Corrosion and Wear Analysis in Marine Transport Constructions

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Abstract – **Corrosion is one of the most common naturally occurring processes studied by thermodynamics, which includes oxidation process, metal disruption, and its chemical and electrochemical effects under environmental influence. Corrosion of metal and equipment accounts for a considerable proportion of total corrosion losses, thus providing the impetus for further investigation and developments related to corrosion protection in order to provide transport systems and industry with corrosion preventive materials and tools.**

Keywords – **Corrosion, maritime transport, metal coatings, wear.**

I. INTRODUCTION

Protection of metals from corrosion is a topical issue affecting all areas of the world's economy. The losses due to the damage associated with marine transport corrosion during the period of construction or operation constitute approx. 50–80 billion USD and approx. 3 % of world GDP [1]. Statistics show that 90% of ship failures are attributed to corrosion [2].

The effects of corrosion are diverse. First, these are irreversible metal losses (When corrosion is widespread and uniform, with steel in seawater a metal loss of about 0.3 mm per year may be expected [3]). The main losses are related to indirect losses – increase in the mass of metal structures due to corrosion enhancements, increase in the amount of works related to construction manufacturing, reduction of their performance, large volume of repairs, etc.

Experience shows that the proper design of ship structures and use of corrosion protection equipment, qualified operation and timely replacement of damaged structures can reduce the damage caused by corrosion by 33 % of this cost could be prevented by the selection and use of an appropriate corrosion protection system [4]. To reduce the metal capacity of ships by reducing the thickness of structures, increasing the carrying capacity and life of ships.

The diversity of vessel structures and operating conditions create certain difficulties in the design and use of methods and tools for corrosion protection. The most effective way to prevent corrosion is by using various methods of protection.

II. INFLUENCE OF THE MARINE ENVIRONMENT

A ship's hull and structures are exposed to the effects of liquid and gaseous corrosion environment (permanent and periodic) [5], [6].

Sea, river and lake water, atmospheric air as well as various gases represent corrosive environments for vessels and other marine constructions.

Seawater means all ocean waters varying in their salinity and chemical composition. Salinity S – the total amount of minerals, g, per 1 kg of water – is expressed in per mille and is from 2 ‰ to 40 ‰. The average sea and ocean salinity is 35 ‰. The relationship between the concentrations of the main ions of 99.9 % of substance dissolved in the seawater is constant [7], [8]. The exception is closed seas, the Baltic Sea, the Azores Sea, the Caspian Sea, etc., with different ratios. To assess the aggressiveness of environmental corrosion, the ion concentration in the given area is determined by salinity data. For example, in the Baltic Sea the salinity of water in the upper layers ranges from

2.0 ‰ to 8.6 ‰; in the Caribbean Sea – from 35.5 ‰ to 36.0 ‰, while in the Mediterranean Sea – from 36.3 ‰ to 39.5 ‰.

Corrosion activity is affected by oxygen, carbon dioxide and hydrogen sulphide. The first and second are dissolved in all sea basins. In the Black Sea, the volume of H_2S is 87 %. There are migration zones ("clouds") as well in other seawaters where the concentration of hydrogen sulphide is high.

The waters of all seas are characterized by a high electrical conductivity γ of 0.5–6.7 S/m, a stable and narrow potential of hydrogen range (pH 7.3–8.6). Seawater is a typical low alkaline electrolyte.

The balance of seawater ions and stability of physico-chemical properties are ensured by high values of buffer volume β (0.8–1.0 meq/L) and alkalinity *Alk* values (2–2.5 meq/L), which is determined by the constant concentration of carbonate ions [9], [10].

Other parameters characterizing the composition of seawater are the freezing point *t* and the ion diffusion coefficient *D* [11].

III. CORROSION MANIFESTATION ON MARITIME TRANSPORT CONSTRUCTIONS

Basic ship structures that are subject to corrosion processes are given in Table I.

TABLE I

SHIP STRUCTURES THAT ARE SUBJECT TO CORROSION PROCESSES

Name of construction	Seawater	Sea atmosphere	Other environment
Ship hull			
Bottom of the ship	A	B	–
Forepeak and afterpeak	A	B	–
Keel, beam, propeller bracket	2A	–	–
Boarding	A	B	–
Kingston crates, lagoons and echoed shafts	2A	2B	–
Freeboard	–	2B	–
Forepeak and afterpeak	–	2B	–
Boarding	–	2B	–
Top deck	–	2B	–
Superstructure	–	2B	–
Engine department space shafts	–	2B	–
Coamings, bulwarks, storm ports, basements	–	2B	–
Cabins / forepeak and afterpeak			
Freshwater tanks	A	B	C
Ballast tanks	2A	B	–
Dry compartments and cofferdams	A	B	–
Double bottom			
Freshwater tanks	A	B	C
Ballast tanks	2A	B	–
Fuel and oil tanks	A	B	C
Dry compartments and cofferdams	A	B	–
Tanks outside the double bottom			
Fresh water tanks	A	B	C
Ballast tanks	2A	B	–

Fuel and oil tanks	A	B	C
Liquid cargo tanks	A	B	C
Cofferdams	A	B	–
Kingstons, shafts of lag and echosounder	A	B	–
Oil tanker cargo tanks	A	B	C
Cargo pallets, twin decks	A	B	C
Dry cargo compartments of dry cargo vessels	A	B	C
Equipment and devices			
Hatch and cargo tank covers	–	B	–
Twin decks hatches	–	B	–
Steering devices			
Steering wheel	2A	–	–
Steering Baller	2A	–	–
Anchor facilities	–	2B	–
Anchors and hawses	A	B	–
Chains and ropes	A	B	–
Shaft	–	B	–
Propeller shaft	A	–	–
Dying pipe	A	B	–
Screwdriver	2A	–	–
Propeller	A	B	–
Propeller conveyor	A	B	–
Systems and Pipelines / *Systems*			
Drainage	–	B	–
Ballast	A	B	–
Liquid cargo	–	B	C
Gas outlet	–	B	C
Ventilation	–	B	–
Fuel	–	B	C
Lubrication	–	B	C
Water Cooling	A	B	–
Drinking water	–	B	C
Compressed air	–	B	–
Steam	–	B	C
Hydraulic	–	B	C
Pipelines			
Air	–	B	–
Gas outlet / overspill	–	B	C
Measuring	A	B	C
Sewage	A	B	C

Using the data on the corrosion rates of metals in the seawater K_A, marine atmosphere K_B and other environments K_C and knowing the relative duration of exposure to the environment τ, it is possible to determine the expected corrosion wear of structural elements by using the following formula (1):

$$V = K_A \tau_A + K_B \tau_B + K_C \tau_C. \tag{1}$$

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Due to the different operating conditions of ship structures, the corrosion of a ship cannot be considered as one whole. All types of ships are subject to contact corrosion, weld corrosion, corrosion resulting from the heat treatment of metal structures.

IV. TYPES OF CORROSION MECHANISMS

There are two types of corrosion mechanisms – chemical and electrochemical corrosion [12].

Chemical corrosion is an arbitrary process of metal exposure to corrosive environment, when metal oxidation and environmental oxidation components regeneration take place simultaneously. It occurs in dry gasses, liquid electrolytes and non-electrolytes. The chemical corrosion mechanism in electrolytes is not discussed in this paper, because electrolytes, in which the corrosion mechanism is observed, are not used in ship building, operation and maintenance. On seagoing vessels, various elements of power plants, fuel combustion products discharged into the system, oil tanks, fuel tanks and other structures are subject to chemical corrosion. In shipbuilding and ship repair, the metal constructions which are processed under high temperatures (e.g., welding, cutting) are subject to corrosion [5], [6].

Electrochemical corrosion is an arbitrary process of metal exposure to corrosive environment (electrolyte) when metal oxidation and environmental oxidation component regeneration do not take place simultaneously – their regeneration speed depends on electrolyte potential.

The thermodynamic probability of electrochemical corrosion is determined by the value of the standard electrode potential process φ_0. φ_0 is a metal potential when the active substances participating in the reaction are equal to 1, that is, when the metal ionization rate and ion recovery rate are equal (2):

$$\Delta G_0 = -n\varphi_0 F, \qquad (2)$$

where

ΔG_0 the change of energy to maintain the balance;
n ionizing metal value;
F Faraday number.

The probability of a corrosion process decreases with the increase of the φ_0 value (from La to Pt), which is determined by the comparative data given in Table II. The electrochemical mechanism includes separate processes for standard shipbuilding metal ionization (Table II) and environmental oxidizing component cathode recovery processes (Table III).

TABLE II

IONIZATION ELECTRODE POTENTIAL OF METAL IN WATER SOLUTIONS AT $T = 25$ °C

Electrode process	φ_0, B	Electrode process	φ_0, B
$La = La^{3+} + 3e$	−2.522	$Cd = Cd^{2+} + 2e$	−0.403
$Nd = Nd^{3+} + 3e$	−2.431	$Co = Co^{2+} + 2e$	−0.277
$Mg = Mg^{2+} + 2e$	−2.363	$Ni = Ni^{2+} + 2e$	−0.250
$Al = Al^{3+} + 3e$	−1.663	$Mo = Mo^{3+} + 3e$	−0.200
$Ti = Ti^{2+} + 2e$	−1.630	$In = In^{+} + e$	−0.139
$Zr = Zr^{4+} + 4e$	−1.539	$Sn = Sn^{2+} + 2e$	−0.136
$Mn = Mn^{2+} + 2e$	−1.179	$Pb = Pb^{2+} + 2e$	−0.126
$V = V^{2+} + 2e$	−1.175	$Fe = Fe^{3+} + 3e$	−0.037
$Nb = Nb^{3+} + 3e$	−1.100	$Bi = Bi^{2+} + 2e$	0.215
$Cr = Cr^{2+} + 2e$	−0.913	$Cu = Cu^{2+} + 2e$	0.337
$Zn = Zn^{2+} + 2e$	−0.763	$Cu = Cu^{+} + e$	0.520
$Cr = Cr^{3+} + 3e$	−0.744	$Ag = Ag^{+} + e$	0.789
$Jn = Jn^{3+} + 3e$	−0.443	$Pt = Pt^{2+} + 2e$	1.188
$Fe = Fe^{2+} + 2e$	−0.440		

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TABLE III

METALS IN SHIPBUILDING AND SHIP CORROSION
BASIC OXIDANT CATHODE RESTORE ELECTRODE POTENTIAL EQUILIBRIUM

Electrode process	φ_0, B	Electrode process	φ_0, B
pH = 7		**pH = 0**	
$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$	+0.268	$2H^+ + 2e = H_2$	0
		$O_2 + 4H^+ + 4e + 2H_2O$	+1.229
$O_2 + 4H^+ + 4e = 4OH^-$	+0.815	$H_2O_2 + 2H^+ + 2e + 2H_2O$	+1.776
$H_2O_2 + 2e = 2OH^-$		**pH = 14**	
$Cl_2 + 2e = 2Cl^-$	+1.360	$2H_2O + 2e = H_2 + 2OH^-$	-0.828
		$O_2 + 2H_2O + 4e = 4OH^-$	+0.401

The probability and mechanism of electrochemical corrosion processes in natural environments and water solutions is determined by a potential dependent on pH. In addition, the φ−pH and metal−water equilibrium system diagram is used.

V. METHOD OF METAL ELECTRICAL POTENTIAL DETECTION

One of the most important electrochemical properties of a material is an electrode potential or electropotential (EP), which appears in a liquid medium. Before starting any anti-corrosion action, it is necessary to determine the EP of the metal to be treated to find the best matching metal coating. Since the deposited coating and the base form a system of two or more different materials, the corrosion resistance will depend on the EP of the coating and base and the difference between them, as in case of electrogalvanical coatings, by determining the type of anode or cathode.

By immersing a metal in an electrolyte solution, a difference of potentials is found between the metal surface and electrolyte, which is called an electrode potential. The EP of unbalanced or irreversible metals are potentials characterized by exchange process involving the participation of not only their own ions and atoms but also the ions and atoms of other metals. These standard EPs are determined according to the standard hydrogen electrode assumed to be "0". In cases when the EP is determined as a relation to another electrode (with known EP), this potential is called a potential for comparison. The EP difference (ΔE_{EP}) of metals in direct contact is of great importance. The corrosion current strength depends on the difference. It affects the durability of the corrosion resistance of the product. From the point of view of minimizing electrochemical corrosion, the allowable ΔE_{EP} of two materials in contact is 0.1 V.

It is not possible to measure a single EP; therefore, to measure the potential of an electrode, a galvanic element, i.e. a system consisting of two electrodes, is used. One of them is a comparative electrode that is insensitive to ionic solutions; its potential is constant and unknown and does not depend on the composition of the electrolyte.

There exists an EP detection device that includes a standard hydrogen electrode and a test electrode embedded in an electrolyte solution [13]. The standard hydrogen electrode consists of a platinum plate coated with a thin layer of platinum and immersed in an acidic solution, which contains hydrogen ions of 1 mol/L and through which very pure gaseous hydrogen at a pressure of 101 325 Pa flows continuously (Fig. 1). Fig. 1 – an electrolytic bridge connecting anode and cathode solutions is indicated by two stripes. Measuring the EP, the normal hydrogen electrode is assumed to be 0. EP relative to 0 is determined on a hydrogen scale.

This device cannot practically be used for determining EP under operating conditions and for mass application. Moreover, it is relatively expensive and time consuming.

The similar device for EP detection consists of a comparator electrode, a test electrode and electrolyte solution.
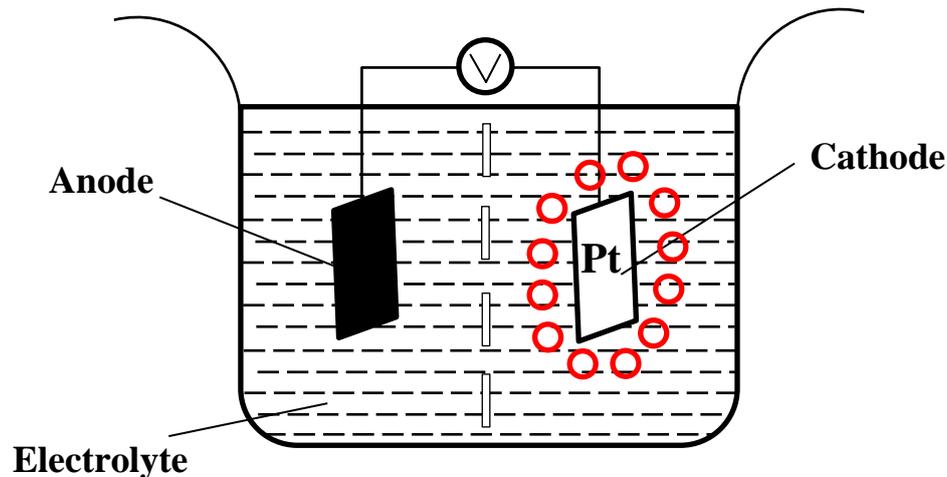

Fig. 1. Potential electrode detection scheme using a standard hydrogen electrode: V – potential detector (potentiometer).

In the operating state, the device is an electro galvanized circuit – a closed system consisting of two electrodes connected to each other by an external circuit – an electron conductor (metal) and an internal circuit – an ion conductor (electrolyte solutions connected with a salt bridge). In the galvanic chain, the oxidation of chemical energy conversion and conversion of renewal processes into electrical energy takes place. An oxidation reaction takes place on an electrode, which is an anode, i.e. an electron yield. Thus, the negatively charged anode sends the electron in the outer circuit. The anode is always an electrode, a material that is easily oxidized, such as an active metal. There occurs a reaction on the cathode, i.e. the attachment of electrons, i.e. the cathode is charged positively in the galvanic circuit and obtains electrodes from the outer circuit. A cathode is an electrode of less active metal, where cations are more readily regenerated.

An electrical circuit is made to determine an EP. This circuit consists of the studied electrode and electrode, the potential of which is known (comparator electrode). At the same time electrolytes, in which both electrodes are immersed, are connected, but the electrodes themselves are disconnected from each other. The registration of changes in the potentials of electrodes is carried out with the help of measuring equipment.

This device can hardly be used to determine the potential in operating conditions and for mass application and this is a time-consuming process. In addition, this device cannot be used to detect the potential of electrodes for massive objects, since electrodes must be submerged in the electrolyte solution during the measurement.

The purpose of the invention is to provide the possibility of determining EP in operating conditions, as well as the possibility of saving time spent on measurements. The device is distinguished by the fact that it is simple for mass application and it is possible to carry out an express analysis, which saves time for measurements [14].
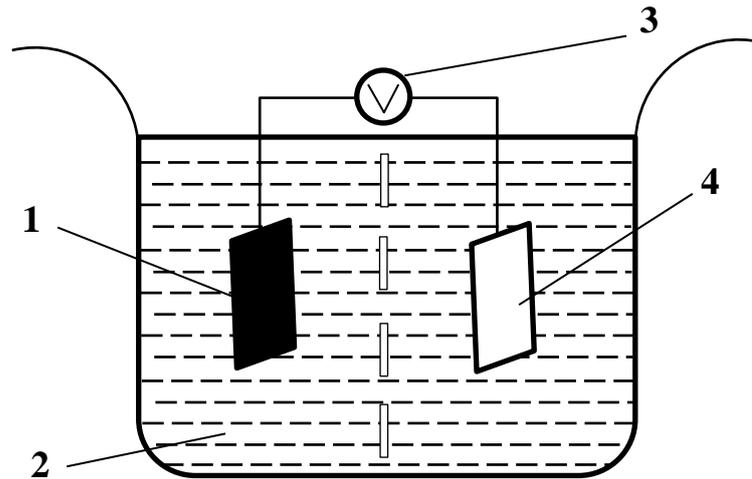
Fig. 2. Scheme of EP detection device: 1 – comparative electrode; 2 – electrolyte; 3 – potentiometer; 4 – research object.

The proposed device is an EP detection device designed for unbalanced EP express detection. The schematic device consists of two tanks (Fig. 3), which are interconnected with a tube so that, if necessary, electrolyte can be pumped from the main reservoir; the pumping process must be performed each time a potential measuring device is disconnected from or added to the test metal. The test surface is connected by a suction cup with a diameter of about 5 mm, but it is sufficient enough for the electrochemical reaction to take place and for measuring the potential value.
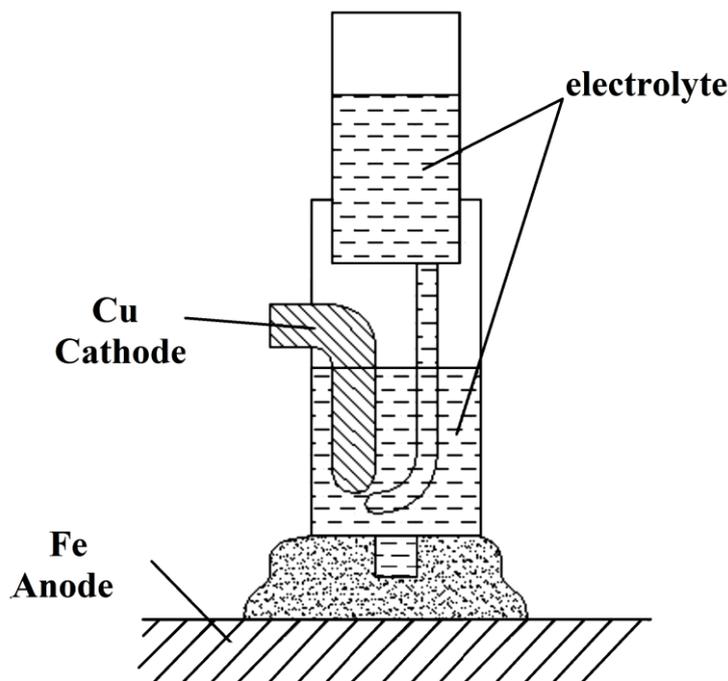

Fig. 3. Scheme of EP measuring device.

Electro technical copper was taken as a reference electrode. The base electrode (Cu) in this potentiometer is not changeable, as a result of which all measurements must be made towards the copper. The electrolyte was supplied with 10 % sodium chloride solution in water (it is also possible to use seawater). The device consists of two medical syringes and a pure Cu electrode, which, if necessary, can be cleaned. The nozzle is made from the same plunger of the syringe (Fig. 4 and Fig. 5). All connections are hermetically sealed to prevent electrolyte leakage.

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Fig. 4. EP measuring device.

Fig. 5. Potential measuring device in disassembled state.

VI. CONCLUSION

There is no classification and objective control methods. Protection characteristics are often determined by a set of different activities. These indicators are determined by mathematical modelling to determine the critical dependencies that bind the changes in the properties of the coatings in laboratory conditions and in real life conditions.

Currently, these issues are not resolved. Therefore, only benchmarking methods are used to assess some of the protection features. All the potential results obtained in the research are unbalanced, which means that the obtained results should not be compared with the standard hydrogen electrode measurement data. The literature provides balanced potential values obtained by using a potential benchmark (standard hydrogen electrode).

After summarizing the potential results, it is easy to choose the coating material for the required component. Steel can be coated with aluminium and then the next layer is selected – the one that falls into the aluminium range, such as tin or lead. This is the only way to create a high-quality multi-component anti-corrosion coating [15], [16].

The proposed EP measuring device, which includes a reference electrode, an electrode under test and electrolyte liquid, differs by the fact that it consists of two containers connected by a tube for pumping electrolyte from the main container in case of necessity. The pumping process is performed each time disconnecting or connecting the potential measuring device from/to the metal being tested with the help of a suction cup, while all unit connections should be hermetically sealed to prevent electrolyte leakage. The proposed device is quite simple, and its use provides the opportunity to perform rapid analysis helping to save considerable time required for measurements.

REFERENCES

[1] NACE – Economic Impact, *Assessment of the Global Cost of Corrosion*. [Online]. Available: http://impact.nace.org/economic-impact.aspx. Accessed on: December 15, 2017.

[2] R. E. Melchers, "Corrosion Uncertainty Modelling for Steel Structures," *Journal of Constructional Steel Research*, vol. 52, no. 1, pp. 3–19, Oct. 1999. https://doi.org/10.1016/S0143-974X(99)00010-3

[3] A. M. Berendsen, *Marine Painting Manual*. Springer Science & Business Media, 1989. https://doi.org/10.1007/978-94-017-2186-8

[4] T. Tezdogan and Y. K. Demirel, "An Overview of Marine Corrosion Protection With a Focus on Cathodic Protection and Coatings," *Brodogradnja/Shipbuilding*, Brodarski Institute, vol. 65, no. 2, 2014.

[5] I. A. Stepnov, *Morskaja Korrozia*. M.: Metallurgia, 1983. p. 512.

[6] V. D. Pirogov *et al.*, *Korrozia i zasita sudov, Spravocnik*. L.: Sudostroenie, 1987. p. 376

[7] R. Yhnevic, E. Valaskovskij, A. Viduhovskij and G. Stankevic, *Tehnika borjbi s korroziej*. Translation from Polish, L.: Himia, 1978. p. 304.

[8] H. D. Racev and S. T. Stefanova, *Spravocnik po Korrozija*. Sofija – Derzavno Izdateljsvo "Tehnika", 1977.

[9] Posiva Oy, *Safety Case for the Disposal of Spent Nuclear Fuel at Olkiluoto*. 2012. [Online]. Available: http://www.posiva.fi/files/3010/Posiva_2012-04web.pdf. Accessed on: December 3, 2017.

[10] Hach Company / Hach Lange GmbH, *pH Alkalinity of Water*, 2nd ed. 2015. [Online]. Available: https://www.hach.com/asset-get.download.jsa?id=29641556307. Accessed on: November 30, 2017.

[11] N. A. Azarenko, S. V. Litovchenko, I. M. Nekljudov and P. I. Stoev, *Korrozija I Zasita Metallov. Cast 1. Himiceskaja Korrozia Metallov*. Ministry of Education and Science of Ukraine. V. N. Karazin Kharkiv National University. p. 187

[12] T. L. Lukanina, I. S. Mihajlova and M. A. Radin, *Himiceskoe Soprotivlenie Materialov i Zasita ot Korrozii*. Saint Petersburg, 2014.

[13] The LibreTexts libraries, *Standard Electrode Potentials*. [Online]. Available: https://chem.libretexts.org/Textbook_Maps/General_Chemistry_Textbook_Maps/Map%3A_General_Chemistry_(Petrucci_et_al.)/20%3A_Electrochemistry/20.2%3A_Standard_Electrode_Potentials. Accessed on: December 10, 2017.

[14] A. Urbahs, K. Savkovs, V. Ņesterovskis and G. Rijkuris, "A Device for Measuring Electrode Potential," LV patent LV 15205 B, July 20, 2017.

[15] A. Urbahs, G. Rijkuris and K. Savkovs, "Corrosion and Wear Resistant Nanostructured Metal Coatings Characteristics Analysis," in *Proceedings of the AES-ATEMA 26th International Conference*, Ottawa, Series – Advances and Trends in Engineering Materials and their Applications, 12–16 October, 2015, pp. 37–42. , ISSN 978-1-927838-21

[16] A. Urbahs, G. Rijkuris and I. Stelpa, "Marine Vessel Structure and Equipment Corrosion Defect Characteristics," *Production and Engineering*, vol. 35, pp. 38–45, 2013.

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