Synthesis and application of manganese dioxide nanoparticles as part of anti-corrosion coatings

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Abstract. The paper presents a study of synthesized manganese dioxide nanoparticles effect on the properties of transparent coatings to protect the rolled metal from corrosion. Capacitive-ohmic measurements of the electrochemical cell formed on the studied coatings demonstrate corrosion processes inhibition under the coating with a nanoparticle content of 0.025\% and higher.

1. Introduction

Issues related to the production of nanoparticles (NPs) dispersions and composite nanoparticles based on various chemical compounds and substances with given sizes, polydispersity, shape, surface and structure characteristics have been one of the most important areas of physical chemistry in recent decades. However, the correct usage of nanostructures in specific applications is an important aspect. One of the ways to develop research in this area is the design and creation of the so-called organo-inorganic nanocomposites that attract increasing attention due to the fact that they demonstrate special thermal, mechanical, electrical, optical and optoelectronic properties [1–11].

As far as paint and varnish industry is concerned the core idea of nano-objects application is that they should be used not as ordinary fillers in paints and varnishes formulations, but as functional additives that give noticeable improvement to the basic characteristics of coatings [12, 13].

One of the key tasks in paint and varnish technology is metals protection from corrosion. Given a highly developed characteristic of nanoparticles surface, the paintwork components used for corrosion protection endowment can achieve a significantly greater anticorrosive effect with smaller amounts of functional substance than when using micro size components.

The studies presented in this article are aimed at demonstrating the possibility of using manganese dioxide nanoparticles synthesized as stable colored dispersions in organic solvent in transparent coatings with an anticorrosive effect.

2. Methods

The nanoparticles synthesis was carried out according to the method developed by the authors. It calls for the usage of available components and the possibility of adjusting the dispersion medium composition for the specific film-forming base. The obtained sol of MnO\textsubscript{2} nanoparticles was characterized by the methods of dynamic light scattering (DLS), optical and electrophoretic
spectroscopy. Measurements by DLS and electrophoretic spectroscopy methods were carried out on ZetaPALS and 90 Plus/BI-MAS instruments manufactured by Brookhaven.

The AS-548 varnish analogue was used as a film-forming base. It is a mixture of solutions of acrylic copolymer 5B with epoxy resin E-40 with addition of resylated glyphthalic resin № 90. The nanoparticle and the binder solution were mixed using a laboratory magnetic stirrer.

In order to study the nanoadditive effect on the structured coatings properties, their physicomechanical and protective properties were determined. Coatings were applied with the help of automatic applicator model 1137 manufactured by Sheen Instruments in 1 layer, onto previously cleaned by P100 sandpaper and fat-free steel plates 150×70×1 mm in size. The coating was formed in a drying chamber for 15 min at 170 °C. The coating thickness determined with the help of a TT210 thickness indicator, was 15± 2 μm.

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Impact strength was determined according to the national standard GOST 4765-73 on a U-1 device, adhesion was evaluated by the method of grating notches according to GOST 31149-2014-1a, relative hardness was determined according to GOST 5233-89 (ISO 1522-73). Barrier properties were evaluated by capacitive-ohmic method in electrochemical cell “painted metal-electrolyte” under static exposure to a 3% sodium chloride solution, according to the procedure described in [14, 15] using an RCL Fluke PM 6303A automatic immittance meter.

Simultaneously, the coatings’ resistance was determined under constant exposure to condensing moisture according to ISO 6270-2 in an artificial climate chamber CH-300 manufactured by Dycometal at a temperature of 40 °C. To determine the anticorrosive effect, we evaluated the behavior of the corrosion potential in the “painted metal-electrolyte” electrochemical cell under the static action of a 3% sodium chloride solution.

3. Results and Discussion
Manganese dioxide nanoparticles were obtained by redox precipitation in a solution of a stabilizing substance in an aqueous-organic medium. During the synthesis, a color change of the reaction mixture was observed, which was recorded by the extinction spectra using a spectrophotometer. Together with optical spectroscopy in the course of nanoparticles synthesis the dispersed characteristics of the reaction mixture were recorded by dynamic light scattering. The characteristic spectra at different time intervals and the size distribution diagram are shown in figures 1 and 2 respectively.

![Figure 1. Absorption spectra of the reaction mixture at various time intervals for the synthesis of nanoparticles: 1 – 0 min, 2 – 5 min, 3 – 10 min, 4 – 15 min, 5 – 30 min.](image)
Figure 2. Histogram of the of MnO₂ particles size distribution.

It can be seen from figure 1 that in the course of reaction the extinction peaks disappear in the wavelength range of 500–600 nm, characteristic of the soluble manganese compound. The reaction completion was monitored by the absence of changes in the absorption spectra upon subsequent addition of a reducing agent, and the solution color change from violet to tan was observed.

Analysis of the histogram of the particle size distribution shown in figure 2 showed that dispersion contains two fractions of particles with sizes of 12.75–18.08 nm, the content of which is 97.08% vol., and particles with sizes 73.15–87.11 nm, the content of which is 2.92% vol. The average particle size of the obtained manganese dioxide particles, determined with the help of Brookhaven ZetaPALS nanoparticle analyzer, was 15.5 nm.

The obtained nanoparticles were included in the composition of coatings based on a mixed film former. The results of determining the physicomechanical properties of nanostructured coatings with different contents of the dispersed phase are shown in table 1.

**Table 1.** Physico-mechanical properties of coatings with different contents of nano-additives.

| Characteristics            | 0   | 0.025 | 0.05  | 0.075 | 0.1  |
|----------------------------|-----|-------|-------|-------|------|
| Relative hardness, conv. units | 0.77 | 0.79  | 0.86  | 0.87  | 0.7  |
| Impact strength, cm        |     |       | 50    |       |      |
| Adhesion score             |     |       | 0     |       |      |

Analysis of the data from table 1 demonstrates high impact strength and adhesion of coatings, and the hardness of the coatings is extremely dependent with a maximum of 0.87 conventional units with a nano-particles content of 0.075%.
Protective coatings of metal substrates that are in contact with corrosive environments during operation must have high barrier properties and the ability to inhibit corrosion processes that can occur on the protected metal surface. The inhibitory ability of manganese-containing pigments has been confirmed by a number of works [16–18]. The change in the barrier properties of coatings was recorded by the kinetics of the electric capacitance (figure 3), determined by the capacitance-ohmic method in the electrochemical cell, and by the appearance of the painted plates (figure 4), tested in a humidity chamber for 120 h.

As a rule, after pouring a 3% solution of sodium chloride into electrochemical cells, an increase in electric capacity occurs within 24 hours due to the swelling of the coating under the action of electrolyte solution, which is obvious for a sample that does not contain NPs. Further kinetics of the electrical capacitance of the coating that does not contain NPs is extremely unstable, and high values of this indicator stand for the possible formation of a microdefect in which direct contact of electrolyte solution with steel substrate takes place. The presence of above mentioned contact should certainly provoke an electric capacitance increase by 1–2 orders of magnitude, however, its decrease is observed due to the filling of the formed defects with corrosion products, leading to a decrease in the diffusion of corrosive substances to the substrate.

![Figure 3](image.png)

**Figure 3.** Kinetic dependences of the electric capacitance in the system painted metal – electrolyte with different contents of nanoparticles.

When analysing the kinetic dependences of coatings containing nanoparticles in the range of 0.025–0.075%, a significant improvement in the insulating ability can be noted. That happens supposedly due to the formation of a more perfect structure and increased adhesion. With an increase in NPs content up to 0.1% of the mass, there is an increase in electric capacity and consequently a decrease in barrier properties. As was said above this fact may be related to the degradation of polymer matrix supramolecular structure due to the excess of some critical concentration, because spherical NPs with particle size of 15.5 nm have specific surface area more than 75 m²/g. Nevertheless, by the end of the test, the electric capacitance value for this sample is stabilized and becomes close to coatings with a lower content of NPs.

Analysis of the samples physical configuration after they have been tested in humidity chamber for 120 hours shows the appearance of proportionate and pinprick-like corrosion lesions on the sample with a coating containing no NPs. Notably, a sample with a coating containing 0.025% of the mass. particles has passed the test successfully.
Figure 4. The physical configuration of coatings with different nanoparticle contents before (a), (b), (c), (d), (e) and after (f), (g), (h), (i), (j) tests in humidity chamber at the temperature of 40 °C for 120 hours.

With further increase of nano-additive concentration in the coating, a strong decrease in resistance to high humidity is not observed, however, after testing, traces of pitting corrosion appear on these samples.

The direct ability of a painted metal to resist corrosion can be determined by measuring the corrosion potential on exposure to electrolyte solution. This indicator monitoring was carried out in electrochemical cell for 500 hours (figure 5) according to the procedure described in [14, 15].

Analysis of the kinetic curves shown in figure 5 makes it possible to conclude that nanostructured coatings in all the studied concentrations of nano-additive contribute to the inhibition of corrosion processes, transferring the metal surface under the coating to passive state.

In this case, the sample covered with the coating containing no nanoparticles shows a downward curve of corrosion potential in the range of $-136 \text{–} (-437) \text{ mV}$ kinetic dependence, thereby indicating active oxidation of iron.
4. Conclusions

In the course of this work, we synthesized MnO$_2$ NPs in organic solvent medium suitable to be further included in the of organic-diluted coatings composition. Barrier and protective characteristics of polymer composite coatings containing synthesized manganese dioxide nanoparticles were studied. The possibility of the coatings protective properties increase by introducing into their composition manganese dioxide nanoparticles in an amount of 0.025–0.075% mass was revealed.

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