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SUMMARY PhD THESIS

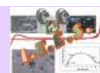
STUDY OF CORROSION DEGRADATION AND IMPROVEMENT OF ANTI-CORROSIVE PROTECTION METHODS OF METAL STRUCTURES IN THE MARINE ENVIRONMENT

PhD Student
Eng. Laurentiu MARDARE

PhD supervisor, Prof. univ. dr. chim. Lidia BENEĂ

Series I 5: Materials Engineering No. 14

GALA I
2019





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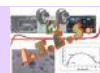
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INTRODUCTION

The experimental researches presented in this study have been initiated and carried out at the **Competences Center for Interfaces Tribocorrosion and Electrochemical Systems (CC-ITES)**, at the Faculty of Engineering within “Dunarea de Jos” University of Galati. The researches presented in this study continue the previous studies regarding the electrochemical methods on-site for evaluating the corrosion resistance of materials in specific environments of use and for improving their performances by applying composite and polymeric anti-corrosive protective coatings.

The general objective of the research presented in this study is to evaluate the corrosion resistance of E32 and EH36 naval steel, the anti-corrosive protection methods by coating with organic polymers (primers and paints) and to improve the anti-corrosive performances of the epoxy polymer primer by reinforcing it with nanoparticles of titanium oxide (TiO₂) in seawater taken from the Black Sea basin.

The specific objectives consisted in:

The study of the corrosion mechanism of E32 naval steel according to the applied protection layers: primer, primer + paint and primer modified in seawater.

The influence of the immersion time on the corrosion behavior of the unprotected steel and on the steel covered with different polymeric anti-corrosive systems.

The influence of dispersed titanium oxide nanoparticles from the modified primer upon the corrosion resistance of EH36 naval steel welded structures in seawater.

The study of the morphology, composition, roughness, micro-hardness, hydrophobicity and the coating thickness of the applied anti-corrosive coatings on the naval steel.

The structure study by X-ray diffraction of the unprotected steel and of the applied protective layers, as well as of the corrosion products resulted by submerging in seawater.

The doctoral thesis has a number of 179 pages and it is structured in two parts: a general part which is approximately 25.13% and an experimental part representing personal contributions in the approached field. The bibliographic references have been listed per chapters. Of the 318 bibliographic references that are presented in the thesis, 6 are personal studies, one of them being ISI indexed (clarivate Analytics). The study has 68 Figures and 26 tables.

The general part of the study (**Chapter I), SYNTHETIC ANALYSIS OF THE ACHIEVEMENTS AT NATIONAL AND INTERNATIONAL LEVEL IN THE FIELD OF THE DOCTORAL TOPIC**, presents a synthesis of the actual stage regarding the



achievements at national and international level in the field of protective coatings for naval steel with aspects focusing on defining, classifying, presenting and characterising the general methods of obtaining chemical composition of composite materials, the study methods of their structures and properties, especially the corrosion resistance. Moreover, the chapter presents research directions resulted from the bibliographic study in the field of the research topic that of obtaining polymeric protective films and protection films reinforced with nanoparticles for protecting naval steel and improving their behaviour in the marine environment.

The second part of the study presents all personal experimental results in nine chapters.

In **chapter II**, entitled **MATERIALS, METHODS AND EXPERIMENTAL TECHNIQUES**, materials, methods and experimental techniques are presented, structured on the two main research directions of the thesis: evaluating the corrosion resistance of naval steel and of unprotected naval steel welded structures covered with different polymeric and nanocomposite coating systems, and developing a polymeric nanocomposite coating by modifying the epoxide primer by adding dispersed titanium oxide nanoparticles (TiO_2).

Both obtaining and characterising the polymeric protection films, as well as the nanocomposite polymeric films, required a rigorous foundation of the electrochemical characterization methods (open circuit potential, linear polarization, potentiodynamic polarization, cyclic voltammetry and electrochemical impedance spectroscopy) which are applied in the field of science and material engineering.

Moreover, the studies were completed with off-site methods for evaluating the roughness, micro-hardness, hydrophobicity, morphology and structure of polymeric and nanocomposite anti-corrosive layers.

In **chapter III**, entitled **THE INFLUENCE OF WORKING PARAMETERS ON THE PROPERTIES OF ANTI-CORROSIVE POLYMERIC PROTECTION FILMS AGAINST CORROSION**, is presented the complex analysis of the E32 naval steel unprotected and covered with protection films. The roughness of the steel and of the applied protection films (**2D**, **3D**), coating thickness of the polymeric and nanocomposite films, micro-hardness and the comparative hydrophobicity of the studied surfaces are analyzed comparatively.

Chapter IV, entitled **MORPHOLOGICAL AND STRUCTURAL CHARACTERIZATION OF THE E32 NAVAL STEEL WITH AND WITHOUT ANTI-CORROSIVE POLYMERIC PROTECTIVE FILMS**, presents comparative studies upon the morphology and composition of the unprotected steel surfaces and the polymeric and nanocomposite protection coatings before and after the corrosion process by coupled electron microscopy with X-ray spectroscopic analysis (SEM-DEX). Their structure is studied by X-ray diffraction (XRD) in order to observe the effect of the TiO_2 nanoparticles on the morphology of epoxy polymer primer films. There has also been noticed results of corrosion formed in seawater on each type of studied surface.



Chapter V, entitled **BEHAVIOUR IN TIME OF NAVAL STEEL CORROSION WITH AND WITHOUT POLYMERIC PROTECTIVE COATINGS IN NATURAL SEAWATER**, is correlated with possible fields to use the polymeric coatings for the naval steel and presents the study of their behaviour to corrosion in the water taken from the Black Sea from three topographic points near the sea-coast area of Romania. The three used solutions were from the area of Agigea, Navodari and Mangalia. Methods of investigation of the coating / solution interface used are the open circuit potential (OCP), Polarization resistance (R_p), electrochemical impedance spectroscopy (EIS), diagrams for the studied systems. The experimental results have been compared for the studied surfaces by mathematical modeling and simulation with equivalent electrical circuits showing the respective interface. The measures and the evaluation were carried out over 98 days. At the end of the chapter the comparative behaviour of the studied surfaces in the seawater taken from three locations is presented.

In **chapter VI**, entitled **IMPROVING THE POLYMERIC PRIMER'S ANTI-CORROSIVE PERFORMANCES BY ADDING DISPERSE TITANIUM OXIDE NANOPARTICLES AND OBTAINING POLYMERIC NANOCOMPOSITES**, it is presented the study of the corrosion behavior of E32 naval steel and its protection coating with polymeric primer and polymeric primer modified by adding dispersed titanium oxide nanoparticles (TiO_2). The chapter highlights the beneficial effect of the titanium oxide nanoparticles dispersed in the epoxide polymeric primer in order to increase the corrosion resistance of the naval steel covered with nanocomposite polymeric films. At the end of the chapter the comparative study of the corrosion resistance of the systems studied in seawater taken from three different locations from the Black Sea shore is presented.

In **chapter VII**, entitled **IMPROVING THE CORROSION RESISTANCE OF WELDED EH36 NAVAL STEEL STRUCTURES BY COATING WITH POLYMERIC PRIMER MODIFIED WITH TiO_2 NANOPARTICLES**, it is presented the behaviour study to corrosion in seawater of EH36 naval steel welded structures and the possibility of increasing the corrosion resistance by protecting with polymeric films of epoxy primer modified with titanium oxide nanoparticles.

In **chapter VIII**, **GENERAL CONCLUSIONS, PERSPECTIVES AND FUTURE RESEARCH DIRECTIONS**, the conclusions on the experimental results of the doctoral thesis are summarized, in the field of developing and characterising the corrosion resistance of polymeric layers of primer, paints and epoxy primer modified with titanium oxide nanoparticles dispersed therein. There are also presented perspectives and new research directions on the research topic addressed.

Chapter IX, **PERSONAL CONTRIBUTIONS AND SCIENTIFIC ACHIEVEMENTS IN THE FIELD OF THE RESEARCH TOPIC**, presents scientific achievements in journals and conference volumes ISI indexed (Clarivate Analytics), publications in journals in international databases and participations at national and international scientific events.



CHAPTER I

SYNTHETIC ANALYSIS OF THE ACHIEVEMENTS AT NATIONAL AND INTERNATIONAL LEVEL IN THE FIELD OF THE DOCTORAL TOPIC

With the development and use of oceanic resources, port facilities, bridges, offshore oil platforms and other marine floating structures are built. A big number of metallic materials are used in the marine environment, depending on their utility. The marine environment is considered one of the most aggressive and hostiles corrosive natural environments. [1.1].

1.1. Main achievements in the field of materials used in shipbuilding

1.1.1. Structures exposed to the action of degradation in marine environment

At present, ships are decisively contributing in supporting the economical activity of the modern world. The world economy depends directly on trade and industrial activities by exploiting the resources of the seas and oceans.

Most of the elements that comprise various equipment to operate and explore the marine environment are made out of metallic materials.

Naval structures that are built from steel and aluminium, like any other dynamically charged metal structure, can always be liable to the challenges of corrosion, weariness and to tear [1.4].

Corrosion is one of the phenomena that seriously affect the deterioration of materials in maritime applications. 30% of damage to ships and other marine equipment is the consequence of marine corrosion, with an annual cost of over 1.8 trillion dollars.

Marine corrosion is categorized as quite aggressive due to its high content of salt and the low electrical resistivity of seawater. The chlorides present in the seawater depassivate metals and their alloys, like: stainless steel, aluminum alloys or titanium alloys even in the absence of oxygen. Also, chlorides are present in the marine atmosphere, which can lead to the corrosion of materials and structures that are not immersed, but where temperature and the seawater salinity, as well as the concentration of dissolved oxygen vary according to the geographic location with its specific conditions [1.5].

The lifespan and the range of space movements of ships expose them to a broad spectrum of different environmental factors, which influence the corrosion speed and the formation of different corrosion forms specific to the marine environment. Complex external



factors (navigating in different areas and on different routes, atmospheric conditions, seawater, etc.) and internal factors (disposal of ballast tanks, dry spaces and cargo warehouses, operating conditions etc.) determine a corrosion tendency that appears to working ships [1.6- 1.7].

1.1.2. Marine corrosion

Corrosion, especially steel corrosion in a marine environment, is an extremely complex phenomenon which depends on numerous environmental and material factors. Environmental factors include bacterias, biofouling, oxygen supply, carbon dioxide, salinity, pH, carbonate solubility, pollutants, temperature, pressure, suspended solids, the speed of water and the waves' action, and material factors include the steel's composition and the surface's roughness. Moreover, the corrosion which is associated with microbiological influences depends on the presence of some adequate bacterial colonies and the availability of the energy sources (electrons) as well as nutrients sufficient to support bacterial metabolism [1.17].

1.1.4. Types of corrosion characteristic to the marine environment

Fontana identified eight forms of corrosion which appear and are characteristic for the marine environment. These are [1.47 -1.48]:

These corrosion forms can be categorized by their identification mode, macroscopic (with the naked eye) and microscopic with special devices.

1.1.5. Risk zones of marine structures for corrosion

The risk zones where the corrosion phenomenon can appear at naval and floating structures that operate in the marine environment are well defined by the ship class records.

Class records, like the American Bureau of Shipping (ABS), Det Norske Veritas (DNV), Bureau Veritas (BV) etc, that are subordinated to the International Association of Classification Societies (IACS), group 6 corrosion zones for ships and floating structures in the marine environment: the submersible zone, the atmospheric zone, the cargo warehouse zone, the splash zone, the ballast tanks zone, interior spaces zone.

1.2. Using anti-corrosion protection methods

Protection against corrosion is a vital concern for the applications in the field of maritime industry, in which metals are used as functional and building materials. It is important that corrosion has been declared as the main mechanism of structural integrity



failure which leads to massive economic losses, safety and environmental problems.

During usage, when the protection barrier is damaged, the corrosive environment can easily penetrate through the coating and as an effect, it causes corrosion and degradation to the metallic parts. Recently, a new generation of intelligent anti-corrosive coatings composed of two functional components has been suggested and investigated. One part is passive, like the coatings with sol-gel and polymeric coating which act as a physical barrier against corrosive species [1.72].

The system that is the most used in the marine environment for anti-corrosive protection for metallic materials and especially for steel is obtained by using different types of organic and anorganic protective coatings and for the submersive zone, coatings combined with cathodic protection (CP) are used. Functional coatings (organic, anorganic and hybrids) are a class of materials that can be adapted for many applications, where they should fulfill a series of well-defined functions [1.73 -1.75]. However, reality shows that this kind of protection system against corrosion is not always enough and that certain zones of ships and marine structures are or can not be protected thoroughly. Hence, corrosion still remains on of the most important degrading mechanism for the structural integrity [1.77].

1.2.2. Organic coatings

The organic anti-corrosion protective coating system integrates epoxides, polyurethanes, oils, acrylics, alchidices, polyesters, silicates, phenols and amines. Pigments and additives are also added in the composition of various coatings in order to improve their performance [1.83]. Paints or coatings act as ionic and electronic barriers [1.84].

Organic anti-corrosion protective coatings are complex products consisting of various discontinuous solid functional additives usually known as “pigments” which are contained in a continuous polymeric phase known as “binders”. Polymeric binder is also important and it supposed to contribute to the adhesion of the coating to the underlayer [1.85].

1.2.3. Polymeric anti-corrosive protective coatings

Protection against corrosion in conventional coatings was generally obtained by using inhibitors like metallic pigments, metal oxides and relatively high concentrations of salts. Due to strict environmental regulations regarding the usage of paints that contain heavy metals, the new class of polyaniline based coatings (PANI) has become much more attractive, being resistant coatings to corrosion and eliminating the necessity of toxic inhibitors. The advantages of polymers to conventional inhibitors are their low, thermal and chemical stability [1.87].



1.5. Research directions resulted from the bibliographic analysis.

Conducting a study from the current specialized literature in the field of corrosion protective coatings in saline environments, especially towards obtaining some polymeric protective coatings resistant to marine corrosion.

The purpose of the present study is in-depth study of corrosion behavior in natural seawater taken from three distinct areas of the Black Sea of some medium alloyed steels coated with polymeric paints resistant to marine corrosion for shipbuilding and improving them by dispersing titanium oxide nanoparticles.

Based on experimental researches of corrosion behavior and the interaction analysis between electrochemical factors, this study suggests an in-depth study of the evolution of corrosion degradation processes that take place at the polymer interface metal coating and lead to destruction by corrosion of naval steel and their protective coatings.

Studies regarding polymeric protective coatings used at large scale in the maritime industry, especially of two-component polymeric primers and of polyurethane epoxy paints.

Study of the electrochemical parameters influence (current density, the stirring speed of electrolyte, the particles concentration in the polymer coating solution and their size) after dispersing in the polymeric matrix the polymeric coating with and without nanoparticles.

Characterising the coating layers by measuring the coating thickness with the help of optical microscopy, measuring the micro-hardness, the roughness, the contact angle.

Interpreting the chemical composition of the obtained coatings by analyzing the EDX spectra.

Characterising the morphological structure of the coatings made by scanning electron microscopy (SEM-EDX).

Studies of corrosion behavior of the coatings reinforced with TiO₂ nanoparticles in comparison with the coatings with epoxy primer by corrosion tests, carried out using electrochemical methods (open circuit potential measurement, polarization resistance, electrochemical impedance, potentiodynamic curves and cyclic voltammetry) using as a corrosive environment seawater taken from three distinct topographic points of the Black Sea's sea-coast.

1.6. Proposed objectives and experimental research program

Preparing the solutions: electrolytes, pickle, scouring, and corrosion liquor.

Preparing the support for the corrosion tests (E32 naval steel): cutting, cleaning, scouring, pickling, insulating, weighing, etc.

Optimising the parameters: the volume of electrolyte in the electrochemical cell, the distance between the anode and the cathode, determining the pH of the electrolyte solutions, working temperature, the applied current density, concentration of particles, stirring speed, etc.

Improving the primers and the polymeric paints by adding TiO₂ nanoparticles with



different particle sizes at varying concentrations.

Characterising the behavior of polymeric coatings to corrosion in natural seawater taken from the Black Sea shore by electrochemical measurements (OCP, Rp, EIS, PD, CV) at well-established time intervals.

Interpreting the obtained data.

Structural and morphological - topographic characterization of polymeric coatings with nanoparticles obtained within the CC-ITES-UDJG laboratory.

1.7. Selective References - chapter I

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CHAPTER II

MATERIALS, METHODS AND EXPERIMENTAL TECHNIQUES

This chapter presents support materials, methods of conducting naval steel samples, polymeric protective coatings, preparing and modifying polymeric primers by adding in the polymeric matrix TiO₂ titanium dioxide nanoparticles, electrolytes liquor and experimental testing procedures by electrochemical methods of corrosion behavior of E32 naval steel in unprotected condition and covered with polymeric protective coatings.

The morphological and elemental characterization of E32 naval steel surfaces unprotected and protected against the corrosive action of natural seawater with polymeric protective coatings was done with the help of scanning electron microscopy with energy dispersive X-ray analysis (SEM EDX).

The structural characterization was done by using an X-ray diffractometer (XRD).

The behavior to corrosion was investigated by using electrochemical methods, using an electrochemical cell with 3 electrodes connected to a potentiostat/ galvanostat.

2.1. Support materials.

2.1.1. Steel and its alloys.



One of the types of steel highly used in various structures in shipbuilding is the E32 steel [2.4 - 2.6]. For the study of this doctoral thesis E32 weak alloy steel – used in shipbuilding and EH36 high strength weak alloy steel – used at large scale offshore platforms, and in the body structures of the ship due to its excellent mechanical properties – was used.

Besides the study of degradation by corrosion and improving the anti-corrosion protection methods of metal structures in the marine environment done on stainless steel E32, this study also covers the improvement of corrosion resistance of the EH36 naval steel butt welded in the PA/1G position. This steel was used for evaluating the corrosion resistance of welded structures and protected with ordinary primer and with primer reinforced with TiO₂ nanoparticles for comparison. For welding, EH 36 steel sheets with a thickness of 10 mm were used, cored wires (with E70C-6MH4 metal powder and E81T1-Ni1MJH4 rutile flux) with 1.2 mm diameter and Corgon 18 gas as auxiliary material. The samples welded in the PA/1G position for a butt welded joint with the thickness of 10 mm were done on a flat ceramic support with concave channel (Br = 9 mm and Hr = 1,3 mm) and with opening the joint between the welding components (boards), b = 5 mm, use of the joint in the form of the narrow letter V (a = 40 0). The samples for the corrosion test were taken from the specimens for the cross-sectional bending with the compressed root (FBB) of the welded joints, after performing the mechanical laboratory tests. After sampling, one of the front surfaces of the specimens was rectified. In order to do the tests the Phoenix 405 Progress puls MM TDM welding equipment and the K-BUG 5102 welding tractor were used.

2.1.2. Polymeric protective coatings

The protective coatings for floating structures from marine environments are coatings with special purpose which are supplied to shipbuilding markets, offshore, repair, and port infrastructure. The used products vary and are unique and are used for severe climatic and immersion conditions. Figure 2.2 presents the protective coating system with barrier properties for the E32 naval steel used to carry out the study of the corrosion behavior of E32 naval steel unprotected with polymeric anti-corrosion protective coatings.

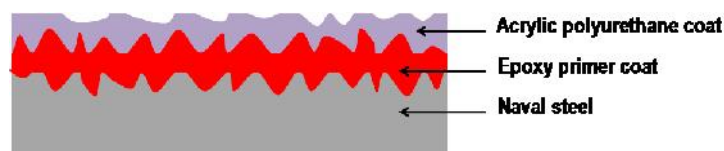


Figure 2.2. The anti-corrosive protective coating system used in the experiment

As a result, a coating system should be applied as uniformly as possible and should provide long-term protection against corrosion and contamination.

2.1.2.1. Epoxy resins



By far, the most important group of epoxy resins is formed by the aromatic types of glycidyl ether. They are manufactured by polycondensation from epichlorohydrin and bisphenol A of the chemical formula $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$. The molecular weight of the individual representatives of this group is only determined by the the mixing ratio of the reactants. The unstable light ether groups formed by the reaction of epichlorohydrin ($\text{C}_3\text{H}_5\text{ClO}$) with bisphenol A limit the use of this group of resins to primers on primed surfaces. The types of ester must continue to be used for surface layers. [2.15].

2.1.2.2. Polyurethane acrylic paint

Polyurethane is one of the most versatile classes of polymers due to its unique properties and it includes an excellent resistance to abrasion, hardness, flexibility, chemical resistance, UV stability, weatherability and solvent resistance. This unusual versatility is not only from their advantageous properties, but also due to a large spectre of applications.

Most anti-corrosive polyurethane polymers consist of a polyacrylic resin (base) and a polysocyanate hardener. The most common polyacrylics have hydroxyl groups as part of their chemical structure [2.22].

The main component of Interthane 990 polyurethane acrylic paint is the urethane acrylate oligomer which is normally prepared by a two-step polymerization process by which it reacts with a polyol (low molecular weight polyether or polyol diol), and with a diisocyanate and then monomeric acrylate vinyl like 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate.

2.1.2.3. Electrolytes used to evaluate corrosion behavior

The Black Sea is a semi-closed basin which communicates with the Mediterranean Sea through the Bosphorus. The Black Sea's coast area is influenced by the contribution of fresh water poured into the sea by the rivers, especially in the North-West part, Danube, Dnieper and Dnister. The agricultural, industrial activities and treatment plants in the coastal area have a huge impact on the influence of the ecosystem. Industrial waste, organic fertilizers, solid household waste, anthropogenic radionuclides, chemicals used in treatment facilities etc. are the main constituents of coastal zone pollution [2.25].

The salinity of the Black Sea varies between 1 and 2.7% ppu, in the coastal areas where the rivers flow. For example, when the Danube flows into the sea, the salinity reaches values below 1% [2.26 - 2.27].

The average pH of the Black Sea is 7.9 [2.28 - 2.29].

The areas' coordinates where the seawater, used as electrolyte was taken are:

Mangalia open sea, - latitude $44^\circ 20' 49.0''$ N, longitude $28^\circ 47' 40.2''$ E

Agigea open sea - latitude $44^\circ 05' 42.1''$ N, longitude $28^\circ 42' 28.0''$ E

Navodari open sea - latitude 43.793632, longitude 28.616974 E



2.2. Methods, techniques for protecting the surfaces

2.2.1. Preparing E32 naval steel samples with and without polymeric protective coating subjected to electrochemical corrosion tests in seawater

In order to study the behaviour to corrosion through electrochemical methods of the unprotected E32 naval steel and with various polymeric protective coatings in natural seawater, a series of operations to prepare and execute them were carried out (gradually).

2.2.2. Obtaining anti-corrosive polymeric protective coatings

2.2.2.1. Mixing of components

Anti-corrosion protective coating with Intergard 269 epoxy primer was made by mixing the two components. A stirrer with a power mixer was used: GRW 12 Professional from BOSCH, Germany. The mixing of the two base components A and the hardener B was done in a mass ratio of 4:1 with a speed of 150 rpm.

Immediately after applying the polymeric protective coating, *on-site* measurement of the thickness of the wet paint layer (WTF - Wet Thickness Film) was done, and after it dried completely the thickness of dried layer (DFT -Dry Thicknes Film) was measured. For this, a device for measuring the thickness of the coating layers, **PCE – CT – 28** coating thickness gauge, was used.

For an in-depth analysis, the layers of the polymeric protective coatings were measured by scanning electron microscope (SEM) on samples in cross section.

2.3. Characterising the corrosion behaviour of the E32 naval steel and of the simple polymeric protective coatings and coatings with polymeric matrix reinforced with titanium dioxide (TiO₂) nanoparticles by electrochemical methods

2.3.1. Equipment and devices used to evaluate corrosion behaviour

The characterization of the E32 naval steel corrosion and of the simple polymeric protective coatings and coatings with polymeric matrix reinforced with titanium dioxide (TiO₂) nanoparticles were done in the Electrochemical and Corrosion laboratory which is integrated in the Competences Center for Interfaces Tribocorrosion and Electrochemical Systems of “Dunarea de Jos” University of Galati.

The evaluation of corrosion behaviour was done in natural water solution taken from the Black Sea from three distinct gathering sites. E32 steel samples without corrosion protection coating and the E32 steel samples with simple polymeric protective coatings and coatings with polymeric matrix



reinforced with titanium dioxide (TiO₂) nanoparticles were submerged in natural seawater and studied through electrochemical methods.

2.4. Experimental methods and techniques for morphological characterization of E32 naval steel with and without polymeric films of corrosion protection

2.4.1. SEM - EDX

The (SEM/ESEM/EDAX) Quanta 200 scanning electron microscope was used to analyze the microstructures of the protective coatings before and after corrosion.

With the help of the SEM, the thickness of the polymeric films with and without TiO₂ nanoparticles applied on the surface of the E32 steel ship with anti-corrosive protection function was measured in cross section.

2.4.2. Roughness

The surfaces' roughness is defined as an assembly of micro-irregularities that have a relatively small step reported to depth and taken together form a well defined relief of the surface. The roughness is a parameter of the degree of surface processing.

The roughness profile of the sample surfaces were measured two-dimensional using a SurfTest SJ-210 roughness tester with inductive probe. The roughness tester is equipped with a probe needle that moves vertically to the surface of the sample so, a 2D profile was obtained. The probe needle has a diamant tip, the measuring speed was 0,25 mm/s, the stroke length was 16 mm and the measurement method was differential inductive and the digital filter which the roughness tester is equipped is Gauss type.

2.4.4. X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique used in characterizing crystalline materials. The method offers information about structures, phases, the orientations of the crystal (texture) and other structural parameters like the average grain size, crystallinity, stems and defects of crystals.

In order to further understand this technique, X-rays are electromagnetic radiations with a wavelength between 0.01 and 100 Å. Therefore, for X-ray diffractions, the wavelength also falls within the given range which is analogous to inter-atomic spacing in a crystal. For example, diffraction generally appears when a material with an ordered arrangement of atoms or molecules it is bombarded by X-ray radiation, as consequence, the generated diffraction pattern is unique for a certain phase of the material.

When a crystal is irradiated with an X-photon beam that has a wavelength similar to the



inter-atomic separation, it emits an X-ray beam with a wavelength equal to that of the incident beam, which then propagates. The scattered waves interfere to generate diffracted waves with higher intensities.

The diffraction effects can be noticed when the electromagnetic radiation affects periodic structures with geometrical variations on the wavelength scale of the radiation.

2.4.5. Evaluating hydrophobic properties of surfaces

Determining and registering the data, which contains values of the contact angle between the surfaces of the E32 naval steel with and without analysed protective coatings and the distilled water drops from these surfaces, was done with the help of contact angle measuring equipment, known as goniometer - OCA 15 EC, Dataphysics, Germany, connected to a computer - SCA20 software used as the computer's interface.

2.5. Partial conclusions

In chapter II, materials, electrochemical and structural investigating methods used for studying the corrosion behaviour of the E32 naval steel with and without commercial and modified polymeric protective coatings by reinforcing the polymer with TiO₂ nanoparticles under conditions specific to the marine environment were presented.

For the study, E32 naval steel used as a support layer for coatings with polyamide epoxy resin, polyurethane acrylic paint and epoxy resin reinforced with TiO₂ nanoparticles was used.

The samples were realized using all the specifications from the standards of international class naval registers.

The E32 naval steel with and without commercial and modified polymeric protective coatings by reinforcing the polymer with TiO₂ nanoparticles samples were investigated regarding the corrosion behavior to corrosion in natural seawater by electrochemical methods.

The characterization of the surface morphology, cross-section and composition of the E32 steel and of the polymeric protective coatings was done by using the scanning electron microscope together with an X-ray analyzer.

The structural characterization of the E32 steel surfaces in sandblasted state without corrosion protective coating, but also with polymeric protective coating was done using an X-ray diffractometer.

By adding the TiO₂ nanoparticles in the polymeric resin, it was observed that the wetting properties, the roughness parameters and the micro-hardness of the polymeric protective films, applied to the E32 steel substrate, modified.

The electrochemical methods proved that were real useful in the study of the corrosion behavior of the E32 steel and of the polymeric protective coatings, offering accurate and detailed information on the behavior to corrosion of the investigated samples.



Combining the electrochemical methods and those of structural and morphological analysis proved a particular importance on-site and off-site of the surfaces properties exposed to the corrosive action of water.

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CHAPTER III

THE INFLUENCE OF WORKING PARAMETERS ON THE PROPERTIES OF ANTI-CORROSIVE POLYMERIC PROTECTION FILMS AGAINST CORROSION

Chapter III approaches the characterization of micro-hardness, roughness and hydrophobicity of E32 naval steel and of polyamide and acrylic polymeric anti-corrosive coatings with and without addition of TiO₂ nanoparticles in the polymeric matrix. Besides these investigations, the thickness of the polymeric protection coatings applied on the surface of the E32 steel was carried out and determined.

The performances of the layers of polymeric anti-corrosive coatings are influenced by a series of factors like: micro-hardness, roughness, crystal structure, thickness, the degree of hydrophobicity of the surface, wear resistance. The characterization was done by summing several tests which role was to evaluate the micro-hardness, roughness, the coatings thickness and the degree of hydrophobicity of the surfaces used to investigate corrosion behavior.

3.1. Micro-hardness of E32 naval steel and that of corrosion protection coatings

A PMT 3 microdurimeter was used to determine the micro-hardness, at an identifier penetration load of 0.1 kgf.

The significant increase of the value of micro-hardness is reported in all the studies presented in the specialized literature. However, the uniform distribution of the TiO₂ nanoparticles contributes to an increase of the micro-hardness. A better and uniform distribution of the TiO₂ nanoparticles in the polymeric matrix determines a significant reduction of the size of nanoparticle agglomerations which considerably improves the values of micro-hardness.

3.2. Coating thickness

The thickness of the polymeric coatings was measured with the help of the FEI Quanta 200 scanning electron microscope (SEM). The average thickness values used as a corrosion



protection layer are given in table 3.2.

After drying the polymer coating layers of the epoxy primer without and with the addition of TiO₂ nanoparticles in the polymeric matrix, the epoxy primer film over which the polyurethane acrylic coating was applied, the dry film thickness - DFT, were analysed in cross section using scanning electron microscopy (SEM) (Figure 3.3). The determined average thickness of each anti-corrosion protection layer was measured in distinct areas for each anti-corrosion protective polymer film for E32 steel. For each area a minimum number of 3 measurements were applied. The average DFT values are shown in table 3.3.

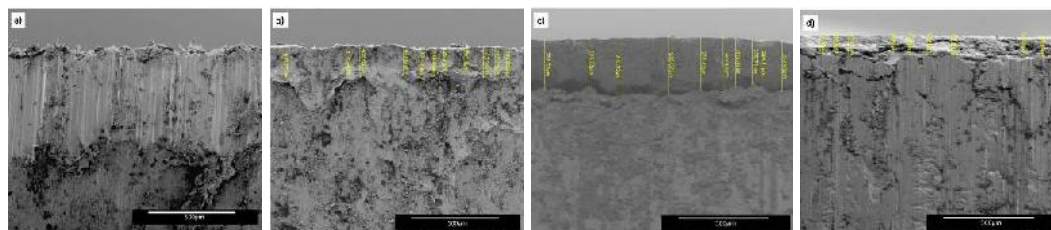


Figure 3.3. SEM micrographs in cross-section, a) sandblasted E32 steel, b) DFT of simple epoxy primer, c) DFT of simple epoxy primer over which polyurethane acrylic paint was applied and d) DFT of epoxy primer coated with TiO₂ nanoparticles

3.3. The roughness of the studied surfaces

It is unanimously recognized that the stability of the substrate coating interface is related to the adhesion forces to the material interface and the electrochemical properties of this region. The relevance of the ratio between roughness and adhesion has long been recognized [3.5]. The 2D roughness profiles were measured with the help of a Mytutoyo Surftest SJ-210 Series roughness tester by displacing the probe needle on the surface of the E32 steel in unprotected condition with the sandblasted surface and of the polymeric protective coatings, on a distance of 4.5 mm and with a speed of 0.5 μm/s. The average values of the roughness parameter R_a were measured for each sample, and are presented in table 3.4.

Tabel 3.4. The measured values of the R_a roughness parameter

| E32 unprotected | E32 with epoxy primer | E32 with epoxy primer + polyurethane acrylic paint | E32 with epoxy primer + nano - TiO ₂ |
|-----------------|-----------------------|--|---|
| 11,113 μm | 2,560 μm | 0,245 μm | 1,127 μm |

The measured 2D roughness profiles of the sample surfaces before being subjected to corrosion tests are presented in Figure 3.4.

The 3D roughness profiles presented in Figure 3.5, were obtained with the help of a software program - ImageJ1.50i by processing the SEM micrographs of the surfaces of the samples analyzed before corrosion presented in chapter 4 (Figure 4.1) by interpreting matrix

images which are composed of pixels.

An increased roughness can be connected to increasing the contact surface area. In the case a low roughness, the stability of the protective coating interface remains and in corrosive environments, the polymeric coatings have values of the roughness parameter R_a at least six times higher than those of the sandblasted surfaces [3.5].

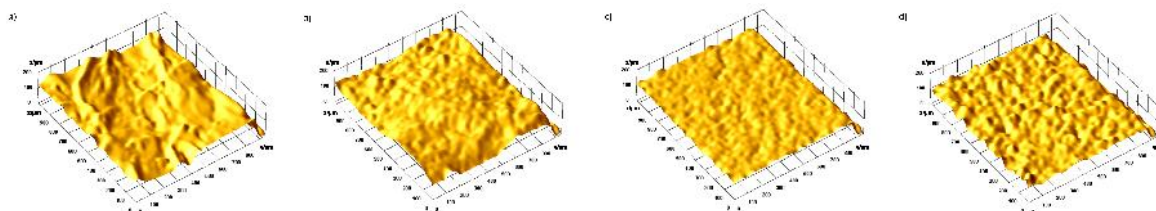


Figure 3.5. 3D roughness surface for: a) unprotected E32 naval steel, b) E32 naval steel covered with epoxy primer, c) E32 naval steel coated with epoxy primer and polyurethane acrylic paint as final layer, d) E32 naval steel coated with epoxy primer reinforced with TiO_2 nanoparticles

Thus, both the protective coatings with a thickness of the polymeric film applied to the surface of the material and those that are thin can lead to high dissemination of the solution depending on the morphology of the applied film. On the other hand, the barrier effect is more significant with thick coatings which have regular surfaces (low roughness) and in this case it could be crucial for reducing the diffusion at coating.

Thus, these two characteristics, thickness and roughness can influence the barrier effect and are relevant for understanding the protection effect of polymeric protective coatings [3.8].

3.4. Hydrophobicity of the studied surfaces

3.4.1. Measuring the contact angle

Contact angle measurements were performed to estimate the effect of hydrophobicity.

The contact angle obtained for the E32 naval steel with sandblasted surface was of 101° even if it has a high roughness. In the specialized literature is confirmed that the sandblasted surfaces have the contact angles between 97° and 116° .

3.4.2. Results obtained for the contact angle of the studied surfaces

The average contact angles measured are represented by the corresponding surface, as shown in Fig. 3.6. It can be seen, from Fig. 3.6., that the contact angles decrease when the roughness increases for polymeric protective coatings. Therefore, the increase of the hydrophilic nature of the polymeric coatings used as a protective layer for corrosion exposure, is attributed to the increased roughness of the sample surface [3.8].

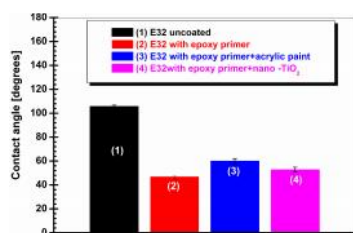


Figure 3.6. The contact angle values of the studied surfaces

3.5. Partial conclusions

From the data presented in chapter III, the following conclusions can be drawn:

After adding >100 nm TiO₂ nanoparticles in the polymer matrix of the commercial epoxy primer - Intergard 269, the Vickers micro-hardness increases significantly from 18.62 HV0.1 to 21.81 HV01. The 2D roughness profiles showed a reduction of the *Ra* roughness parameter values for the nanocomposite coating of epoxy primer reinforced with TiO₂ nanoparticles versus epoxy primer coating without addition of TiO₂ nanoparticles.

Adding TiO₂ nanoparticles lead to the modification of the hydrophobic properties for the polymer primer reinforced with TiO₂, the roughness parameters and to the micro-hardness of the polymeric protective films applied to the E32 steel substrate, due to adding the nanoparticles in the polymeric matrix.

The degree of hydrophobicity obtained by measuring the contact angle of the analyzed surfaces revealed that by adding TiO₂ nanoparticles in the polymer matrix of the commercial epoxy primer that was applied on the surface of the E32 naval steel, more hydrophobic properties of the surface coated with epoxy primer modified by adding TiO₂ nanoparticles to the simple epoxy primer.

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CHAPTER IV

MORPHOLOGICAL AND STRUCTURAL CHARACTERIZATION

In this chapter was analysed the morphology of the studied surfaces before and after the corrosion process by scanning electron microscopy and energy dispersive X-ray (EDX) compositional analysis.

4.1. Morphological characterization of the surfaces by electron microscopy scanning

4.1.1. Morphological characterization of the surfaces before the corrosion

Morphological characterization of anti-corrosive protective polymeric coatings and the surface of E32 naval steel used as substrate were done with the help of the scanning electron microscope (SEM). The morphological characterization of the E32 naval steel samples with and without polymeric protective coating was done before and after carrying out the corrosion tests by electrochemical methods.

Fig. 4.1. the SEM micrograph images of the E32 steel surface with the sandblasted surface (Figure 4.1(a)); (Figure 4.1 (b)) presents the SEM micrograph of the epoxy primer polymer coating on the E32 steel surface; (Figure 4.1.(c)) shows the protective coating applied on the steel surface with epoxy primer over which polyurethane acrylic paint was applied and (Figure 4.1. (d)) the SEM micrograph of the bicomponent epoxy primer coating in which TiO₂ nanoparticles were added.

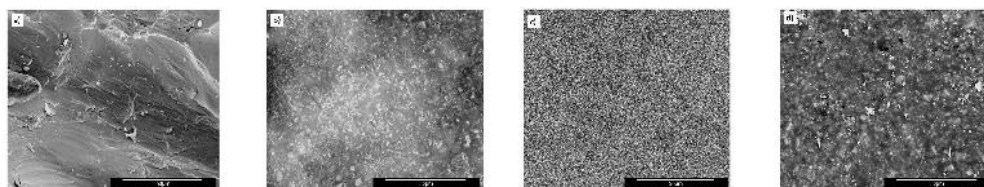


Figure 4.1. SEM micrographs according to the surfaces before the corrosion testings by electrochemical methods in seawater, a) sandblasted E32 steel, b) sandblasted E32 steel covered with epoxy primer, c) sandblasted E32 steel covered with epoxy primer and polyurethane acrylic paint and d) sandblasted E32 steel covered with epoxy primer layer reinforced with TiO₂ nanoparticles

In the Figure 4.1(a)) the SEM image shows that the surface of the sandblasted steel is rough and profiled and the polymeric coatings (Figure 4.1.b,c and d) are compact and

completely cover the surface of the E32 steel.

From the analysis of the recorded SEM micrographs of the surfaces it can be observed that the samples do not present on their surfaces products or traces of corrosion products, the surfaces being clean.

4.1.2. Morphological characterization of the surfaces after the corrosion

As expected, after immersion in seawater, significant quantities of rust, as well as rust blisters were noticed on the surface of the balsted E32 steel. In order to continue to observ the surface of polymeric coatings for corrosion protection, submerged in seawater, another set of SEM analysis were taken and the results are shown in Figure 4.2. It is obvious that the initial coatings (Figure 4.1. (b,c,d)) have a smooth surface and a similar texture, here without superficial gaps and holes uniformly distributed, probably attributed to the evaporation of the solvent during curing strengthening.

The appearance on the coating of epoxy primer reinforced with TiO₂ nanoparticles of a layer of TiO₂ that has a high anti-corrosive protection role explained the excellent anti-corrosive performances of the coating due to the presence of the TiO₂ nanoparticles added to the polymeric matrix in a concentration of 0.5 % are (Figure 4.2.(d)) [4.1. - 4.7].

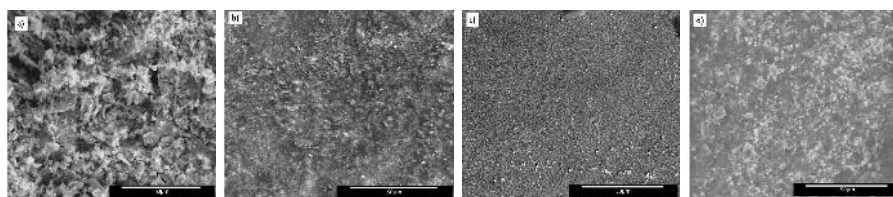


Figure 4.2. SEM micrographs according to the surfaces after the corrosion testings by electrochemical methods in seawater, a) sandblasted E32 steel, b) sandblasted E32 steel covered with epoxy primer, c) sandblasted E32 steel covered with epoxy primer and Polyurethane acrylic paint and d) sandblasted E32 steel covered with epoxy primer layer reinforced with TiO₂ nanoparticles

4.2. SEM – DEX compositional analysis

SEM – DEX compositional analysis carried out on the surfaces of the E32 steel samples and of the anti-corrosive protection films for the E32 steel match the SEM micrographs presented in subchapters 4.1.1 and 4.1.2. These SEM – DEX compositional analysis offer the perspective of better edifying images of the chemical composition from the surfaces of the E32 steel samples and of the anti-corrosive polymeric protection films in the marine environment.

4.2.1. Compositional analysis of the E32 steel surface unprotected

As it can be seen from Figure 4.3., it is clear that the majority element is iron with a percentage

of 71.94%, the elements of carbon and oxygen being considerably smaller, with a percentage of 3.72% for carbon and 24.33 for oxygen. The high content of oxygen is a result of the formation of corrosion products mainly from Fe_2O_3 and Fe_3O_4 , as it turned out also from EDX analysis.

4.3. X-ray diffraction (XRD)

Types of oxides and hydroxides of amorphous or crystalline nature, in particular, $\text{FeO}(\text{OH})$ in amorphous state (goethite) is very abundant in corrosion layers and has been widely reported in the specialized literature [2.27]. However, XRD offers better characterization of existing compounds in corrosion products (rust) [4.18 – 4.20].

Before beginning the corrosion tests, the surface of the E32 naval steel sample without anti-corrosive protection with sandblasted surface was analysed with a diffractometer to identify the majority chemical elements present on the sample's surface. Analysing the E32 sample without protective coating with the XRD iron (Fe) was identified, as noted in Figure 4.7. a) with 1, using the COD - Crystallographic Open Database with the 96-110-0109 standard (Figure 4.7. a)).

After stopping the corrosion tests on the surface of the same E32 steel sample without protective coating iron hydroxide ($\text{FeO}(\text{OH})$, (Fe III) or goethite was identified which appeared on the sample's surface as a consequence of the corrosion process, as noted in Figure 4.7. b) with 1. According to the obtained date the COD no 96-100-8767 standard was identified. The angles of the most intensive peaks were $2\theta = 21,19^\circ$, $2\theta = 33,22$ and $2\theta = 26,62$ as it can be seen in Figure 4.7 b).

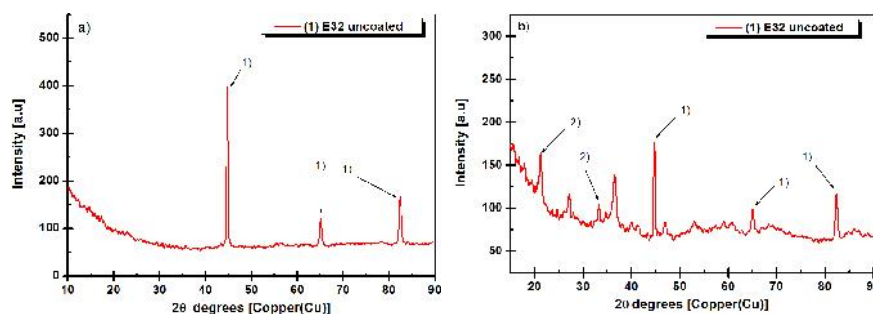


Figure 4.7. XRD diffractogram corresponding to the unprotected E32 naval steel sample:
a) before the corrosion, b) after the corrosion

The XRD images obtained on the surface of the submerged sample in seawater showed that oxygen and iron have identical positions on the surface of the E32 naval steel without protective coating resulting in the fact that the iron oxides have uniformly covered the E32 naval steel sample without protective coating. For the E32 naval steel sample covered with an anti-corrosion protection layer with epoxy primer, the E32 naval steel sample without protective coating was analysed with XRD and the chemical element bisphenol A with the chemical formula $\text{C}_{15}\text{H}_{16}\text{O}_2$ was identified.

After testing the sample with electrochemical corrosion by submerging in natural seawater it was noticed the efficiency of the anti-corrosive protection in the sense that on the surface covered with the polymeric coating layer, namely the epoxy primer, no other additional peaks specific to the corrosion products have been identified.

4.4. Partial conclusions

Following structural and compositional analyzes performed using scanning electron microscope (SEM) and elemental analysis by energy dispersion X-ray spectroscopy (EDX) of E32 naval steel samples with and without polymeric corrosion protective coatings tested by electrochemical corrosion, the following conclusions were drawn:

The SEM morphologies of the polymeric protection coatings applied on the surface of the E32 naval steel used as a substrate showed a smooth surface, without cover defects like gaps and tears spread all over the E32 steel surface. In the case of the unprotected E32 steel with sandblasted surface exposed to corrosion tests in natural seawater it was noticed that after exposure to corrosion on the surface exposed to the seawater, a dense and compact layer of corrosion products is formed throughout the surface.

For the anti-corrosive polymeric protective coating, epoxy primer applied to the surface of the E32 steel after the exposure to electrochemical corrosion, the surface remained clean without traces or agglomerations, stains with corrosion products. This demonstrates that this epoxy coating has good performances regarding the corrosion protection of naval steels which interact with seawater, respectively the marine environment.

The polyurethane acrylic coating that was applied over the epoxy primer to protect the E32 steel maintains its smooth surface observed at SEM before carrying out the electrochemical corrosion tests without traces of corrosive attack or the presence of corrosion products on the exposed surface. By adding the TiO₂ nanoparticles in the polymeric matrix of the epoxy primer, the surface's morphology changed as opposed to unmodified epoxy primer coating and this was due to the formation of a TiO₂ film following the exposure of the corrosive attack exerted by seawater.

Elemental analysis by X-ray spectroscopy by energy dispersion (EDX) and the mass percentages obtained from this analysis highlighted the presence of corrosion for the unprotected E32 naval steel sample with sandblasted surface.

Using the XRD analysis, the chemical compounds of the epoxy primer and the polyurethane acrylic paint specified in their technical data sheet were identified.

XRD analysis showed that the TiO₂ nanoparticles used for epoxy primer modification were pure crystalline anatase.

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CHAPTER V

BEHAVIOUR OF NAVAL STEEL CORROSION WITH AND WITHOUT POLYMERIC PROTECTIVE COATINGS IN NATURAL SEAWATER

In this chapter, the corrosion behaviour of the E32 naval steel without anti-corrosive protective coating and with organic coatings with polymeric films with and without TiO₂ nanoparticles is investigated. The corrosion characterization was done by using electrochemical methods monitoring the time influence on the corrosion process resulted after the interaction between the E32 steel with and without anti-corrosive protective coating. In this case, 98 days was the monitoring period.

In the last part of this chapter, the influence of TiO₂ nanoparticles on corrosion resistance of the layer of the anti-corrosive protective coatings to the action of the natural seawater taken from the Black Sea was analysed.



5.1. The influence of time in the E32 naval steel corrosion process with and without corrosion protective coatings

The corrosion resistance of the E32 naval steel with sandblasted surface and without anti-corrosive polymeric protective coating was determined in a seawater solution taken from the Black Sea, Mangalia open sea, coordinates - latitude 44°20'49.0" N, longitude 28°47'40.2"E. The solution had a pH = 8.3, 21 mS/cm conductivity and 12.8 [‰] ppt salinity.

The evaluation of the corrosion resistance of the E32 naval steel with sandblasted surface and without anti-corrosive protective coating was done by using electrochemical methods and it was compared with the corrosion resistance of the surfaces of the E32 naval steel covered with anti-corrosive polymeric protective films, respectively E32 naval steel with the surface covered with epoxy primer over which polyurethane acrylic paint was applied.

5.1.1. Open circuit potential – OCP

Open circuit potential monitoring was the first electrochemical method initiated after submerging the samples subjected to corrosion tests with the purpose to observe the behavior to corrosion of the submerged surfaces in corrosive solution (natural seawater). The total duration of the OCP monitoring was 98 days, in order to reach a stationary value of the potentials characteristic of the E32 naval steel with and without polymeric protective coatings. The Open circuit potential – OCP was measured directly relative to an Ag / AgCl electrode using a PGZ 301 potentiostat / galvanostat (VoltaLab). The corrosion tests started by monitoring the evolution of the open circuit potential, after submerging the samples in the testing solution and until the stationary state were reached. The open circuit potential measurements of the three different surfaces studied in seawater are presented in Figure 5.1.

In the case of the unprotected E32 naval steel with sandblasted surface it can be clearly seen that the OCP tendency is to slightly shift towards negative values than the initial submersion values of $E = -637$ mV, at the beginning of the corrosion evaluation tests by OCP monitoring, towards a potential value of $E = -671$ mV compared to Ag / AgCl at the end of the 98 days of immersion in electrolyte. It can be seen in Figure 5.1. that the E32 naval steel has a tendency of continuous shift towards more negative values. Gurappa attributes this fact to the inability of the unprotected steel to keep corrosion products formed on its surface [5.1].

For the E32 steel sample covered with epoxy primer it can be noticed a continuous shift of the open circuit potential from positive values from $E = -515$ mV registered at the end of the 98 days of testing, to a value of $E = -492$ mV. After a period of evolution of the potential for 77 days the open circuit potential equilibrium was reached.

The E32 naval steel sample covered with epoxy primer as an intermediate layer of the protection system, the value of the open circuit potential at the beginning of monitoring the



corrosion tests had a value of $E = -415,01$ m. It can be seen that in Figure 5.1. that the open circuit potential had a slight tendency towards positive values reaching the equilibrium state at a value of $E = -415$ mV after a 80 day period of submersion in electrolyte.

After the evolution of the open circuit potential – OCP it was established that E32 steel with anti-corrosive polymeric protective coatings has the open circuit potential shifted towards positive values than the unprotected steel with sandblasted surface which indicates a nobler corrosion behavior.

5.1.2. Polarization resistance - R_p

The evolution of the polarization resistance, R_p , was carried out by measuring 100 linear polarization curves around the open potential with a very small potential difference (± 40 mV) in order to maintain the steady state surface. As mentioned in the specialized literature, the polarization resistance is the only monitoring method of the corrosion which makes possible to measure directly the corrosion speed (put as loss of thickness over time) in real time.

The measurement of the polarization resistance (R_p) was used in order to determine the protection capacity of the polymeric coatings used as anti-corrosive protection for the E32 naval steel because the measured values of the R_p which were registered are inversely proportional to the corrosion current (a higher polarization resistance means a lower corrosion current). Corrosion resistance can be defined as oxidation resistance of the material during the application of an external potential.

The corrosion current determined by this method represents the current that appears at the metal interface/corrosive environment when the metal is submerged in solution, and represents instantaneous corrosion current. The higher the polarization resistance is the lower the corrosion speed is [5.2 - 5.5].

The polarization resistance, R_p , and the corrosion speed V_{cor} were evaluated with the help of the VoltaMaster 4 software.

As it can be seen in Figure 5.2., the minimum value of the polarization resistance (R_p) is reached by the E32 naval steel without protective coating, this starting value being $1,322$ $kohm \cdot cm^2$.

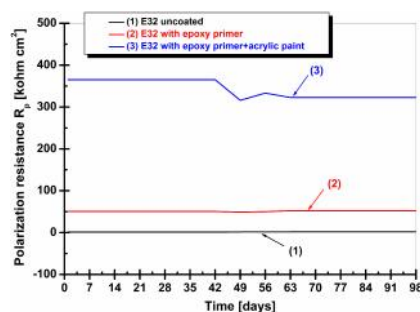


Figure 5.2. Evolution of polarization resistance for: 1) E32 naval steel without protective coating with sandblasted surface, 2) E32 naval steel coated with epoxy primer, 3) E32 naval steel coated with epoxy primer as intermediate layer and polyurethane acrylic paint as final layer during seawater immersion

This R_p value corresponding to the E32 naval steel without protective coating remains constant for 35 days in the immersion period in the seawater, then it starts to easily increase

reaching, after 42 days, the value of $1.609 \text{ kohm} \cdot \text{cm}^2$ and after 56 days it stabilizes at a value of $1.759 \text{ kohm} \cdot \text{cm}^2$.

The polarization resistance values for E32 covered with epoxy primer as a anti-corrosive protective coating registered a value in the beginning R_p equal with $50,450 \text{ kohm} \cdot \text{cm}^2$ and this value has easily dropped, reaching $48,975 \text{ kohm} \cdot \text{cm}^2$ and at the end of the 98 days of testing in the electrolyte, the R_p was $52.29 \text{ kohm} \cdot \text{cm}^2$.

The final polyurethane acrylic coating from the surface of the E32 naval steel sample had the value of $365,297 \text{ kohm} \cdot \text{cm}^2$ at the beginning of the test, after a period of 42 days the R_p value dropped at $315,972 \text{ kohm} \cdot \text{cm}^2$. After a period of 7 days it started to easily increase, reaching a final value of $322,634 \text{ kohm} \cdot \text{cm}^2$.

5.1.3. Evaluating corrosion resistance by electrochemical impedance spectroscopy method – EIS

The Electrochemical Impedance Spectroscopy measurements were done around the open circuit potential in natural seawater solution and the data analysis was done in the “Zview 3.4f” specialized software which numerically correlates spectrum data with an equivalent electrical circuit associated to the structure of the analyzed superficial surface layer. The EIS data were represented in the Nyquist diagram (the imaginary component of the impedance as a function of the actual component of the impedance: $-Z_{im} = f(Z_{real})$) and in the Bode diagram (the impedance module respectively the phase angle depending on the logarithm of the frequency: $\lg |Z| = f(\lg f)$; $\phi = f(\lg f)$).

In the field of high frequencies the semicircles from the Nyquist diagram are capacitive and constant over time, being determined by the charge transfer resistance and double-electric layer capacity

On the other hand, the diagrams of the E32 steel covered with protection films present a capacitive loop of high-frequency depressive semicircle and a large loop of low-frequency.

This behavior may be associated with the penetration of the electrolyte into the coating.

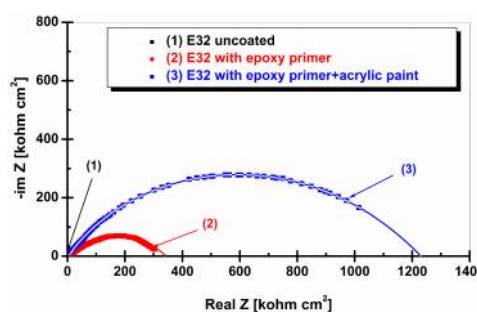


Figure 5.5. The Nyquist diagram of the measured impedance spectra (individual points) and simulated (solid line) recorded for 1) E32 naval steel without protective coating with sandblasted surface, b) E32 naval steel covered with epoxy primer, c) E32 naval steel covered with epoxy primer as an intermediate layer and polyurethane acrylic paint as a final layer

The polarization resistance of the unprotected E32 steel versus the polarization resistance for the E32 covered with epoxy primer and E32 covered with epoxy primer and polyurethane acrylic paint is very small in comparison and it was necessary to zoom in on the diagram shown in Figure 5.5 and in Figure 5.6.

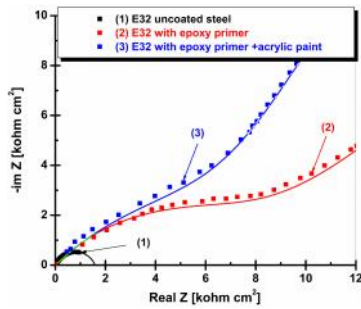


Figure 5.6. Magnification of the high frequencies for: 1) E32 naval steel without protective coating with sandblasted surface, 2) E32 naval steel covered with epoxy primer, 3) E32 naval steel covered with epoxy primer as an intermediate layer and polyurethane acrylic paint as a final layer

5.2. Evaluating the evolution of polarization resistance from EIS data during the 98-day immersion period

The polarization resistance of the surfaces of the E32 naval steel with and without anti-corrosive protective coatings subject to corrosion tests in water for 98 days was concluded by the experimental results obtained with the help of the electrochemical impedance spectroscopy and with the help of the equivalent electrical circuit. As it can be seen from Figure 5.10., the analysis for the experimental data made possible to highlight three periods in the corrosion evolution for the E32 naval steel with an without anti-corrosive polymeric protective coatings in natural water taken from the Black Sea.

The first stage, up to approximately 6 weeks of continuous submersion in seawater, the corrosion was relatively slow and the average values of the polarization resistance being constant. In the second stage, between week 6 and 8 of immersion, an increase of deterioration of the unprotected E32 naval steel surface was registered – the corrosion speed increased. After passing this time period, the corrosion speed started to decrease for the E32 naval steel samples.

The possible explanation of this phenomenon could be that after a period of immersion, which is quite long (in this case being of 9 weeks of immersion) the oxide layer formed on the surface of the unprotected E32 steel with sandblasted surface was thick and compact enough, and its pores have been plugged with insoluble salts present in the seawater which had formed due to the oxygen present in the air. With these conditions being met, it can be assumed that surface corrosion products can function as a layer with barrier properties that slow down subsequent corrosion.

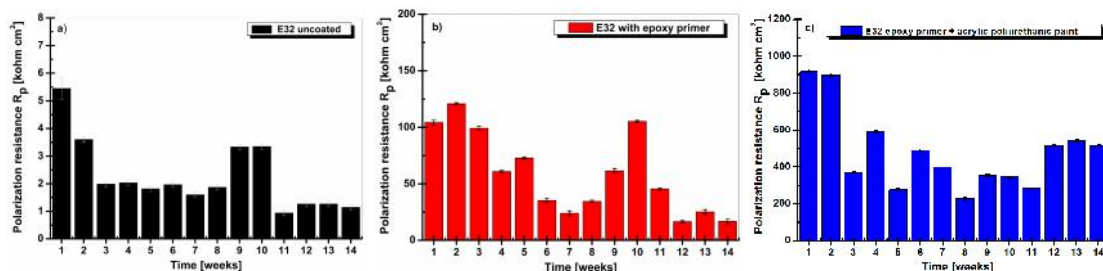


Figure 5.10. Evolution of polarization resistance in seawater from electrochemical spectroscopic impedance data for: 1) E32 naval steel without protective coating with sandblasted surface, b) E32 naval steel covered with epoxy primer, c) E32 naval steel covered with epoxy primer as an intermediate layer and polyurethane acrylic paint as a final layer during seawater immersion.

Like it is mentioned in the specialized literature [5.1 - 5.15], after reaching a certain thickness of the oxide layer present on the E32 steel surface its adherence to the steel surface decreases a lot, in the product layer, tears appear and some of the oxides detach from the surface.

For the epoxy primer coating of the E32 naval steel from the evaluation of the polarization resistance obtained by ... the experimental data for 14 weeks, there are also distinguished, as in the case of the E32 steel without protective coating, three steps. However, the polarization resistance values of the epoxy primer coating are bigger in comparison with those registered on the E32 steel surface submerged in seawater, which indicated a higher resistance. The first stage is smaller in comparison with the evolution stage of E32 steel corrosion without protective coating (Figure 5.10.b)). It can also be noticed the same constant evolution of the corrosion until week 6, and after in week 7 and 8 there are slight increases of the polarization resistance values which stabilize without significant increases until the end of the immersion period, i.e. 14 weeks.

The highest values of the polarization resistance were registered for the E32 steel covered with polyurethane acrylic paint. The corrosion evolution in time for the polyurethane acrylic paint coating applied as a final layer over the intermediate layer of epoxy primer of the anti-corrosive protective coating system present the same three stages in the corrosion evolution for the samples submerged in seawater for a period of 14 weeks. The beginning stage in which the corrosion was very slow and constant until week 6 followed by week 7 by a slight decrease, and in week 8 there is a very sensitive increase of the polarization resistance value. After this period, the corrosion easily decreases, the polarization resistance values being constant until the end of the testing period by natural seawater immersion, i.e. 14 weeks.

5.3. Partial conclusions

Following the analysis of the data presented in chapter V, the following conclusions can be distinguished:

The corrosion behavior in water from the Black Sea for the E32 naval steel for 3 types of surfaces with and without anti-corrosive protective coatings for 98 days has been studied. For evaluating the corrosion behavior in time, natural seawater was used, taken from the Black Sea, Mangalia open sea area. For the studies regarding the corrosion behavior and evolution, electrochemical analysis methods have been used.

The evaluation of open circuit potential – OCP monitored for 98 days for the E32 naval steel samples with and without polymeric protective coatings showed for the E32 naval steel without anti-corrosive protective coating a slight shift towards negative values without reaching the state of equilibrium. This fact indicates that it is not capable of forming an oxide layer that forms a passive layer of protection against corrosion attack.

For the E32 steel samples with anti-corrosive polymeric protective coatings, i.e. coating with epoxy primer and that with polyurethane acrylic paint which were submerged for 98



days in Black Sea water, the potential of the two types of coatings had more positive values than the surface of the unprotected E32 naval steel. It can be concluded that both types of coatings of the E32 naval steel surface had nobler potentials.

From monitoring, in time, of the polarization resistance R_p determined by linear polarization method, three stages can be distinguished in the corrosion evolution during the 98 days in natural seawater, for each analysed surface with the help of this method. The first stage followed by a continuous and slow decrease for 42 days, followed by a slight decrease for 4 days of the polarization resistance values, and after this second stage, follows a slight increase of the polarization resistance values and stabilization of recorded values. The polarization resistance values R_p at the end of the 98 days registered for the surface of the E32 naval steel without protective coating have been $2,25 \text{ kohm}\cdot\text{cm}^2$. The higher values of the polarization resistance R_p have been registered at the end of the same period like in the case of the E32 steel sample without protective coating.

The highest values of the polarization resistance have been registered for the anti-corrosive protective coating of the E32 steel surface made out of the epoxy primer coating used as an intermediate layer over which polyurethane acrylic paint was applied, the values showing, at the end of the 98 days of immersion in seawater, $322,63 \text{ kohm}\cdot\text{cm}^2$.

The corrosion speed evolution V_{cor} indicated as loss of thickness in time registered over the 98 days of immersion in water from the Black Sea for the analysed samples, showed the same evolution tendency in three stages at the same time periods like in the case of the polarization resistance.

The electrochemical impedance spectroscopy – EIS showed that the anti-corrosive protective coating of the E32 naval steel surface made out off epoxy primer over which polyurethane acrylic paint was applied, had the best performances against the corrosive environment's attack, i.e. the natural seawater taken from the Black Sea in comparison with the epoxy primer coating.

The evaluation of the polarization resistance R_p in time obtained from the registered data and of the simulated data of the EIS in time is consistent with those obtained by the linear polarization method.

However, it can be admitted that the three surfaces immersed for 98 days in seawater behave similarly in the Black Sea water.

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CHAPTER VI

IMPROVING THE POLYMERIC PRIMER'S ANTI-CORROSIVE PERFORMANCES BY ADDING DISPERSE TITANIUM OXIDE NANOPARTICLES AND OBTAINING POLYMERIC NANOCOMPOSITES

This chapter looks at the influence of the TiO_2 titanium dioxide nanoparticles which were integrated in the polymeric resin of the Intergard 269 commercial epoxy primer, in order to obtain a higher corrosion resistance of the protective coating against corrosion for weak alloyed naval steels, triggered by the aggressiveness of the marine environment.

For the corrosion tests of this chapter, seawater from N vodari area was used. The reason for this choice was the existing maritime traffic in the port area, which serves Petromidia Refinery and Petrochemical plant from N vodari and can influence the characteristics of the seawater having the effect of degrading the metallic structures.

The coating thickness for protection was of 110 μm for the unmodified epoxy primer coating and 90 μm for the epoxy primer coating reinforced with TiO_2 nanoparticles.

The following electrochemical methods were used to evaluate the corrosion behavior according to the experimental protocol presented in chapter II.

6.2. The influence of the polymeric primer reinforced with TiO_2 nanoparticles on the comparative potentiodynamic polarization curves

In Figure 6.2. (a), is presented the potentiodynamic polarization curves for the three surfaces studied in seawater. Because the potentiodynamic polarization curves registered for the E32 naval steel with polymeric protective coating and with nanocomposite polymer being almost perfectly overlaid, for a better visualization of the passive domain in the



Figure 6.2. (b) an increase in the field of lower values of current densities is presented.

From Figure 6.2., it can be observed that for the unprotected E32 naval steel the registered polarization curve is characterized by a narrow passive region, like it is showed in 6.2. (b). The end of this narrow passive region has a value of 0,3 mV.

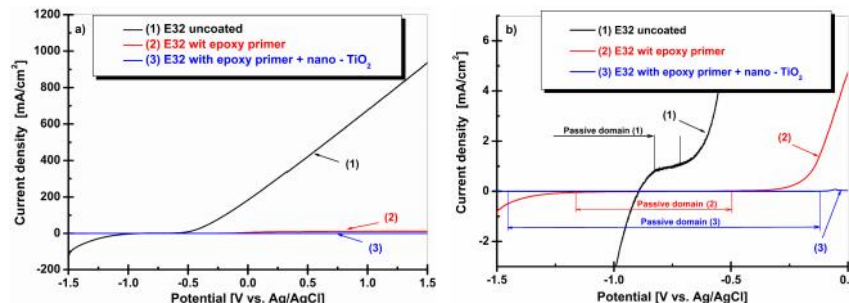


Figure 6.2. Potentiodynamic polarization curves for: 1) unprotected E32 naval steel, 2) E32 naval steel covered with epoxy primer, 3) E32 naval steel covered with epoxy primer reinforced with TiO_2 nanoparticles immersed in seawater. (a) throughout the potential field and b) increase in the field of small values of current densities.

This is indicated by the fast increase of the density of transverse current without any sign of the oxygen's evolution, as a result of the degradation of the passive layer formed on the surface and the dissolution of the steel. These narrow passive regions of unprotected E32 naval steel undoubtedly reflect the severity of the localized corrosion attack induced by Cl anions, as compared to the steel protected by the polymeric coatings.

In the case of polymeric coating, it can be noticed extended passive fields, the biggest passive field seen at the E32 naval steel covered with epoxy primer reinforced with TiO_2 nanoparticles, which once again indicates that TiO_2 nanoparticles added in the epoxide resin improves the corrosion resistance performance in comparison with the surface of the unprotected E32 naval steel.

6.3. The influence of adding TiO_2 nanoparticles in the polymeric primer on the comparative cyclic voltammetry curves

In Figure 6.3., the cyclic voltammetry curves drawn for the unprotected steel and the polymeric protective films are shown. From the Figure 6.3., it can be seen that in the case of the naval steel samples without polymeric protection, submerged in natural seawater from N vodari, at the beginning of the transpassive region, the current continues to increase until the potential is inversed and the curve turns to the initial potential over the drawn curve, indicating susceptibility to localized corrosion.

6.4. The influence of adding TiO₂ nanoparticles in the polymeric primer on the corrosion resistance evaluated by electrochemical impedance spectroscopy (EIS)

The Electrochemical Impedance Spectroscopy (EIS) measurements were done in the open circuit potential in the frequency range between 100 kHz-10 mHz with a sine wave amplitude of 10 mV. The spectra were represented in Nyquist diagrams (Figure 6.4 - 6.5) and in Bode representation (Figura 6.6 – 6.7).

In Figure 6.4., the Nyquist diagrams are presented corresponding to the surface of the unprotected E32 naval steel without protective coating as well as the EIS diagrams corresponding to the surface of the polymeric coatings and anti-corrosive nanocomposite protective coatings applied on the surface of the E32 steel submerged in seawater.

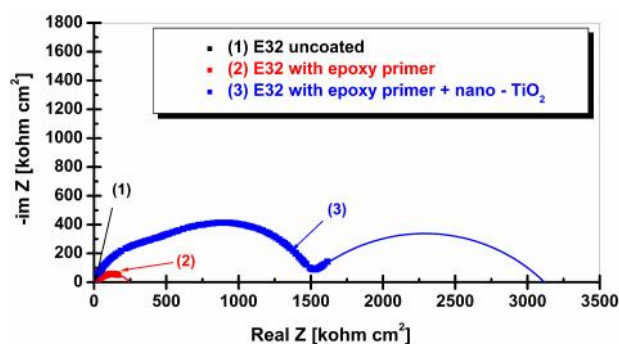


Figure 6.4. Nyquist diagram of measured (individual points) and simulated (continuous line) impedance spectra recorded in seawater for: (1) unprotected E32 naval steel, (b) E32 naval steel covered with epoxy primer, (c) E32 naval steel covered with epoxy primer modified with TiO₂ nanoparticles

As it can be seen in Figure 6.4., the semicircles presented in the Nyquist diagram for the E32 naval steel with polymeric protective coatings are big in comparison with the semicircle of the E32 naval steel without protective coating and for a better view, Figure 6.5. shows a zoom of the chart in the high frequency range.

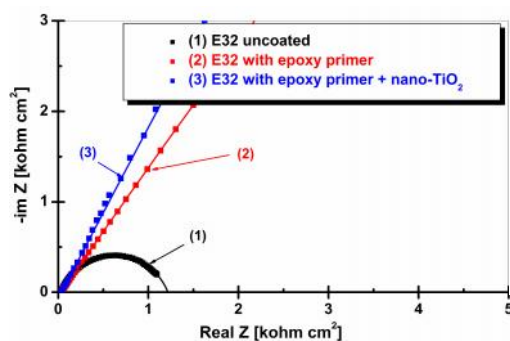


Figure 6.5. Magnification in the high frequency field of the electrochemical impedance spectroscopy chart drawn in seawater for: 1) unprotected E32 naval steel, 2) E32 naval steel covered with unmodified epoxy primer, 3) E32 naval steel covered with epoxy primer modified with TiO₂ nanoparticles

6.5. The influence of adding TiO₂ nanoparticles in the polymeric primer on the corrosion resistance evaluated in three locations in the Black Sea water

In this chapter, the destructive role of the marine environment in the Romanian sea-coast area upon metallic materials which are an integral part of different elements of metallic

structures, which can be found in marine economic-industrial units was highlighted. Hence, a comparison of the corrosion resistance of E32 naval steel with and without protective coatings under the aggressive action of the marine environment from three different geographic areas has been made. The physico-chemical parameters of seawater taken from the three points are mentioned in chapter II. N vodari, Agigea, Mangalia axis is known for its great concentration of industrial units, the great urban agglomeration (where metallic materials are integrated as construction or architectural elements permanently exposed to the interaction with the marine atmospheric environment), port areas, shipyards.

Figure 6.8. presents values resulted from modeling and simulation of diagrams measured by electrochemical impedance spectroscopy of polarization resistances R_p for the three surfaces of the E32 naval steel with and without polymeric protective coatings, respectively the simple epoxy primer coating and the modified primer by integrating TiO_2 nanoparticles in the polymeric matrix submerged in seawater taken from three distinct topographic areas of the Black Sea, namely Mangalia, N vodari and Agigea.

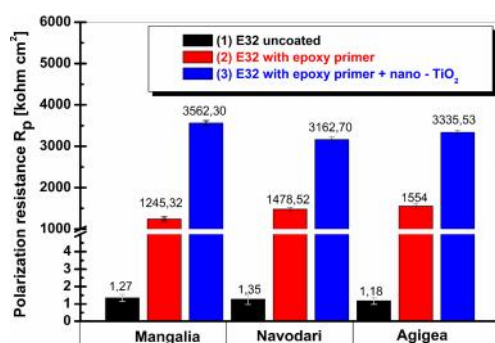


Figure 6.8. R_p polarization resistance values resulting from the modeling of electrochemical spectroscopic impedance diagrams measured for: (1) unprotected E32 naval steel, (2) E32 naval steel covered epoxy primer, (3) E32 naval steel covered with epoxy primer modified with TiO_2 nanoparticles submerged in seawater taken from three geographical areas

In Figure 6.6., it can be seen that the polarization resistance registered for the E32 naval steel covered with epoxy primer modified with TiO_2 nanoparticles submerged in seawater taken from three areas, the R_p values are equally sensitive even if the measured parameters for each seawater sample are relatively different. The effect of the TiO_2 nanoparticles added in the polymeric matrix of the epoxy primer have clearly improved the corrosion resistance of the nanocomposite primer coating, regardless of the characteristics of the seawater taken from three geographical areas, two times in comparison with the simple epoxy primer coating.

From the experimental data it can be said that the epoxy primer coating modified by incorporating TiO_2 nanoparticles into the polymeric matrix forms a much more effective protective barrier than the unmodified epoxy primer.

6.6. Partial conclusions

Monitoring the open principal at immersion of the three surfaces in seawater showed an improvement in the case of the epoxy primer coatings reinforced with dispersed TiO_2 nanoparticles in the polymeric matrix.

By tracing the potentiodynamic polarization curves, it was observed that the passive

field with the widest range was obtained for the naval steel covered with modified primer with the TiO₂ nanoparticles dispersed in the polymeric matrix of the epoxy primer.

From the cyclic voltammetry was pointed out that the unprotected steel is susceptible to localized corrosion showing specific hysteresis. The steel covered with epoxy primer in which TiO₂ nanoparticles had been added, does not show the transpassive field (the anodic current did not increase) and reveals the absence of hysteresis specific to localized corrosion.

The EIS results showed that TiO₂ nanoparticles mixed in the polymeric primer forming nanocomposite coatings have significantly improved the performances of the anti-corrosive polymeric coatings, in comparison with the unmodified polymeric primer.

Due to the TiO₂ nanoparticles insulating effect, the barrier properties of the primer coating have been increased thus, reducing the electrolyte transport and passing through the E32 naval steel coating system and reducing the corrosion process of the seawater.

The corrosion electrochemical tests indicate that the epoxy primer mixed with TiO₂ nanoparticles significantly improves the anti-corrosive performances of the coatings with epoxy primer, in comparison with the epoxy primer without TiO₂ nanoparticles.

Polymeric coating of steel structures intended for use in marine applications is essential for reducing the corrosion phenomenon in seawater.

Polymeric coatings increase the lifespan of steel structures which operate in marine environments and could contribute to the safety of their operation and at lower maintenance costs.

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CHAPTER VII

IMPROVING THE CORROSION RESISTANCE OF WELDED EH36 NAVAL STEEL STRUCTURES BY COATING WITH POLYMERIC PRIMER MODIFIED WITH TiO₂ NANOPARTICLES

In this chapter, the influence of the titanium oxide nanoparticles introduced in the polymer primer on the corrosion resistance of welded EH36 steel structures used for shipbuilding was investigated. The evaluation of the corrosion resistance was performed comparatively.

The coding of the samples is: (i) EH36 steel without protective coating used as base material with the EH36PM code, (ii) EH36 butt-welded joint in PA/1G position without



protective coating with the sample code EH36PAWJ, (iii) EH36 butt-welded joint in PA/1G position covered with unmodified polymeric primer, code EH36PAWJEP and (iv) EH36 butt-welded joint in PA/1G position covered with polymeric primer in which TiO₂ nanoparticles were dispersed, code EH36PAWJEP+TiO₂. The corrosion behavior was done by using electrochemical methods following the nanoparticles' influence on the corrosion process result of the interaction between EH36 welded steel with and without anti-corrosive protective coating in seawater. The thickness of the applied organic coatings was measured with the PCE – CT – 28 tool and the dry thickness film – DFT resulted with a value of 100 μm.

7.1. Roughness and micro-hardness of the studied surfaces

The roughness profile of the surfaces of the samples studied was measured using a Mitutoyo Surftest SJ-210 roughness meter. The following average values of surface roughness were obtained: Ra = 2.864 μm for the EH36PM steel sample base material, Ra = 3,125 μm for the EH36PAWJ with welded joint without protective coating, Ra = 2,485 μm for the EH36PAWJEP sample covered with epoxy primer.

For the EH36PAWJEP + TiO₂ sample covered with primer mixed with TiO₂ nanoparticles the average value of the surface roughness was Ra = 1.753 μm.

By comparing the parameters of the determined roughness it can be seen that the average roughness values are proximate for all studied surfaces, only for the epoxy primer mixed with TiO₂ nanoparticles the average roughness value of the surface slightly decreases at 1.753 μm confirming an improvement of the surface's quality.

7.4. The influence of TiO₂ nanoparticles from the modified polymer primer on the corrosion resistance evaluated by drawing the electrochemical impedance spectroscopy diagrams (EIS)

The electrochemical impedance spectroscopy (EIS) is the most efficient method used to obtain important information regarding the protection mechanism at corrosion provided by the protection coatings and by the passive films formed on the materials' surface.

Figure 7.4. (a, b) presents electrochemical impedance spectroscopy graphics in Nyquist representation of the tested surfaces. Because the curves for EH36PM and EH36PAWJ are very small and can not be seen clearly in Figure 7.4 (a) they are separately presented in Figure 7.4 (b).

In the Figure 7.4 (a), it can be seen the polarization resistance obtained for covering the steel with primer mixed with dispersed TiO₂ nanoparticles, code cod EH36PAWJEP + TiO₂ which has a value of approximately 1200 kohm·cm².



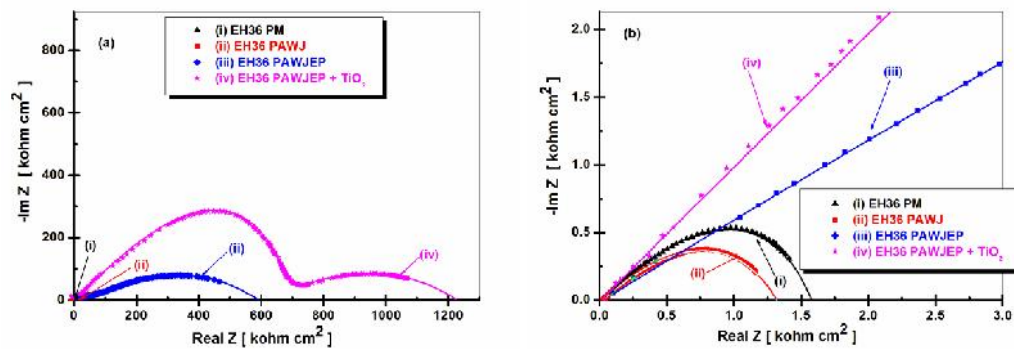


Figure 7.4. EIS diagrams in Nyquist representation for the investigated samples in seawater throughout the frequency range (a) and zoom in the high frequency range (b) for: (i) EH36PM without protective coating used as base material, (ii) EH36PAWJ without protective coating, (iii) EH36PAWJEP acovered with polymeric primer and (iv) EH36PAWJEP + TiO₂ covered with polymeric primer and TiO₂ nanoparticles. Simple symbols represent experimental data, while lines represent simulated results.

[L. Mardare data in process of publication]

The proper primer has a value of approximately 600 kohm·cm², code EH36PAWJEP, offering a lower polarization resistance in comparison with that of the primer mixed with dispersed TiO₂ nanoparticles.

7.5. Partial conclusions

From the data presented in chapter VII, the following conclusions can be clearly highlighted:

The polymeric coating of metallic structures destined for marine environment usage is essential for reducing the corrosion speed of various steels used in the naval industry at the action of the seawater.

Monitoring the open potential for the four surfaces submerged in seawater showed a shift of the open potential towards nobiler values in the case of coatings with epoxy primer coatings layers improved with TiO₂ nanoparticles.

Monitoring the polarization resistance evolution demonstrates a significant increase for the welded naval steel and covered with nanocomposite primer and the corresponding decrease of the corrosion speed.

The EIS showed that TiO₂ mixed in the epoxy primer to form nanocomposite coatings significantly improved the anti-corrosive performance of the polymeric layer compared to the epoxy primer without nanoparticles. Due to its insulating effects, the barrier properties of the TiO₂ nanoparticles, of the primer coating, reduce the transport channels for the electrolyte to pass through the coating system of the submerged samples in seawater.

Adding a low concentration of TiO₂ nanoparticles significantly improves the corrosion resistance of standard primer coatings.

The primer coatings where TiO₂ nanoparticles were added, showed an increased

resistance to corrosion when it was applied on EH36 welded steel exposed to corrosive marine environment. Hence, it was demonstrated that dispersed TiO₂ nanoparticles have an important role in protecting the modified primer coating against corrosion.

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CHAPTER VIII

GENERAL CONCLUSIONS, PERSPECTIVES AND FUTURE RESEARCH DIRECTIONS

8.1. General conclusions

8.1.1. General conclusions regarding the corrosion behaviour of E32 naval steel immersed in natural seawater

The corrosion behavior of the E32 naval steel without anti-corrosive protection and with polymeric protective films submerged in natural seawater was done in water taken from three distinct topographical areas of the Black Sea.

The purpose of the research was comparative evaluation of the corrosion behavior in natural seawater of unprotected steel, protected with different polymeric coatings and improving the polymeric primer by reinforcing with dispersed nanoparticles of titanium oxide.

The electrochemical methods to evaluate the corrosion resistance offered precious information about the corrosion behavior of the E32 naval steel without protective coating and about the polymeric surfaces for anti-corrosion protection of the E32 steel surface submerged in natural seawater.

Monitoring the open circuit potential – OCP showed that the E32 naval steel without anti-corrosive protective coating potential, submerged in natural seawater, does not reach the equilibrium state and the potential has the tendency to move towards negative values which indicates that it is not capable to main on its surface formed corrosion products.

Anti-corrosive polymeric protective coatings, epoxy primer, polyurethane acrylic paint and nanocomposite epoxy primer reinforced with TiO₂ nanoparticles coating showed a tendency of the potential towards positive values, indicating a nobler behavior of these coatings, a better resistance to corrosion.

Monitoring the time evolution of the polarization resistance determined by the method of linear polarization, three stages in the evolution of the corrosion for 98 days in natural



seawater are distinguished, for each analyzed surface using this method. The first stage followed by a continuous and slow decrease until 7 weeks, followed by a slight decrease for 2 weeks of the polarization resistance values and after this second stage, follows a slight increase of the polarization resistance values and stabilization of the values recorded at the end of the electrolyte test period.

The polarization resistance values recorded by the Electrochemical Impedance Spectroscopy - EIS method are in accordance with those recorded by the linear polarization method.

Analysis of the 2D profilometry of the surfaces roughness of the naval steel samples with and without anti-corrosive polymeric protective coatings, highlighted that by adding TiO₂ nanoparticles, and their dispersion in the polymeric matrix of the epoxy primer led to a reduction of surface roughness covered with epoxy primer reinforced with TiO₂ nanoparticles in comparison with the surface covered with simple primer.

Increasing the thickness of the polymeric protective film of the E32 steel increased the resistance to corrosion.

The micro-hardness of the E32 steel surface covered with epoxy reinforced with TiO₂ nanoparticles increased, compared to the surface covered with simple primer, after adding the TiO₂ nanoparticles.

The evaluation of the degree of hydrophobicity of the surface showed the more hydrophobic character for the surface covered with epoxy primer reinforced with TiO₂ nanoparticles compared to the surface covered with simple epoxy primer which indicates an increase of the corrosion resistance, correlating well with the corrosion evaluation results.

Analysis using X-ray diffraction method (XRD) showed the presents of corrosion products on the surface of the unprotected E32 steel after the corrosion test in natural seawater taken from the Black Sea. The presence of oxygen on the surface confirmed the appearance of corrosion products (FeOOH).

Moreover, the XRD analysis showed that the E32 naval steel samples with the surface covered with polymeric protective films did not show signs of corrosion products after the test in seawater.

The SEM micrographs confirmed the results obtained after the XRD analysis, the E32 naval steel surface being totally covered by a compact and dense layer of corrosion products after electrolyte testing, respectively natural seawater.

By tracing the potentiodynamic polarization curves, an extension of the passive potential range was observed for all the applied polymeric coatings with the widest interval for the TiO₂ nanoparticles dispersed in the polymeric matrix of the epoxy primer.

The cyclic voltammetry measurements proved a better behavior of the steel covered with epoxy primer where TiO₂ nanoparticles were dispersed in its polymeric matrix, which shows that they have the largest passive domain in the potential of the scanned potential. Also from the cyclic voltammetry, it was highlighted that the unprotected steel is susceptible to localized corrosion.

The EIS results showed that the TiO₂ nanoparticles mixed in the polymeric primer forming nanocomposite coatings improved significantly the performances of the anti-corrosive polymeric coating compared to the unmodified polymeric primer.

Due to the insulating effect of TiO₂ nanoparticles, the barrier properties of the primer



coating were increased thus, reducing the transport channels for the corrosion electrolyte to pass through the E32 naval steel coating system.

The better behavior of E32 naval steel coated with epoxy primer reinforced with TiO₂ nanoparticles is marked out by cyclic voltammetry measurements. The polarization diagrams did not show any increase of the current density over the entire polarization domain.

The polymeric coatings increase the lifespan of steel structures which operate in marine environments and could contribute to the safety of their exploitation and to lower maintenance costs by increasing the operating lifespan of these structures.

8.1.2. General conclusions regarding the corrosion behaviour and the increased corrosion resistance of welded EH36 steel structures

Polymeric coating of metallic structures for marine environment usage is essential for reducing the corrosion speed of various steel used in the naval industry to the seawater's action.

Monitoring the open potential of the four surfaces submerged in seawater showed a shift of the open potential towards nobler values in the case of coatings with epoxy primers improved with TiO₂ nanoparticles.

Monitoring the evolution of the polarization resistance demonstrates a significant increase in the case of welded naval steel covered with nanocomposite primer and the corresponding decrease of corrosion speed.

The EIS results showed that TiO₂ mixed in the epoxy primer to form nanocomposite coatings significantly improved the anti-corrosive performances of the polymeric coating compared to the epoxy primer unmixed with nanoparticles. Due to its insulating effects, the barrier properties of the TiO₂ nanoparticles, of the primer coating, reduce the transport channels for the electrolyte to pass through the samples' coating system submerged in seawater.

Adding a low concentration of TiO₂ nanoparticles significantly improves the corrosion resistance of standard primer coatings.

The primer coatings where TiO₂ nanoparticles were added showed a higher corrosion resistance when it was applied on EH36 welded steel exposed to corrosive marine environment. Hence, it has been demonstrated that dispersed TiO₂ nanoparticles have an important role in protecting the modified polymer coating of primer against corrosion.

8.2. Perspectives and future research directions

Diversifying the research studies regarding the corrosion behavior to seawater with different salinity concentrations from different geographical areas for naval steel.

Research studies regarding corrosion evaluation of welded joints of naval steel.

Behavior analysis to marine corrosion of sandblasted naval steel with laser.

Behavior evaluation to marine corrosion of naval steel surfaces after deformation due to mechanical stress.



Developing new polymeric protective coatings for naval steel resistance to marine corrosion.

Adhesion properties evaluation of anti-corrosive organic protective coatings for naval steel.

Evaluation of the wear resistance of organic coatings for naval steel.

Tribocorrosive evaluation studies of organic coating systems for naval steel.

Behavior evaluation of the polymeric coatings at biocorrosion by studying the effects produced by the algae from the Black Sea sea-coast.

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CHAPTER IX

PERSONAL CONTRIBUTIONS AND SCIENTIFIC ACHIEVEMENTS IN THE FIELD OF THE RESEARCH TOPIC

9.1. Personal contributions

Carrying out an extensive bibliographic study based on scientific articles from the specialized literature, on marine corrosion behavior of metallic materials, especially on naval steel and anti-corrosive protection methods used in the naval field.

Establishing a methodology by developing a working plan to ensure the optimization of corrosion behavior evaluation of the E32 naval steel and of its polymeric organic coating.

Obtaining a coating with improved corrosion resistance properties in the marine environment by using an epoxy primer modified by adding TiO₂ nanoparticles.

Identifying the seawater harvesting areas in the coastal area of the Black Sea according to its specific characteristics.

Morphological and structural characterization of E32 steel and the polymeric coatings used as anti-corrosive protective coatings.

Corrosion evaluation in time of E32 steel submerged in natural seawater taken from 3 distinct topographical areas from the Black Sea.

Evaluation of the properties of TiO₂ titanium dioxide nanoparticles to study their influence on the corrosion resistance in natural seawater taken from the Black Sea.

Identifying the electrochemical methods and their parameters in order to carry out an optimal evaluation of the properties of the E32 naval steel and its polymeric protective coatings against marine corrosion.



Developing a research plan which allows the evaluation of anti-corrosive properties of the anti-corrosive organic protective coatings.

Interpreting experimental data resulted after using behavior evaluation methods of marine corrosion of the E32 steel without protective coating and also with organic coatings using polymeric films.

Disseminating the obtained results from the researches by publishing them in scientific articles in specialized journals and participating in international and national scientific conferences.

9.2. Scientific achievements in the research field

9.2.1. Publications in ISI journals (Clarivate Analytics) – 1

1) L Benea, L Mardare, Nicoleta Simionescu, **Anticorrosion performances of modified polymeric coatings on E32 naval steel in sea water**, *Progress in Organic Coatings* 123 (2018) 120 - 127, <https://doi.org/10.1016/j.porgcoat.2018.06.020>, **Q1, I.F. = 3.420**, WOS:000444357000013

9.2.2. Publications in ISI Proceeding Volume - 4

1) L. Mardare, L. Benea, Development of Anticorrosive Polymer Nanocomposite Coating for Corrosion Protection in Marine Environment, 2017 IOP Conf. Ser.: Mater. Sci. Eng. 209 012056 DOI: 10.1088/1757-899X/209/1/012056; WOS:000423732100056

2) Laurențiu Mardare, Lidia Benea, Valentin Dumitra cu, **Behavior of naval steel with polymer protective coatings in sea water**, Proceedings of 16th International Multidisciplinary Scientific GeoConference SGEM 2016, Book 6 – Nano, Bio and Green – Technologies for a Sustainable Future, Vol. 2 – Green Buildings Technologies and Materials, Green Design and Sustainable Architecture, p. 49–56, 2016, ISSN: 1314-2704. DOI: 10.5593/SGEM2016/B62/S26.007.; WOS:000391650000007

3) Valentin Marian Dumitra cu, Lidia Benea, Laurențiu Mardare, **Influence of anodizing voltage on the morphology and corrosion resistance of 1050 aluminum alloy**, Proceedings of 16th International Multidisciplinary Scientific GeoConference SGEM 2016, Book 6 – Nano, Bio and Green – Technologies for a Sustainable Future, Vol. 1 – Micro and Nano Technologies, Advances in Biotechnology, p. 167–174, 2016, ISSN: 1314-2704. DOI: 10.5593/SGEM2016/B61/S24.022.; WOS:000391648800022

4) Doinița Pîrvu-Neagu, Lidia Benea, Valentin Marian Dumitra cu, Laurențiu Mardare, **Some corrosion problems in municipal waste water collection system of Galati**, Proceedings of 16th International Multidisciplinary Scientific GeoConference SGEM 2016, Book 5 – Ecology, Economics, Education and Legislation, Vol. 2 – Ecology and Environmental Protection, p. 743– 750, ISSN: 1314-2704. DOI: 10.5593/SGEM2016/B52/S20.096.; WOS:000391519600096

9.2.3. Publications in journals indexed in international databases - 5

1) L Mardare, L Benea, Marine corrosion behavior of EH 36 steel in the Black Sea, 2019 IOP Conf. Ser.: Mater. Sci. Eng. 572 012007, DOI: 10.1088/1757-899X/572/1/012007



2) Laurentiu Mardare, Lidia Benea; **Corrosion of architecture and infrastructure elements in Romanian Black Sea littoral area**; pp. 73-80. 17th International multidisciplinary scientific geoconference, SGEM 2017, Conference proceedings, Volume 17. Nano, bio and green – technologies for a sustainable future, Issue 62, Section Green Buildings Technologies and Materials, 29 June - 5 July, 2017, Albena, Bulgaria. ISSN 1314-2704. <https://doi.org/10.5593/sgem2017/62>.

3) Laurențiu MARDARE, Lidia BENEĂ. **Electrochemical Corrosion of Stainless Steels in Commercially Soft Drinks**. THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI, FASCICLE IX. METALLURGY AND MATERIALS SCIENCE, No. 2 - 2016, p. 19- 24. ISSN 1453 – 083X.

4) Laurentiu MARDARE, Lidia BENEĂ, Eliza D N IL , Valentin DUMITRA CU. **Polymeric coatings used against marine corrosion of naval steel EN32**. Key Engineering Materials 2016, Volume 699, Pages:71-79. <https://doi.org/10.4028/www.scientific.net/KEM.699.71>

5) Adrian Diaconu, C t lin Solomon, Lidia Benea, Valentin Dumitra cu, Lauren iu Mardare.. **Corrosion Resistance of Zinc Coated Steel in Sea Water Environment**. THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI. FASCICLE IX. METALLURGY AND MATERIALS SCIENCE, No . 3 – 2015, pag. 43 - 48. ISSN 1453 – 083X.

9.2.4. Oral communications and posters presented at international congresses, workshops and seminars - 17

1) L. Mardare, L Benea, **Marine corrosion behavior of EH 36 steel in the Black Sea**, EUROINVENT ICIR 2019 International Conference on Innovative Research May 16 th to 17th, 2019 Iasi – Romania. <http://www.euroinvent.org/cat/ICIR2019.pdf>

2) Laurentiu MARDARE, Lidia BENEĂ, Stefan Nabi FLORESCU, Danut MIHAILESCU, **Corrosion behavior in Black Sea water of welded joints processed on EH36 naval steel after bending deformation with root compression**. The 8th CONFERENCE ON MATERIAL SCIENCE & ENGINEERING, October 11-13, 2018, Galati Romania. <http://www.ugalmat.ugal.ro/BOOK%20OF%20ABSTRACT-UGALMAT2018%20.pdf>

3) Laurentiu MARDARE, Lidia BENEĂ, **Corrosion behaviour of two types of naval steel in Black Sea water protected with modified polymeric coating by addition of TiO₂ nanoparticles**, The 8th CONFERENCE ON MATERIAL SCIENCE & ENGINEERING, October 11-13, 2018, Galati, Romania. <http://www.ugalmat.ugal.ro/BOOK%20OF%20ABSTRACT-UGALMAT2018%20.pdf>

4) Stefan Nabi FLORESCU, Danut MIHAILESCU, Marius Corneliu GHEONEA, Laurențiu MARDARE, Lidia BENEĂ, **Macroscopic, microscopic and microdurty vickers HV1 analyzes of MAG-M mechanized deposited welding cords in horizontally position with solid and flux-cored wires**. The 8th CONFERENCE ON MATERIAL SCIENCE & ENGINEERING, October 11-13, 2018, Galati, Romania. <http://www.ugalmat.ugal.ro/BOOK%20OF%20ABSTRACT-UGALMAT2018%20.pdf>

5) Marius Corneliu GHEONEA, Stefan Nabi FLORESCU, Danut MIHAILESCU, Laurențiu MARDARE, Lidia BENEĂ, **Analysis of corrosion resistance of EH36 and butt welded joints in sea water**. The 8th CONFERENCE ON MATERIAL SCIENCE & ENGINEERING, October 11-13, 2018, Galati, Romania. <http://www.ugalmat.ugal.ro/BOOK%20OF%20ABSTRACT-UGALMAT2018%20.pdf>

6) Laurentiu Mardare, Lidia Benea, **Impact Of Marine Environment On Behavior Corrosion Polymer Coatings In Constanta Port Area**. 18th International Multidisciplinary Scientific GeoConference SGEM 2018, 24. Section Micro and Nano



Technologies, 30 June - 9 July, 2018, Albena, Bulgaria.

https://www.sgem.org/documents/programme/Day7_Programme_POSTER.pdf

7) Laurentiu Mardare, Lidia Benea, **Development of Anticorrosive Polymer Nanocomposite Coating for Corrosion Protection in Marine Environment**, International Conference on Innovative Research. May 25th to 26th, 2017. Iasi – Romania.

DOI: 10.1088/1757-899X/209/1/012056

http://www.euroinvent.org/conference/doc/Program_ICIR_2017.pdf

8) Laurentiu Mardare, Lidia Benea, **Corrosion Of Architecture And Infrastructure Elements In Romanian Black Sea Littoral Area**,

17th International Multidisciplinary Scientific Geoconference, SGEM 2017, 29 June - 5 July, 2017, Albena, Bulgaria, Section: Green Buildings Technologies and Materials.

https://www.sgem.org/documents/programme/Day5_Programme_WIND%20Hall.pdf

9) Laurentiu Mardare, Lidia Benea, **Degradation Of Marine Structures By Corrosion And Prevention Methods**, The IVth edition of the international conference of young researchers, 25th - 27th October 2017, Galati, Romania.

http://www.teme.ugal.ro/Program_TEME_2017.pdf

10) Lauren iu MARDARE, Lidia BENE. **The corrosion behavior of naval steel covered with polymeric paints in seawater**. Section I: Advanced Materials and Technologies (TMA 2016).

7th edition of International Conference on Material Science & Engineering - UgalMat 2016, 19 - 21 Mai 2016, organized by Department of Material Science and Engineering, Faculty of Engineering, "Dunarea de Jos" University of Galati, Romania.

<http://www.ugalmat.ugal.ro/>

<http://www.ugalmat.ugal.ro/Poster/FINAL%20PROGRAMME%20UgalMat2016.pdf>

11) Lauren iu MARDARE, Lidia BENE. **Effect of ZnO nanoparticles on different polymer coatings for marine corrosion**. Session: NanoEngineering, NANO-37.

11th International Conference on Surfaces, Coatings and Nanostructured Materials – NANOSMAT 2016, 6 – 9 Septembrie 2016, Aveiro, Portugal.

<http://www.nanosmat-conference.com/default.asp>

[http://www.nanosmat.co.uk/Downloads/Programme%20NANOSMAT%202016%20\(FINAL\).pdf](http://www.nanosmat.co.uk/Downloads/Programme%20NANOSMAT%202016%20(FINAL).pdf)

12) Lauren iu MARDARE, Lidia BENE. **Influence of polymer coatings against marine corrosion**. Session: Marine Corrosion, O-65837, pg. 77 – Scientific Programme.

The European Corrosion Congress – EUROCORR 2016, Advanced in linking scienceto engineering, Le Corum - Montpellier Conference Centre, 11 – 15 Septembrie 2016, Montpellier, Fran a.

<http://eurocorr.org/eurocorr2016.html>

http://eurocorr.org/eurocorr_media/EUROCORR+2016+Scientific+Programme.pdf

13) Lauren iu MARDARE, Lidia BENE. **The behavior of galvanized steel used in specific marine environment**. Session: Marine Corrosion, P-65727, pg. 54 – Scientific Programme.

The European Corrosion Congress – EUROCORR 2016, Advanced in linking scienceto engineering, Le Corum - Montpellier Conference Centre, 11 – 15 Septembrie 2016, Montpellier, Fran a.

<http://eurocorr.org/eurocorr2016.html>

http://eurocorr.org/eurocorr_media/EUROCORR+2016+Scientific+Programme.pdf

14) Laurentiu MARDARE, Lidia BENE, Valentin DUMITRA CU, Eliza D N IL .

Polymeric coatings used against marine corrosion of naval steel EN32,

Symposium 3, Session 2: Polymers, Functional Surface and Interfaces II, PPE2015-35.

The 3th International Conference on Polymers Processing in Engineering - PPE 2015, 24 – 26 Septembrie



2015, Universitatea "Dun rea de Jos,, din Galați, România.

<http://www.if.ugal.ro/PPE2015/>

<http://www.if.ugal.ro/PPE2015/Program.html>

15) Lauren iu MARDARE, Valentin DUMITRA CU, Lidia BENEĂ.

Advanced materials and coatings for marine corrosive environment – improving the corrosion resistance of naval steel by polymeric coatings.

The 3rd International Conference of Young Researchers - New Trends in Environmental and Material Engineering - TEME 2015, 21 - 23 Octombrie 2015, Universitatea "Dun rea de Jos,, din Gala i, România.

<http://www.teme.ugal.ro/>

<http://www.teme.ugal.ro/Program%20TEME%202015.pdf>

16) C t lin SOLOMON, Adrian DIACONU, Lidia BENEĂ, Laurentiu MARDARE. **Corrosion resistance of zinc coated steel in sea water environment.**

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<http://www.teme.ugal.ro/Program%20TEME%202015.pdf>

17) Lauren iu MARDARE, Doini a PÎRVU (NEAGU), Eliza D N IL , Lidia BENEĂ, **Nothing stays the same for ever: The environmental degradation and corrosion of materials – applications and protection methods in marine media**, 3th International Workshop on Achievement and Challenges for Functional Surfaces Obtained by Electrochemical Methods – Processing and Characterization, NanoSurf 03/2014 jointly with PERFORM, 23 – 25 July 2014, Gala i, România.

http://www.cc-ites.ugal.ro/Invitation_Workshop_NanoSurf_03_-2014_&_PERFORM_2014.pdf

9.2.5. Oral communications and posters presented at national congresses - 3

1) Lauren iu MARDARE, Lidia BENEĂ.

The influence of TiO₂ nanoparticles added to polymeric coatings on corrosion behaviour of coated naval steel in marine environment.

Section 1: Advanced research in mechanical engineering, industrial engineering, electrical engineering and systems engineering, O.P. 1.6, pg. 8 – Book of Abstract.

Scientific Conference of Doctoral Schools, SCDS-UDJG. Perspectives and challenges in doctoral research! IOSUD-UDJG, Galati, 8 - 9 of June 2017.

www.cssd-udjg.ugal.ro

http://www.cssd-udjg.ugal.ro/files/2017/Detailed_Conference_Programme_2.pdf

2) Lauren iu MARDARE, Lidia BENEĂ.

The corrosion behavior of naval steel covered with polymeric paints in marine environments.

Section 3: Functional Materials & Nanotechnologies, O.P. 3.4, pg. 44 – Book of Abstract.

Scientific Conference organized by the Doctoral Schools of "Dun rea de Jos" University of Galați (CSSD-UDJG 2016), Fourth Edition of Scientific Conference of Doctoral Schools from UDJ Galați, 2 - 3 Iunie 2016, Galați, România.

<http://www.cssd-udjg.ugal.ro/>

<http://www.cssd-udjg.ugal.ro/index.php/abstracts>

3) Laurentiu MARDARE, Lidia BENEĂ, **Degradation of materials in specific saline environments with temperature differences and prevention methods.**

Session 3 : Functional Materials & Nanotechnologies, O.P. 3.6, p. 44-45 – Book of Abstract.

Scientific Conference organized by the Doctoral Schools of "Dun rea de Jos" University of Galați (CSSD-UDJG 2014), Fourth Edition of Scientific Conference of Doctoral Schools from UDJ Galați, 15 – 16 Mai 2014, Galați, România.

<http://www.cssd-udjg.ugal.ro/>

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9.2.6 Research results awards from the Executive Unit for Financing Higher Education, Research, Development and Innovation for the article - 1

1) L Benea, L Mardare, Nicoleta Simionescu, **Anticorrosion performances of modified polymeric coatings on E32 naval steel in sea water**, *Progress in Organic Coatings* 123 (2018) 120 - 127, <https://doi.org/10.1016/j.porgcoat.2018.06.020>, **Q1, I.F. = 3.420**.

WOS:000444357000013. Nr. curent 94, Lista 10.

<https://uefiscdi.gov.ro/resource->

[80293?&wtok=&wtkps=XY1RDsIgEETvwrffLpSWbu9gTDxBBawYLVhaMTheXeip0a+d7Myb6bHGV0C OJFhNuoAVQwKVf7MQ/n52se7BjpVfymMt26GAZpAXxQsIz3aKIROAxOabQAFZpDKIk2URqjYHGIRa+3F/2PKmZJLJUsiVSOj3s2EAggNw4GutWKNdHwMlkt9g2o1m3U3q5vRyNdRNA13MyQalLX1YE2k/zVa5K+neHw==&wchk=b330d4c966bfffdeca666071794baf014e053347](https://uefiscdi.gov.ro/resource-80293?&wtok=&wtkps=XY1RDsIgEETvwrffLpSWbu9gTDxBBawYLVhaMTheXeip0a+d7Myb6bHGV0C OJFhNuoAVQwKVf7MQ/n52se7BjpVfymMt26GAZpAXxQsIz3aKIROAxOabQAFZpDKIk2URqjYHGIRa+3F/2PKmZJLJUsiVSOj3s2EAggNw4GutWKNdHwMlkt9g2o1m3U3q5vRyNdRNA13MyQalLX1YE2k/zVa5K+neHw==&wchk=b330d4c966bfffdeca666071794baf014e053347)

9.2.7 ISI citations (Clarivate Analytics) - 3

1) L Benea, L Mardare, Nicoleta Simionescu, **Anticorrosion performances of modified polymeric coatings on E32 naval steel in sea water**, *Progress in Organic Coatings* 123 (2018) 120 - 127, <https://doi.org/10.1016/j.porgcoat.2018.06.020>, **Q1, I.F. = 3.420**.

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Citted twice in ISI indexed journals.

1.1. Foteinidis G, Tsirka K, Tzounis L, Baltzis D, Paipetis A.S. *The Role of Synergies of MWCNTs and Carbon Black in the Enhancement of the Electrical and Mechanical Response of Modified Epoxy Resins*. 2019, *Applied Sciences*, 9(18), 3757. doi:10.3390/app9183757.

1.2. Radhamani A, Lau H.C, Ramakrishna S. *Nanocomposite coatings on steel for enhancing the corrosion resistance: A review*. 2019, *Journal of Composite Materials*, 002199831985780. doi:10.1177/0021998319857807.

2) L. Mardare, L. Benea, **Development of Anticorrosive Polymer Nanocomposite Coating for Corrosion Protection in Marine Environment**, 2017 IOP Conf. Ser.: Mater. Sci. Eng. 209 012056
DOI: 10.1088/1757-899X/209/1/012056

WOS:000423732100056

citedd once in ISI indexed journals.

2.1. Paredes M, Padilla-Rivera A, Güereca L. *Life Cycle Assessment of Ocean Energy Technologies: A Systematic Review*. *Journal of Marine Science and Engineering*, 2019, 7(9), 322. doi:10.3390/jmse7090322.

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