PIOTR WARSZYŃSKI[1]
ORCID: 0000-0001-5449-9060

KRZYSZTOF SZCZEPANOWICZ[1]
ORCID: 0000-0002-9927-5869

GRZEGORZ MORDARSKI[1]
ORCID: 0000-0002-6832-2685

MARTA SZCZĘCH[1]
ORCID: 0000-0003-3013-6585

PAWEŁ NOWAK[2]
ORCID: 0000-0003-2068-7068

MAGDALENA LIPKA[2]

DARIA NOWAK[2,*]
ORCID: 0000-0003-0725-767X

TOMASZ SAŁEK[2]

RAFAŁ STAŃCZYK[2]

[1] Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Cracow, Poland

[2] ABC Colorex sp. z o.o., Cracow, Poland

[*] Corresponding author, e-mail: d.nowak@colorex.pl

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The influence of surface treatment with triethoxymethylsilane and triethoxyethylsilane sols on the permeability of powder coatings

Wpływ obróbki powierzchniowej zolami trietoksymetylosilanu i trietoksyetylosilanu na przepuszczalność pokryć farbami proszkowymi

The objective of the research described in the present paper is the powder coatings prepared with the use of the low-cost polyester resins and their possible application on aluminum elements for the service in the harsh environment: marine and offshore atmosphere, swimming pools where chlorine is used for disinfection, chemical industry. Pores, cracks and pinholes in the final powder coating are the weak points of an undamaged coating, the points where the process of corrosion could begin. Clogging them should decrease the probability of blistering due to hydrogen evolution caused by the contact of the metal surface with the aggressive media. With the application of the electrochemical impedance spectroscopy authors showed that treatment of the surface of a coating with the sol of either triethoxymethylsilane or triethoxyethylsilane causes the decrease in the water uptake in the first step of water sorption by the coating, which was ascribed to the clogging of the pores by the sol particles.

<u>Keywords</u>: powder coatings, powder painting, triethoxymethylsilane, triethoxyethylsilane

Przedmiotem badań opisanych w artykule są pokrycia organiczne farbami proszkowymi otrzymywane z tanich polimerów poliestrowych oraz możliwości ich użycia do ochrony antykorozyjnej wyrobów aluminiowych przeznaczonych do pracy w agresywnym środowisku: w transporcie morskim, na terenach nadmorskich, w basenach, w których wciąż używa się chloru do dezynfekcji, czy w przemyśle chemicznym. Pory, pęknięcia i dziury w końcowej powłoce proszkowej – to słabe punkty nieuszkodzonej powłoki, w których może rozpocząć się proces korozji. Zamknięcie ich powinno zmniejszyć prawdopodobieństwo powstawania pęcherzy w wyniku wydzielenia się wodoru wskutek kontaktu powierzchni metalu z agresywnymi czynnikami. Za pomocą elektrochemicznej spektroskopii impedancyjnej wykazano, że obróbka powierzchniowa pokrycia proszkowego zolem trietoksymetylosilanu lub trietoksyetylosilanu powoduje obniżenie zdolności pochłaniania wody w pierwszym etapie sorpcji wody przez powłokę na skutek wypełnienia porów i pęknięć w pokryciu cząsteczkami zolu.

<u>Słowa kluczowe</u>: powłoka proszkowa, malowanie proszkowe, trietoksymetylosilan, trietoksyetylosilan

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1. Introduction

For a long time corrosion of metals has been becoming more and more serious problem all over the world [1, 2]. That problem is especially important in the marine and offshore environments, where the metal objects meet the harsh atmosphere. Covering with the organic coatings is the most widely applied technology of corrosion prevention. However the traditional coatings contain relatively large amounts of volatile organic compounds (VOC) and their application creates thread for the people and the environment. In order to comply with VOCs reducing policy of European Union, the coating industry has designed different types of products such as waterborne coatings, high-solid coatings and powder coatings [3]. These types of formulation have been largely developed; however, the market for low VOCs coatings is still growing. It is projected to grow by roughly 130% in five years in terms of United States Dollar (USD) [4]. However, due to the complexity of the system: coating–substrate and the big number of factors affecting the performance and service life of anticorrosive coatings the understanding of the anticorrosive coatings degradation and long-term protection of metals from aggressive environments is still an up-to-date subject [3, 5].

The objectives of the research described in the present paper is the powder coatings prepared with the use of the low-cost polyester resins and their possible application on aluminum elements for the service in the harsh environment: marine and offshore atmosphere, swimming pools where chlorine is used for disinfection, chemical industry. The technology of powder coatings has been developed for a long time since the publication of the patent authored by Gustin and Wainio [6], but there is still the place to make the improvements.

Pores, cracks and pinholes in final powder coating are the weak points of an undamaged coating, the points where the process of corrosion could begin. They are the paths for water, oxygen, Cl^- ions and other corrosive species to reach the surface of the coated metal. Therefore, clogging them should decrease the probability of blistering due to hydrogen evolution caused by the contact of the metal surface with the aggressive media. We proposed to use, as the clogging elements, the ormosil nanoparticles, formed by the hydrolysis of either triethoxymethylsilane (TEMS) or triethoxyethylsilane (TEES) in a sol-gel process. The above mentioned compound hydrolyze at the presence of water, giving finally alcohol and alkylsilicates:

$$\begin{aligned} R–Si(–OR)_3 + H_2O &\rightarrow R–Si(–OR)_2(–OH), \\ + H_2O &\rightarrow R–Si(–OR)(–OH)_2, \\ + H_2O &\rightarrow R–Si(–OH)_3 + 3ROH. \end{aligned}$$

Hydrolysis is catalyzed both by H^+ and by OH^- ions and by many other species, also by the surface of a solid body (for example glass), however in contact with very pure water or the surface of PP containers alkoxysilanes are stable [7, 8]. Products of hydrolysis may polymerize, either with the liberation of the molecule of water (for example):

$$\begin{gathered} R–Si(–OR)_2(–OH) + R–Si(–OR)(–OH)_2 \rightarrow \\ \rightarrow (RO–)(HO–)R–Si–O–Si–R(–OH)(–OR) + H_2O, \end{gathered}$$

or with the liberation of the molecule of alcohol (for example):

$$\begin{gathered} R–Si(–OR)_2(–OH) + R–Si(–OR)(–OH)_2 \rightarrow \\ \rightarrow (RO–)(HO–)R–Si–O–Si–R(–OH)(–OR) + R–OH. \end{gathered}$$

In the above given reactions R means an alkyl. When polymerization proceeds, linear, planar and spatial oligomeric structures are formed [9, 10]. Finally transparent hard substance called organic glass is obtained, which found multiple applications. Oligomeric particles, after entering the pores may grow further there, clogging the pores completely. Hydrolyzed alkoxysilanes may also form the bonds with the surface of solids, covering the surface with the "carpet" of adsorbed silane species, providing that the surface exposes –OH groups [7, 8].

We assumed that the presence of pores, cracks etc. in the coating would cause fast uptake of water at the beginning of contact of the coating with the aqueous solution, due to the filling of the pores with the solution, followed by slower increase of the water concentration in the coating due to diffusion of water through the polymer. Such phenomenon was observed by Krzak et al. [11] and interpreted in terms of accelerated uptake of water by the polymer due to the presence of pores in the coating. To control if the expected process of clogging pores really occurs we needed a method which could estimate the concentration of water in the coating in relatively short time. The method of choice is the electrochemical impedance spectroscopy (EIS), a method which can measure the capacitance of the coating *in situ* during the contact of the coating with the solution. Due to the big difference in dielectric constants between water (80) and polymers (4–8) even small concentration of water in the polymer can increase the capacitance of the polymer layer significantly.

Electrochemical impedance spectroscopy is nowadays routinely used in the investigations on corrosion and corrosion protection due to the versatility of this method and quantitative character of generated data, contrary to the accelerated corrosion test methods which require visual assessment of the results. In comparison to accelerated corrosion test methods, which last hundredths or even thousands of hours, EIS gives similar results but in a very short time, as showed lastly by Kunce, Królikowska, and Komorowski [12], for example. Application of electrochemical measurements for the characterization of the organic coatings has long tradition [13]. Examples of the application of EIS to the characterization of corrosion performance of powder coated aluminum alloy may be found in the papers of Morabedini et al. [14, 15].

2. Experimental

All experiments were performed at the room temperature. Demineralized water was used to prepare the solutions. Triethoxymethylsilane (CAS No 2031-67-6) (>99%) and triethoxyethylsilane (CAS No 78-07-9) were purchased from Merck-Poland, NaCl was purchased from Chempur (Poland). In the electrochemical experiments 3.5% NaCl solution was used. Either Potentiostat Galvanostat EIS Analyser PARSTAT 4000 (AMETEK, USA) or LCR meter LCR-8101G (GW Instek, Taiwan) were used in the electrochemical measurements. The thickness of the coatings was measured with the use of Qnix 1500 meter (Automation Dr. NIX, Germany).

TEMS and TEES sols were prepared by gently stirring the mixture of water and TEMS or TEES in a polypropylene (PP) container by a magnetic stirrer. Strong agitation was avoided for not to form micellar solutions. Specific density of TEMS or TEES is much lower than that of water and during stirring it floats on the surface of water. Therefore PP container should be closed during stirring for not to lose silane by evaporation. The concentration of the sol was controlled by the spectrophotometric analysis. Sol sample of the volume of 1 ml was mixed with 10 ml of 30% H_2O_2 and 20–30 mg of NaOH in the form of microgranules was added. Then the mixture was heated to the temperature of 95°C during 1 h to oxidize silane to SiO_2, diluted and analyzed by the Heteropoly Blue Method, using DR1900 spectrophotometer (Hach, USA). Fig. 1 shows the kinetics of the sol formation. The time to reach stable concentration depended on temperature and concentration (higher concentration requires longer time). For the TEMS concentration of 2% it took ~24 h (Fig. 1). To serve their purposes the particles of the sol should be as small as possible, whereas they grow on standing (Fig. 2). Therefore we used in the experiments

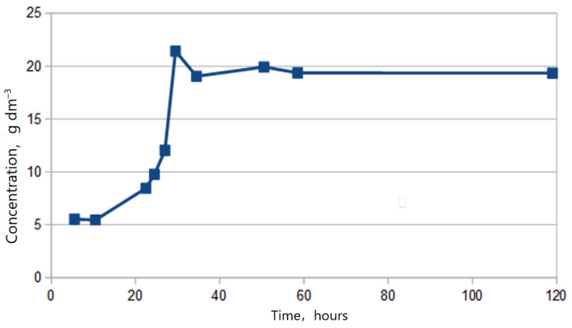

Fig. 1. Kinetics of the formation of TEMS sol of the nominal concentration 20 g dm^{-3}

Rys. 1. Kinetyka tworzenia zolu TEMS o stężeniu nominalnym 20 g dm^{-3}

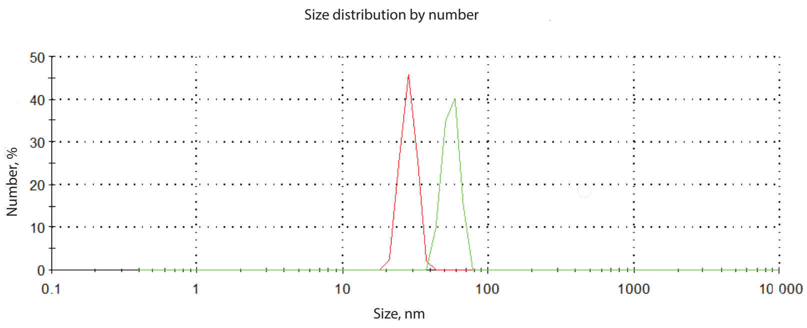

Fig. 2. Dispersion of the TEMS sol particle diameter: one day (red line) and twelve days (green line) after preparation

Rys. 2. Rozkład wielkości cząstek w zolu: jeden dzień (czerwona linia) i dwanaście dni (zielona linia) po przygotowaniu

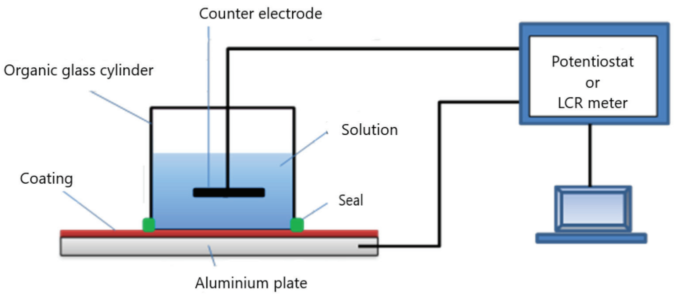

Fig. 3. Schematic presentation of the measuring cell

Rys. 3. Schemat układu pomiarowego

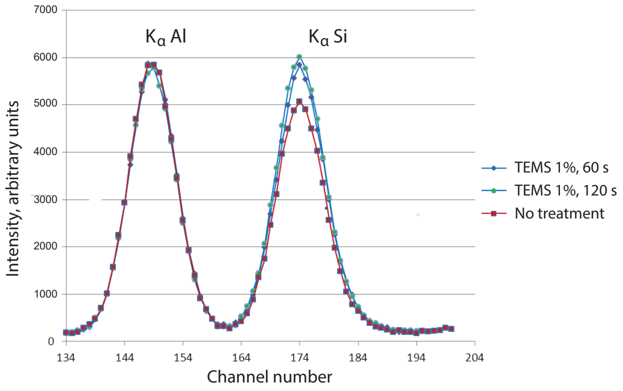

Fig. 4. EDX spectra of a sample not treated and two samples treated by spraying in TEMS sol of the concentration of 1% during 60 s and 120 s

Rys. 4. Widma EDX próbki nieobrabianej i dwóch próbek obrabianych powierzchniowo poprzez natrysk zolem TEMS o stężeniu 1% przez 60 s i 120 s

always freshly prepared sols. The stability of the sols was investigated with the use of Zetasizer Nano-ZS (Malvern, USA). The presence of TEMS or TEES at the surface of the samples was controlled with the application of the XRF spectrometer EDX 3600H Alloy Analyzer (Skyray Instruments, USA).

Aluminum (AA 5005) samples of the dimensions 150 × 50 × × 1 mm were processed on the production line together with the elements painted for clients. The process consisted of: acidic etching (twice) – washing with tap water (twice) – washing with demineralized water – chrome free passivation – washing with demineralized water – drying – powder painting – polymerization. Nabudur 158 and Nabudur 158 E were used for washing whereas Nabutan 810 was used in passivation. These chemicals were supplied by NABU Poland. In most cases the samples painted by AE30017704420 (Axalta, Poland) powder were used in the experiments. Thickness of the coating changed and was confined between 50 µm and 140 µm. TEMS and TEES sols were applied on the surface of the samples either by spraying or by sprinkling. In the former case the Bosch PFS 500 sprayer was used. After the application of the sol the samples were left in the air to dry.

In the electrochemical experiments 3.5% NaCl solution was used. Fig. 3 presents the measuring cell. Investigated sample served as a working electrode, the counter-electrode was a platinum foil of the surface area of ca. 10 cm^2. It was checked that at all frequencies the impedance of the counter-electrode was negligibly small in comparison with the impedance of the sample, so in almost all cases either potentiostat or LCR meter were used in two-electrode configuration, which reduced noises in comparison to the three-electrode configuration. Cylinder made of organic glass of the internal diameter 4.6 cm and height 5 cm, pressed to the sample through the sealing served as the measuring vessel. The working area of the sample electrode was 13.85 cm^2.

3. Results and discussion

3.1. Identification of TEMS presence at the surface by EDX

Fig. 3 shows the examples of X-ray fluorescence spectra of two samples treated by TEMS sol and one not treated in the sol. In all three spectra strong emission lines of both Al and Si may be seen. The source of Al emission is, at least partially, aluminum from the substrate, but the presence of Al in the powder forming coating, as a filler or pigment cannot be excluded. Indeed, we analyzed more than 20 different formulations of powders and in every analyzed powder significant concentration of Al was measured. We met similar situation in the case of silicone emission line. However in the case of Al line, every kind of coating, treated with the sol or not treated, showed the same concentration of Al whereas in the case of silicone emission line, samples treated with TEMS or TEES sol showed significantly more silicone in comparison to not treated samples (Fig. 4). Unfortunately, quantitative estimation of the concentration of silane at the surface was not possible, because we have not known the magnitude of the matrix effect [16].

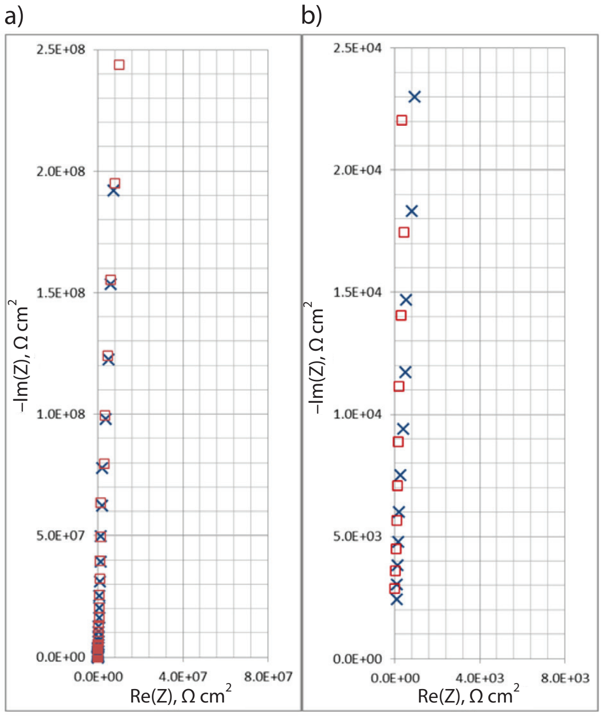

Fig. 5. Impedance spectra in 3.5% NaCl solution of a not treated sample registered in the frequency range 10 Hz–1 MHz, 1 h (red squares) and 24 h (blue ×) after the contact of the sample with the solution: a) full spectrum, b) high frequency part of the spectrum, expanded to emphasize the high frequency data

Rys. 5. Widma impedancyjne próbki nieobrabianej w zolu, zarejestrowane w zakresie częstotliwości od 10 Hz do1 MHz, po 1 godzinie (czerwone kwadraty) i po 24 godzinach (niebieskie ×) od kontaktu próbki z 3,5-proc. roztworem NaCl: a) całe widmo, b) część widma o wysokiej częstotliwości, rozszerzona w celu podkreślenia danych

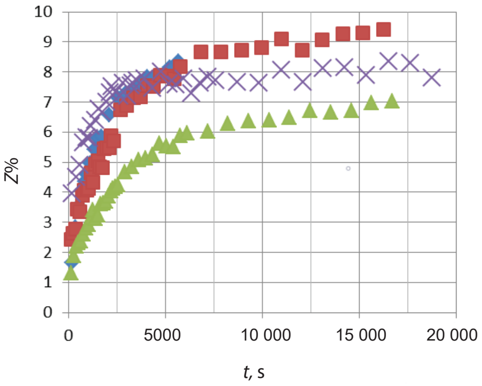

Fig. 6. Change of the parameter *Z*% in time in 3.5% NaCl solution for four different not treated samples

Rys. 6. Zmiana parametru *Z*% w czasie w 3,5-proc. roztworze NaCl dla czterech różnych nieobrabianych próbek

3.2. The shape of the impedance spectrum

Fig. 5 presents the impedance spectra of one sample (not treated) after one hour and after 24 hours of contact with the solution. From Fig. 5 one may judge that even at as low frequency as 10 Hz changes of the real part of impedance is negligibly small in comparison with the change of the imaginary part of impedance. Evidently the impedance response of the samples of aluminum covered by the coating was dominated by the capacitive behavior of the coating. To register significant changes of the real part of impedance one should make measurements at the frequencies several orders of magnitude lower. However, acquisition of an EIS spectrum at the low frequency requires long time, whereas we wanted to register fast changes occurring at the beginning of the contact between the coating and the solution. Moreover, the principal condition of the application of EIS is the stationarity of the system. No meaningful spectrum may be measured, if the properties of the system change during the spectrum acquisition. Therefore, we decided to make measurements in the range of high frequencies, recording the answer of the system: coating–solution to the sinusoidal excitation of one frequency.

Most frequently the measurements were conducted at the frequency of 500 kHz and amplitude 100 mV. The measurements were conducted in such a way that after having assembled the cell the solution was introduced quickly to the cell and impedance measurements started immediately. Impedance was measured repeatedly at predetermined time intervals during predetermined time period (up to five hours). Naturally such manual triggering introduced some uncertainty, but the changes of the impedance were not so fast that it could influence the results. We assumed that the first reading represented the properties (capacitance) of the dry coating whereas the difference between the first reading and the particular reading represents its change, caused by the sorption of water by the polymer. Because impedance and capacitance of a condenser are connected by a very simple formula, and the exact value of dielectric constant of the polymer is not known, instead of calculating the capacitance of the coating we considered just the values of impedance modulus as read from the measuring device or calculated from the impedance data. Moreover, to compensate for the differences in the capacitance of the coatings, due to (for example) differences in the coating thickness, we normalized the data dividing the difference between values of impedances by the first reading of impedance. Finally we present the data in the form given by formula (1):

$$Z\% = 100\,\frac{|Z_{t=0}| - |Z_t|}{|Z_{t=0}|}. \tag{1}$$

Note that *Z*% is positive when the impedance diminishes in time (what was usually observed).

3.3. Changes of the parameter Z% in time

The parameter *Z*% may be considered a measure of the water content in the coating layer (bigger *Z*% means more water in the coating). Fig. 6 shows the change of the parameter *Z*% in time in 3.5% NaCl solution for four different not treated samples. It may be seen that the impedance undergoes fast change at the beginning (up to ca. one hour), followed by the period of much slower but still significant changes. According to our opinion this fast change at the beginning in much part is due to the uptake of water by pores, crashes etc. The change is quite high, as expected. Despite the normalization (formula 1) the differences between samples presented in Fig. 6 are significant. We ascribe that to uncontrolled differences between different samples.

Fig. 7 shows the change of the parameter *Z*% in time for three samples treated in different manner and one untreated sample. In each case of treated samples the change of parameter *Z*% is significantly lower than in the case of the untreated sample (compare also Fig. 6 and 7). Note the strong influence of the presence of anionic surfactant (SDS) on the behavior of the sample in electrochemical measurements. Evidently lowering the surface tension makes the penetration of the pores by the sol particles easier.

Practically no difference between the sol of TEES and TEMS was observed, so most of the experiments were performed with the application of TEMS. As already stated, the repeatability of the results

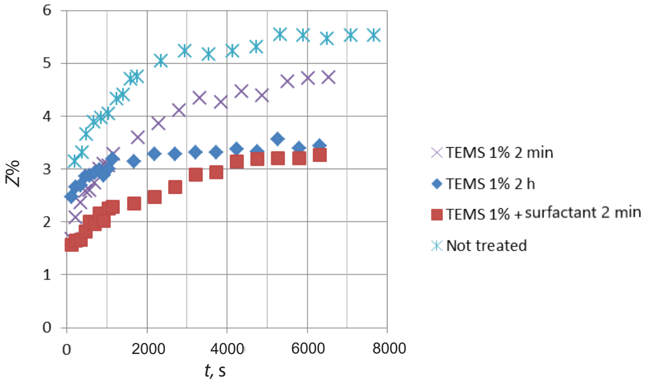

Fig. 7. Change of the parameter Z% in time in 3.5% NaCl solution for one not treated sample and three samples treated in different manner: 2 min in 1% TEMS sol, 2 h in 1% TEMS sol and 2 min in 1% TEMS sol containing additionally anionic surfactant sodium dodecylsulfate (SDS)

Rys. 7. Zmiana parametru Z% w czasie w 3,5-proc. roztworze NaCl dla jednej próbki nieobrabianej i trzech próbek obrabianych w różny sposób: 2 min w 1-proc. zolu TEMS, 2 h w 1-proc. zolu TEMS i 2 min w 1-proc. zolu TEMS zawierającym dodatkowo anionowy środek powierzchniowo czynny dodecylosiarczan sodu (SDS)

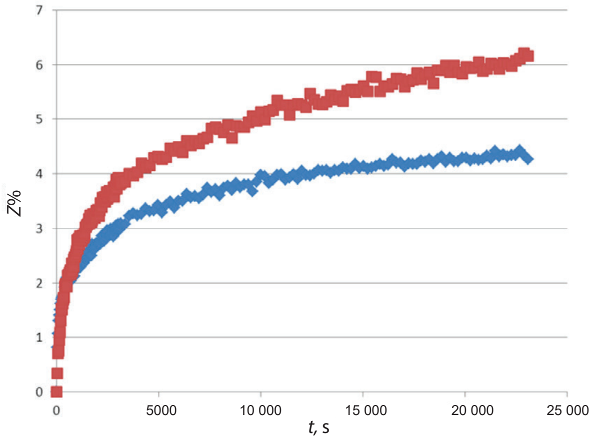

Fig. 8. Change in time of the parameter Z% in 3.5% NaCl solution for samples sprayed by TEMS sol of the concentration 1% during 2 min (blue squares) and the samples not treated (red squares); every line presents averaged results of four identical but independent measurements

Rys. 8. Zmiana parametru Z% w czasie w 3,5-proc. roztworze NaCl dla próbek natryskiwanych zolem TEMS o stężeniu 1% w ciągu 2 min (niebieskie kwadraty) i próbek nieobrabianych (czerwone kwadraty); w każdym wierszu przedstawiono uśrednione wyniki czterech identycznych, ale niezależnych pomiarów

of the electrochemical measurements was rather low. That may be increased by repeating the same measurement several times and averaging. Such a case is presented in Fig. 8, which confirm that even as short contact with the sol as two minutes is long enough to cause significant decrease in the water sorption.

4. Conclusions

Sorption of water by powder coatings, prepared with the use of the low-cost polyester resins, and the influence of treatment of the surface of a coating with the sol of either triethoxymethylsilane or triethoxyethylsilane was investigated with the application of electrochemical impedance spectroscopy. The following conclusions may be drawn on the basis of presented results:

- Powder coatings contacted with the aqueous solutions absorb water in two steps: first, up to approximately 1 h rather fast, then rather slowly. According to our opinion during the first step mainly filling of pores, crashes etc. occurs whereas during the second step, much slower, waters enters the bulk of polymer by diffusion.
- Sorption of water by polymer coating may be followed by measuring the electrical capacitance of the coating layer.
- Treating the surface of the coating with the sol of either TEMS or TEES causes sorption of the sol particles at the surface of the coating, which was confirmed by EDS.
- Treating the surface of the coating with the sol of either TEMS or TEES diminishes the uptake of water especially in the first, fast step. The most probable explanation of that observed phenomenon is clogging the pores, cracks etc. with the sol particles.

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BIBLIOGRAPHY

[1] G. P. Bierwagen. 1996. "Reflections on Corrosion Control by Organic Coatings." *Progress in Organic Coatings* 28(1): 43–48. DOI: 10.1016/0300-9440(95)00588-9.

[2] P. A. Sørensen, S. Kiil, K. Dam-Johansen, C. E. Weinell. 2009. "Anticorrosive Coatings: A Review." *Journal of Coatings Technology and Research* 6: 135–176. DOI: 10.1007/S11998-008-9144-2.

[3] K. Pélissier, D. Thierry. 2020. "Powder and High-Solid Coatings as Anticorrosive Solutions for Marine and Offshore Applications? A Review." *Coatings* 10(10): 916. DOI: 10.3390/coatings10100916.

[4] V. Kumar, A. Bhattacharya. 2020. "Demand for Low-VOC Coatings Continues to Rise." https://www.pcimag.com/articles/107370-demand-for-low-voc-coatings-continues-to-rise (access: 11.03.2023).

[5] S. B. Lyon, R. Bingham, D. J. Mill. 2017. "Advances in Corrosion Protection by Organic Coatings: What We Know and What We Would Like to Know." *Progress in Organic Coatings* 102, part A: 2–7. DOI: 10.1016/j.porgcoat.2016.04.030.

[6] D. S. Gustin, A. W. Wainio. 1945. *Electrostatic Coating Method and Apparatus*. U.S. Patent No. 2,538,562. Serial No. 596, 728.

[7] B. Arkles, J. R. Steinmetz, J. Zazyczny, P. Mehta. 1992. *Factors Contributing to the Stability of Alkoxysilanes in Aqueous Solution*. In: K. L. Mittal (ed.). *Silanes and Other Coupling Agents*. Utrecht: VSP.

[8] F. D. Osterholtz, E. R. Pohl. 1992. "Kinetics of the Hydrolysis and Condensation of Organofunctional Alkoxysilanes: A Review". *Journal of Adhesion Science and Technology* 6(1): 127–149. DOI: 10.1163/156856192X00106.

[9] M. M. Sprung, F. O. Guenther. 1955. "The Partial Hydrolysis of Ethyltriethoxysilane." *Journal of the American Chemical Society* 77(15): 3996–4002. DOI: 10.1021/ja01620a014.

[10] M. M. Sprung, F. O. Guenther. 1955. "The Partial Hydrolysis of Methyltriethoxysilane." *Journal of the American Chemical Society* 77(15): 3990–3996. DOI: 10.1021/ja01620a013.

[11] M. Krzak, Z. Tabor, P. Nowak, P. Warszyński, A. Karatzas, I. A. Kartsonakis, G. C. Kordas. 2012. "Water Diffusion in Polymer Coatings Containing Water-Trapping Particles. Part 2: Experimental Verification of the Mathematical Model." *Progress in Organic Coatings* 75(3): 207–214. DOI: 10.1016/j.porgcoat.2012.05.008.

[12] I. Kunce, A. Królikowska, L. Komorowski. 2021. "Accelerated Corrosion Tests in Quality Labels for Powder Coatings on Galvanized Steel – Comparison of Requirements and Experimental Evaluation." *Materials* 14(21): 6547. DOI: 10.3390/ma14216547.

[13] F. M. Geenen. 1991. *Characterisation of Organic Coatings with Impedance Measurements: A Study of Coating Structure, Adhesion and Underfilm Corrosion*. Doctoral thesis. Delft, Netherlands: Delft University of Technology.

[14] S. M. Mirabedini, S. Moradian, J. D. Scantlebury, G. E. Thompson. 2003. "Characterization and Corrosion Performance of Powder Coated Aluminium Alloy." *Iranian Polymer Journal* 12(4): 261–269.

[15] S. M. Mirabedini, G. E. Thompson, S. Moradian, J. D. Scantlebury. 2003. "Corrosion Performance of Powder Coated Aluminium Using EIS." *Progress in Organic Coatings* 46: 112–120. DOI: 10.1016/S0300-9440(02)00218-7.

[16] J. L. de Vries, B. A. R. Vrebos. 2002. *Quantification by XRF Analysis of Infinitely Thick Samples*. In: R. E. Van Grieken, A. A. Markowicz (eds.). *Handbook of X-ray Spectrometry: Methods and Techniques*. New York: Marcel Dekker.