цинку, а його ефективність знаходиться на рівні відомого інгібувального пігменту.

Ключові слова: епоксидна ґрунтовка; поверхнево модифікований наповнювач; інгібувальні пігменти; корозійна стійкість.

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