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RESEARCH ON ORGANIC COATINGS DESIGNED FOR UNDERWATER APPLICATIONS

Underwater steel structures require periodic maintenance. In the case of vessels, anti-corrosion works are carried out in the shipyard, where very good conditions for applying organic protective coatings can be provided. Very good surface preparation can be obtained by the use of abrasive blasting. The well-prepared metal surface is free from impurities (particularly inorganic salts). Suitable conditions for the application and renovation of coatings are also ensured (creating appropriate climatic conditions, drying the air, setting the appropriate air temperature). However, there are underwater constructions that cannot be transferred above the water level and, therefore, their conservation against corrosion can take place only under the surface of the water, which significantly hinders the execution of renovation works. In this work, protective coatings for underwater application were tested. The application of coatings on selected steel surfaces over and under the water was carried out. Physico-mechanical and electrochemical tests were carried out in order to assess the quality of the obtained corrosion protection. The possible difficulties faced when applying coatings in marine conditions were discussed.

Keywords: organic coatings, underwater application, offshore

1. Theoretical introduction

Many underwater structures require anti-corrosive protection. The most commonly used type of protection is cathodic as well as an application of organic protective coatings. In case of sailing vehicles in maritime transport, most of the works are carried out in the shipyard, resulting in the fact that all of the maintenance activities related to anti-corrosive protection are relatively simple [1-4]. However, problems begin to emerge when it comes to underwater structures, which cannot be lifted to the surface. All of the maintenance works must be performed below sea level, which significantly hinders their performance. In case of implementing coating protection, works related to the development of formulas of coating sets designed for underwater application have been carried out for many years. The first coating of this type was introduced to the market in 1962 by the Shell Chemical Company, and it is mainly used in the splash zone [5,6]. All of the available coating sets are based on an epoxy bonding agent.

Throughout the years, three generations of applicable underwater epoxies have been developed. The surface of epoxies of the first generation was able to be applied and hardened under water. It is characterized by high viscosity and the consistency of chewing gum and a short shelf-life period. Another generation

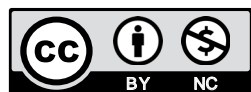
contributed to the creation of an appropriate coating, but it had been confirmed that there were troublesome issues related to toxicity. It is characterized by a high adhesion below the water surface and the possibility of the occurrence of crystallization if the product was inappropriately stored. Its chemical content includes a large amount of solvent. Epoxies of the third generation successfully solved these problems, as they are non-toxic, they do not undergo crystallization, and most importantly they are efficient [4,7-9]. Anti-fouling coatings are also used for underwater applications (Drisko, 1977).

Currently, in the market, there are many types of epoxy paints, which are applied in underwater conditions [12]. The producers assure the high quality of the products and offer a warranty for multiple years.

The application of protective coatings under the surface of the water requires a previous planning of the process. When selecting a method for the application of coatings, a user needs to consider the depth at which a given object is located, its size, and the material with which the object is made. Applying layers under water requires the involvement of a qualified team of divers. Before the coating is applied, it is necessary to remove pollutants located on the surface of the structure. The cleaning might be done with the use of an abradant, a stream of water, or high pressure air.

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1.1. Applying the coating with a brush

Applying a protective coating with the use of a brush is only possible if the painting product is characterized by a low or mediocre viscosity. The product, in that case, is fluid, which enables spreading it onto the surface of a coated element. By using brushes, a user is able to produce thin coatings [13-15]. The use of a brush makes it possible to paint spots with difficult access. Moreover, the applied paint equally penetrates the pores and irregularities of a coated substrate. The method is labor-intensive and poorly effective, and that is why it is used for small-sized surfaces. While working in the water environment, we want the coating application time to be as short as possible.

1.2. Using an applicator

A device used to apply protective layers on underwater structures comprises an applicator in the form of a round brush or a perpendicular spatula, which are connected with a pressure pump. Due to the use of the pressure pump, the painting product is released from a nozzle of the applicator with increased speed and exerts pressure. It beneficially influences the adhesion of a coating to a substrate and provides the appropriate water tightness. One of the advantages of this method is a low spread of the paint and gradual release of the product, which enables the user to save painting material. This method is convenient for a person who applies the layer because the product is released directly from the applicator. It does not require carrying separate containers for paint. The working time of a diver becomes shortened, and the emission of harmful substances for living organisms is possible to be avoided. Previously, a coating was applied with the use of a brush or a trowel, which was not the most comfortable solution. The protective layer often did not adhere to the used tools, leading to its decomposition even before applying it to structures, thereby causing product loss. Moreover, the decomposed coating limited divers' visibility.

Applying the coating with a roller

This method proves itself in the case of covering large and smooth surfaces. In other cases, the irregularities may cause the coating to poorly adhere to the substrate. Brushes should be distinguished by high absorbability. Painting with the use of a brush is distinguished by high efficiency, which allows its users to save time.

The aim of the research conducted in this work was to determine the properties of protective coatings painted under water in relation to their application over a water surface.

2. Experimental part

The subject of the research was two epoxy coatings (red (A) and gray (B) color) designed to be used for painting under water. The coatings are ultimately to be applied to the underwater parts of offshore drilling platforms. The choice of the tested organic coatings was made on the basis of offers from paint suppliers.

The coatings were applied to steel plates under as well as above the water surface. The layers were applied to the surface of steel, which were cleaned by the blasting technique. The substrate represented an SA2½ class in terms of preparation.

The coatings were applied under water using a brush. The water environment simulated seawater conditions, and the NaCl concentration was 3.5%. The height of the liquid column was 0.5 m. After the application of the coating, the samples were always below the water level until the coating had fully cured. Coatings applied above the water were also applied with a brush to simulate similar application conditions.

While applying, both of the coatings were characterized by their good adhesion to the surface of the sample materials. Figure 1a shows steel samples painted below the water surface, and Figure 1b shows steel samples painted about the water surface.

In order to assess the quality of the applied coatings, tests of the following elements were carried out:

- Thickness. The thicknesses of the coatings were tested with a use of Phynix Surfex measuring equipment.

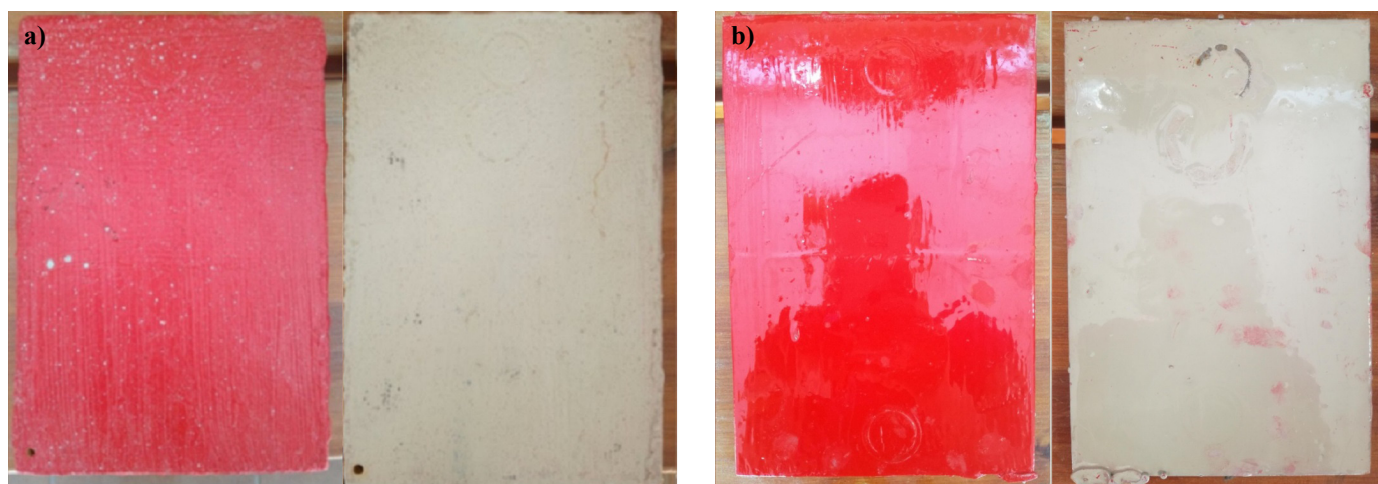


Fig. 1. Steel painted samples: a) below the water surface; b) above the water surface

- Hardness. The tests for hardness were done with the use of the Barcol test.
- Adhesion (pull-off method). The adhesion measurement was done by using the pull-off method by Erichsen Adhesion Tester.
- Impedance spectroscopy. Impedance spectroscopy measurements were done with the use of equipment for electrochemical measurement – Gamry Instruments – Reference 600.

3. Measurement results

3.1. Coating thickness measurement

Table 1 shows the results for the thicknesses of the tested coatings

TABLE 1

Thicknesses for tested coatings

Coating application method	Number of applied layers of coating	Acquired values for coating thickness [μm]						Average thickness of a coating
coating (A) – red color								
Under a water surface	I	134	190	143	137	97	135	139
	II	245	226	217	232	230	224	191
Over a water surface	I	90	125	151	97	111	123	116
	II	300	370	306	335	226	289	304
coating (B) – gray color								
Under a water surface	I	80	81	97	105	97	85	91
	II	245	302	215	178	155	226	220
Over a water surface	I	100	106	135	117	102	126	114
	II	190	255	283	216	204	272	237

The acquired values for the thicknesses of coatings diverge from those found in the safety data sheets. When painting be-

low the water surface, the thickness of a layer should be equal to 200-400 μm. The values contained within this range were acquired only for coatings applied about the water surface after applying two layers. By comparison of the methods of coating application, it is observed that the acquired values for single layers are comparable, but after applying yet another layer, thicker coatings were obtained when painting above the water surface.

3.2. Coating hardness measurement

The results of the tests are shown in Table 2.

The performed tests did not show significant differences in the case of layers applied above the water surface as well as below the water surface, proving that the hardening process in both cases was normal.

TABLE 2

Hardness of testes coatings

Coating application method	Number of applied coating layers	Average coating hardness
coating (A) – red color		
Under a water surface	I	48
	II	57
Over a water surface	I	36
	II	65
coating (B) – gray color		
Under a water surface	I	66
	II	75
Over a water surface	I	36
	II	62

3.3. Adhesion test (pull-off method)

This method enables determining the strength of material layers against the influence of a force that causes the material to be detached from a substrate. Figure 2 shows the condition of the samples after the measurement was done.

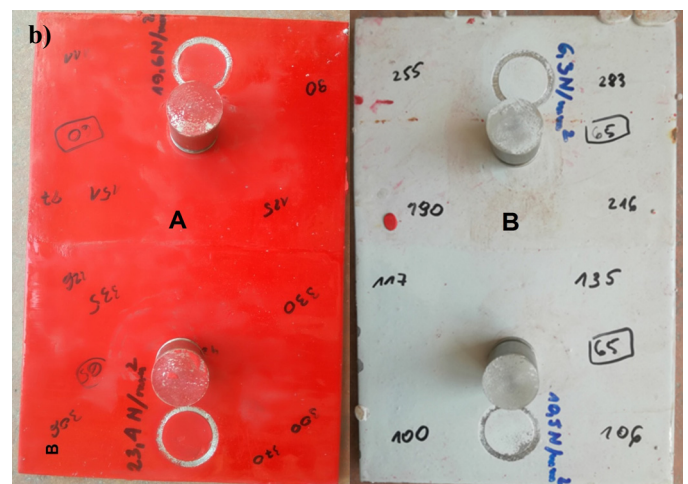
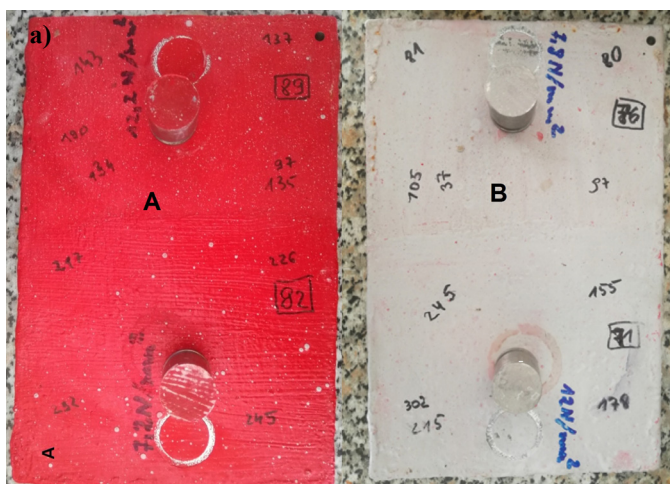


Fig. 2. Condition of the surface of samples after testing with the use of pull-off method a) above the water surface, b) below the water surface

Table 3 shows the results of the tests for coating adhesion.

TABLE 3

Results of test for coating adhesion

Coating application method	Number of applied layers of coating	Force at which the samples were detached [N/mm^2]
coating (A) – red color		
Under a water surface	I	12.2
	II	7.2
Over a water surface	I	19.6
	II	23.4
coating (B) – gray color		
Under a water surface	I	7.8
	II	12.0
Over a water surface	I	10.5
	II	6.3

In the case of all of the measurements, the adhesive detachment of the coatings occurred. Generally, it is assumed that if the adhesion of the coating to the substrate is lower than $2 \text{ N}/\text{mm}^2$, the adhesion of the coating to the substrate is insufficient. In all of the examined cases, the value of $2 \text{ N}/\text{mm}^2$ was higher, which indicates the very good adhesive properties of the tested coatings.

Testing coatings with the use of the impedance spectroscopy method

Exemplary impedance spectrum in Bode's system, acquired in the impedance spectroscopy measurement, is shown below.

The test showed that there is a one-time constant of the acquired impedance spectra. Therefore, in order to analyze them, an electrical equivalent circuit was used and is shown in Figure 4.

Based on the analysis of the obtained impedance spectra with the use of the electrical equivalent circuit shown in Fig. 4, it was possible to determine the capacitance and resistance of the tested paint coatings. The results are shown in Table 4.

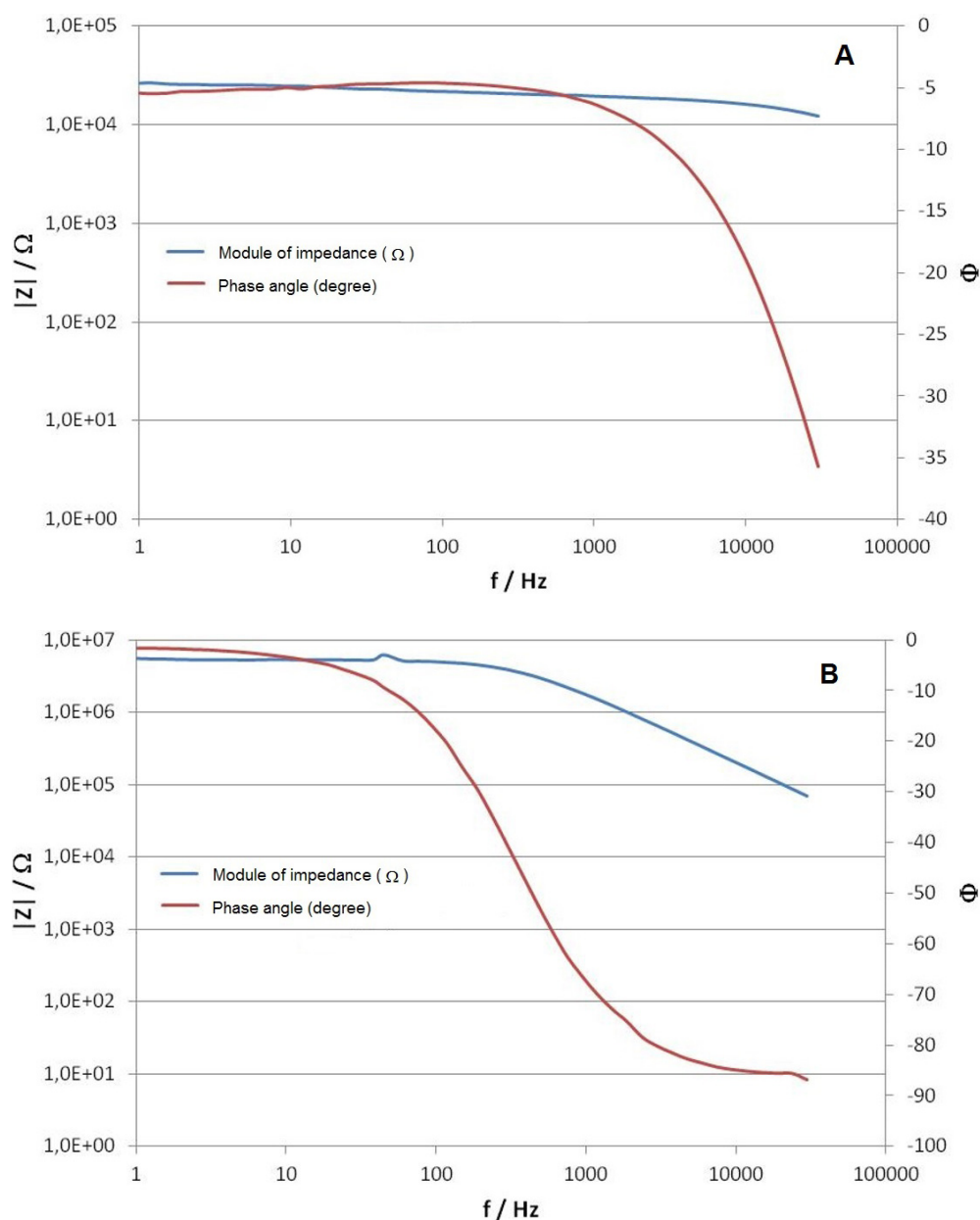


Fig. 3. Impedance spectra from the measurements of a coating applied below the water surface: a) one coating layer; b) two coating layers

TABLE 5

Thicknesses of coatings after repainting

Coating application method	Number of applied coating layers	Obtained values of a coating thickness [μm]						Average thickness of a coating
coating (A) – red color								
Under a water surface	III	256	205	295	297	317	195	261
	IV	421	378	394	351	335	353	372
Over a water surface	III	286	216	278	267	234	236	253
	IV	605	584	540	445	544	503	537
coating (B) – gray color								
Under a water surface	III	200	203	194	197	199	215	201
	IV	362	390	353	295	289	343	334
Over a water surface	III	267	289	360	312	315	299	307
	IV	326	475	380	331	455	350	386

TABLE 6

Results presenting resistance and capacitance of a coating after application of the third and fourth

Coating application method	Number of applied coating layers	Capacitance of a coating [F]	Resistance of a coating [Ω]
coating (A) – red color			
Under a water surface	III	$9.6 \cdot 10^{-11}$	$3.4 \cdot 10^6$
	IV	$1.1 \cdot 10^{-9}$	$4.4 \cdot 10^6$
Over a water surface	III	$5.6 \cdot 10^{-12}$	$3.4 \cdot 10^{11}$
	IV	$2.9 \cdot 10^{-12}$	$5.4 \cdot 10^{11}$
coating (B) – gray color			
Under a water surface	III	$1.4 \cdot 10^{-9}$	$6.5 \cdot 10^6$
	IV	$7.4 \cdot 10^{-11}$	$1.2 \cdot 10^{10}$
Over a water surface	III	$1.2 \cdot 10^{-10}$	$2.2 \cdot 10^9$
	IV	$2.5 \cdot 10^{-11}$	$2.9 \cdot 10^{10}$

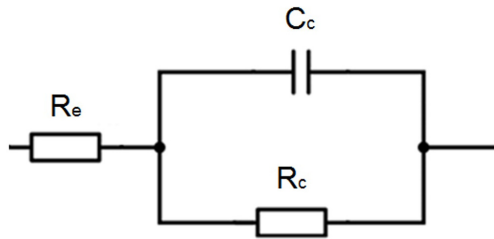


Fig. 4. Electrical equivalent circuit used for the acquired impedance spectra. R_e – electrolyte resistance; C_c – capacitance of a paint coating; R_c – resistance of a paint coating

TABLE 4

Results of resistance and capacitance of coatings

Coating application method	Number of applied coating layers	Coating capacitance [F]	Coating resistance [Ω]
coating (A) – red color			
Under a water surface	I	$9.1 \cdot 10^{-10}$	$1.4 \cdot 10^4$
	II	$8.1 \cdot 10^{-11}$	$5.2 \cdot 10^6$
Over a water surface	I	$2.2 \cdot 10^{-10}$	$7.0 \cdot 10^8$
	II	$4.9 \cdot 10^{-11}$	$2.1 \cdot 10^{10}$
coating (B) – gray color			
Under a water surface	I	$2,138 \cdot 10^{-6}$	1615
	II	$1,266 \cdot 10^{-10}$	$5,841 \cdot 10^6$
Over a water surface	I	$1,632 \cdot 10^{-10}$	$1,143 \cdot 10^5$
	II	$1,511 \cdot 10^{-10}$	$5,716 \cdot 10^5$

It is generally assumed that, if the resistance of a coating is lower than $1 \cdot 10^6 \Omega$, then the coating has insufficient barrier properties. The test results indicate that, in general, the resistance of the coatings tested is low, especially the B coating; the coating applied above and below the water surface has a low resistance below $1 \cdot 10^6 \Omega$, (with the exception of two layers of coating applied below the water surface). In the case of coating A, the low resistance is too low for one layer of the coating applied under water. For this reason, it was decided to coat the tested samples with more layers.

Table number 5 shows the results of thicknesses of the tested coatings after being repainted.

The achieved results of the coating thicknesses after repainting the samples are more satisfactory. All of the thicknesses of coatings after repainting are contained within the range of thicknesses provided in the safety data sheets. It was established that the minimal number of coating layers is equal to 3. The impedance tests of coatings applied below as well as above the water surface were repeated, and the results of the analyses with the use of an electrical equivalent circuit are shown in Table 6.

Based on the performed analyses and in the case of three and four layers of a coating painted above and below the water surface, the resistance of the coatings is higher than $1 \cdot 10^6 \Omega$.

4. Summary

The tests have shown that the application of the tested coatings under water did not show worse barrier, adhesive (Table 3),

and strength (Table 2) properties in relation to the application above the water surface. No significant differences were found in the parameters of both of the coating sets tested. When applying one or two layers of the coating after performing the test of coating thicknesses, the acquired values were lower than the values recommended by the producer. The insufficient thickness of the coatings was confirmed based on impedance spectroscopy tests (Table 4). It was found that the coating resistance was too low (below $1 \cdot 10^6 \Omega$), which indicates weak barrier properties. The application of another layer (III and IV coating layer) on the remaining samples provided the appropriate thickness, which efficiently isolated them from the exposure environment. Therefore, when the coatings are applied under water, the coating thickness measurement is important because if the coating thickness is insufficient, the barrier properties are very poor and may, in a short time, result in the occurrence of corrosion processes. When testing adhesion with the pull-off method (Table 3), the acquired results were satisfying for the coatings applied under water as well as above water. Considerably high values of the acquired results confirm that the adhesion of the coatings to the substrate is good. The tests have also shown that the process of the coating application under water with the use of a brush may

be relatively difficult to perform when taking into account the necessity to apply at least three layers of a coating. The costs of painting works, due to the necessity to perform many long-lasting diving works, which are characterized by high prices, suggest that the use of protective coatings applied under water seems to only be advisable for works performed locally (on a relatively small surface), especially in mechanical damage zones of the coating or after NDT tests in which it was necessary to remove the coating from the steel surface.

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