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Comparative Study of Porphyrin Systems Used as Corrosion Inhibitors

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1. Introduction

Fundamental research in durability of materials and structures have shown great potential for enhancing the functionality, serviceability and increased life span of our civil and mechanical infrastructure systems and as a result, could contribute significantly to the improvement of every nation's productivity, environment and quality of life. The intelligent renewal of aging and deteriorating civil and mechanical infrastructure systems includes efficient and innovative use of high performance composite materials for structural and material systems. [Monteiro et al, 2002]

The word corrosion is as old as the earth, but it has been known by different names.

Corrosion is known commonly as rust, an undesirable phenomena which destroys the luster and beauty of objects and shortens their life. A Roman philosopher, Pliny (AD 23-79) wrote about the destruction of iron in his essay 'Ferrum Corrumpitar'. Corrosion since ancient times has affected not only the quality of daily lives of people, but also their technical progress. There is a historical record of observation of corrosion by several writers, philosophers and scientists, but there was little curiosity regarding the causes and mechanism of corrosion until Robert Boyle wrote his 'Mechanical Origin of Corrosiveness.'

Philosophers, writers and scientists observed corrosion and mentioned it in their writings:

- Pliny the elder (AD 23-79) wrote about spoiled iron.
- Herodotus (fifth century BC) suggested the use of tin for protection of iron.
- Austin (1788) noticed that neutral water becomes alkaline when it acts on iron.
- Thenard (1819) suggested that corrosion is an electrochemical phenomenon.
- Hall (1829) established that iron does not rust in the absence of oxygen.
- Davy (1824) proposed a method for sacrificial protection of iron by zinc.
- De la Rive (1830) suggested the existence of microcells on the surface of zinc.

The most important contributions were later made by Faraday (1791-1867) who established a quantitative relationship between chemical action and electric current. Faraday's first and second laws are the basis for calculation of corrosion rates of metals. Ideas on corrosion control started to be generated at the beginning of nineteenth century. Whitney (1903) provided a scientific basis for corrosion control based on electrochemical observation. As

early as in eighteenth century it was observed that iron corrodes rapidly in dilute nitric acid but remains intact in concentrated nitric acid. Schonbein in 1836 showed that iron could be made passive. It was left to U.R. Evans to provide a modern understanding of the causes and control of corrosion based on his classical electrochemical theory in 1923. Corrosion laboratories established in M.I.T., USA and University of Cambridge, UK, contributed significantly to the growth and development of corrosion science and technology as a multi disciplinary subject. In recent years, corrosion science and engineering has become an integral part of engineering education globally. [Ahmad, 2006]

The strong damaging effects of corrosion require establishing and taking some control measures. In accordance with the ways in which corrosion manifest, the supporting material and the specific local conditions, corrosion control can take different forms. Surely that here should also be added the use of materials maximum resistant to corrosive environment in order to limit the corrosion effects.

The practice of corrosion prevention by adding substances which can significantly retard corrosion when added in small amounts is called inhibition. Inhibition is used internally with carbon steel pipes and vessels as an economic control alternative to stainless steels and alloys, and to coatings on non-metallic components. One unique advantage is that adding inhibitor can be implemented without disruption of a process. The addition of an inhibitor (any reagent capable of converting an active corrosion process into a passive process) results in significant suppression of corrosion.

Corrosion inhibitors are substances when added in small amounts in a corrosive environment reduces significantly the corrosion rate for metallic material in contact with the environment.

A typical good corrosion inhibitor will give 95% inhibition at concentration of 80ppm, and 90% at 40ppm. Some of the mechanism of its effect are formation of a passivation layer (a thin film on the surface of the material that stops access of the corrosive substance to the metal), inhibiting either the oxidation or reduction part of the redox corrosion system (anodic and cathodic inhibitors), or scavenging the dissolved oxygen.

Some corrosion inhibitors are hexamine, phenylenediamine, dimethythanolamine, sodium nitrite, cinnamaldehyde, condensation products of aldehydes and amines, chromates, nitrites, phosphates, hydrazine, ascorbic acid, and others.

The corrosion inhibitors are added not only in aqueous solutions, but also in oils and fuels, the liquid cooling etc. can also be organic additives and coatings (varnishes, paints) on metallic surfaces.

The presence of a chemical compound in an environment, even in small concentrations, can lead to significant changes in speed and form of corrosion of a metallic material in contact with the environment. The acceleration or inhibition of corrosion processes are specific methods, dependent of metal-corrosive environment characteristics.

Corrosion inhibitors are selected on the basis of solubility or dispersibility in the fluids which are to be inhibited.[Rahimi,2004]

Porphyrins are well-known for their biological, catalytic, and photochemical properties. Considerable effort has been devoted to confining porphyrin molecules in microporous

inorganic matrixes because such a hostguest approach can improve the efficiency of photoinduced charge separation by preventing back electron transfer. Moreover, organic-inorganic composite materials sometimes offer unique properties that are not available in any of the individual parts.[Bose et al,2002].

In this paper we intend to test the corrosion resistance of two other types of organic inhibitors and to study in which conditions they behave similarly to an anticorrosive paint. The corrosion resistance was studied by cyclic voltammetry, in 20% Na_2SO_4 electrolyte solution, Tafel tests and in the salt spray chamber, using diverse exposure conditions.

The two types of organic inhibitors used in this study for comparison are:

- 5,10,15,20 tetrakis(1-methyl-4pyridyl)21H,23H-porphine,tetra-p-fosylate salt
- 4,4′,4′,4′′′(porphine-5,10,15,20-tetrayl)-tetrakis (benzeric sulfonic acid)
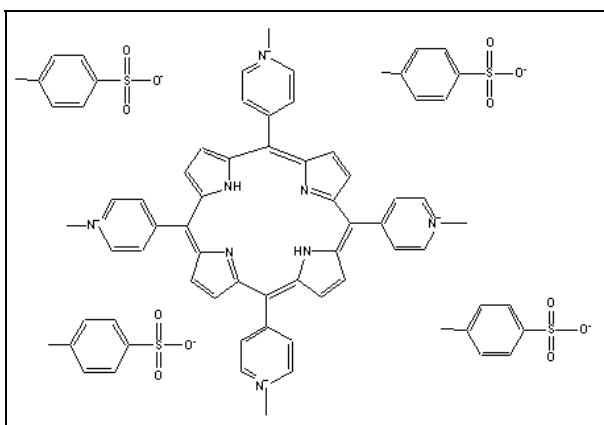
Fig. 1. Structure of 5,10,15,20 tetrakis(1-methyl-4pyridyl)21H,23H-porphine,tetra-p-fosylate salt.
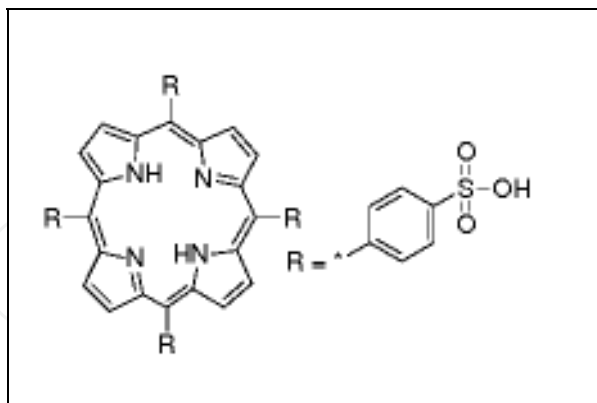
Fig. 2. Structure of 4,4′,4′,4′′′(porphine-5,10,15,20-tetrayl)-tetrakis (benzeric sulfonic acid).

2. Experimental

The initial data consisted of 2 types of porphyrins dissolved KOH, H_2SO_4 and benzonitrile, as presented bellow, as the first set:

a. 0.2 g of Na_4TFP Ac porphyrin ($C_{44}H_{26}N_4Na_4O_{12}S_4 \times H_2O$) dissolved in 40 ml 10% KOH, mentioned as system A.

b.   0.2 g of Na$_4$TFP Ac porphyrin (C$_{44}$H$_{26}$N$_4$Na$_4$O$_{12}$S$_4$ × H$_2$O) dissolved in 40 ml 10% H$_2$SO$_4$, mentioned as system B.

c.   0.2 g of H$_2$TPP porphyrin (5,10,15,20 tetrakis 4 phenyl-21H,23H) dissolved in benzonitrile, mentioned as system C.

System C presented the best anticorrosive properties.

The **second set** consists of:

a.   0.2 g of 5,10,15,20 tetrakis(1-methyl-4pyridyl)21H,23H-porphine,tetra-p-fosylate salt dissolved in 40 mL benzonitrile, mentioned from this point forward as **system I**

b.   0.2 g of 4,4′,4′,4′′′(porphine-5,10,15,20-tetrayl)-tetrakis (benzeric sulfonic acid) dissolved in the same solvent namely benzonitrile (40mL) mentioned from this point forward as **system II.**

Various apparatuses were used, like the DCTC 600 salt spray chamber or the Dynamic EIS Voltalab. The results are presented as mm/year corrosion speed, thus evaluating the different coating systems.

The electrochemical studies namely cyclic voltammetry and Tafel curves carried out to test the protective layer were conducted using the PGZ 402 Dynamic EIS Voltalab. For the data acquisition the Voltamaster 4, version 7.08, was used. This specialized software can determine, based on references, from the Tafel test's values, the exact corrosion speed, measured in mm/year.

The voltammetry measurements, the Tafel tests, were conducted between -1000 and 1000 mV potentials at a sweep rate of 100 mV/s. Before each experiment, the working electrodes were polished with a series of wet sandpapers of different grit sizes (320, 400, 600, 800, 1000 and 1200). After polishing, the carbon-steel electrode are washed with ultrapure water and dried at room temperature and then the active part was immersed in porphyrin solution.

The working electrode is the carbon-steel electrode, (prepared as mentioned earlier) with 0,28 cm² active surface, (coated or uncoated); platinum counter electrode with 0.8 cm² active surface and saturated calomel electrode, (SCE), as reference electrode; all of which connected to the PGZ 402 Dynamic EIS Voltalab, from Radiometer Copenhagen.

20% Na$_2$SO$_4$ solution was used as base electrolyte.

The thickness loss and weight loss tests were not conducted, due to the relatively small size of the electrodes.

To test the corrosion resistance of the porphyrin systems eighteen electrodes were used.

For a good repeatability and accuracy the eighteen electrodes are pretreated as follows:

Three electrodes are uncoated/untreated, three electrodes are immersed for 5 minutes in **system I,** three electrodes are immersed for 60 minutes in **system I,** three electrodes are immersed for 5 minutes in **system II,** three electrodes are immersed for 60 minutes in **system II,** three electrodes are coated with anticorrosive paint. The porphyrin systems are dissolved and then applied on the electrodes; the electrodes are immersed in the solution for 5, respectively for 60 minutes, thus simulating a shorter and a longer exposure time.

After testing the porphyrin systems by electrochemical studies, the DCTC 600 dry salt spray chamber, (Figure 2) and the ASTM B 117 method (dry salt spray corrosion test), were used. The method establishes the spraying and drying times respectively the spraying and drying frequencies; in our case, the 5% NaCl solution is sprayed for 5 minutes at 35°C, afterwards is dried at 50°C for 55 minutes. The salt solution was prepared using 1 kg of pure NaCl dissolved in 20 liters of distilled water, resulting the 5% NaCl solution, mentioned earlier.

The exposure time in the salt spray chamber of the probes was 336 hours.

3. Results and discussions

Regarding the electrochemical studies of the corrosion resistance of the protective layers formed from the first set of porphyrin it has been demonstrated that the electrodes which have been treated with the system C (0.2 g of H_2TPP porphyrin (5,10,15,20 tetrakis 4 phenyl-21H,23H) disolved in 40 mL benzonitrile) gave the best results. The immersion time was 5 minutes.

Parameters	Electrodes			
	Uncoated	System A	System B	System C
$i^{\rightarrow}_{peak}\,[mA/cm^2]$	290	190	90	280
$\varepsilon^{\rightarrow}_{pic}\,[mV]$	900	750	600	1300
$i^{\leftarrow}_{peak}\,[mA/cm^2]$	-	60	100	85
$\varepsilon^{\leftarrow}_{peak}\,[mV]$	-	50	100	50
$\varepsilon_{O2}\,[mV]$	1500	1500	1500	1500
$\varepsilon_{pas}\,[mV]$	1350	900	850	1600
$i_{pas}\,[mA/cm^2]$	25	8	0	50

Table 1. Results of cyclic voltammograms.

Parameters	Electrodes			
	Uncoated	System A	System B	System C
$i_{cor}\,[mA/cm^2]$	0.7666	0.9792	0.6506	0.0718
$v_{cor}\,[mm/year]$	8.99	11.48	7.63	0.842
Rp	50.91	129.51	59.57	147.67
C	0.9962	0.9996	0.9997	1.000

Table 2. Results of Tafel test.

The notations from the table: $i^{\rightarrow}_{peak}$ – peak current density for anodic polarization; $\varepsilon^{\rightarrow}_{peak}$ – peak potential for anodic polarization; $i^{\leftarrow}_{peak}$ - peak current density for cathodic polarization; $\varepsilon^{\leftarrow}_{peak}$ - peak potential for cathodic polarization; ε_{O2} - oxygen generation potential; ε_{pas} - passivation potential; i_{pas} - passivation current.

Continuing with the tests, after we have demonstrated that porphyrin (5,10,15,20 tetrakis 4 phenyl-21H,23H) had the best results, we have realized a study to compare this porphyrin with other two types of porphyrins, namely: 5,10,15,20 – tetrakis(1-methyl-4pyridyl)21H,23H-porphine,tetra-p-fosylate salt and 4,4′,4′′,4′′′(porphine-5,10,15,20-tetrayl)-tetrakis(benzeric sulfonic acid); also used as organic inhibitors.

From the obtained voltammograms were determined the anodic i_{peak} and ε_{peak} and from the Tafel curves were determined the corrosion current, polarisation resistance (Rp), corrosion rate and the correlation coefficient.

We continued the studies, cyclic voltammetry and Tafel method for carbon steel electrodes treated in different ways.
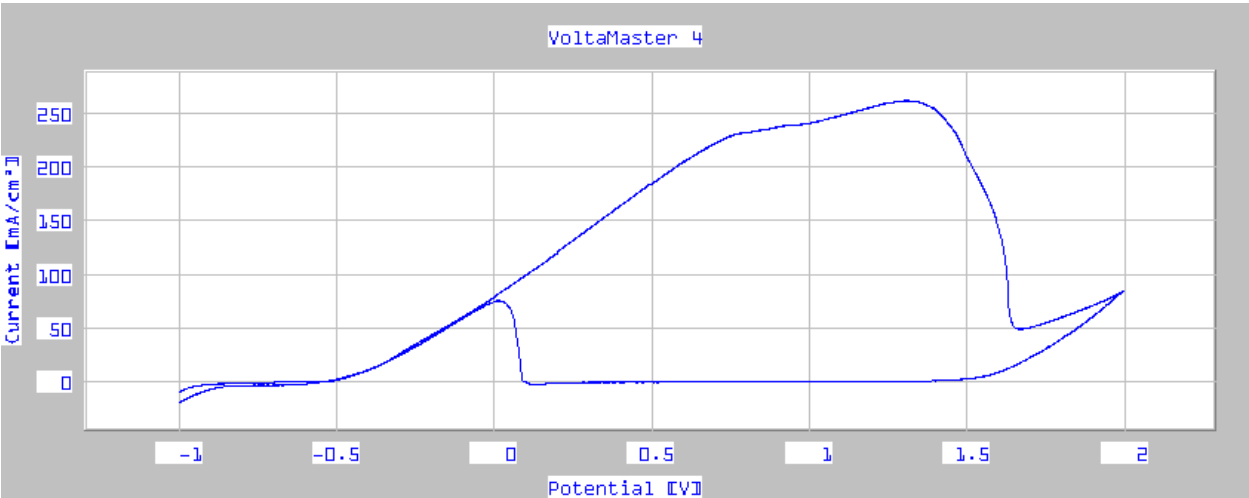
Fig. 3. Cyclic voltammograms of coated electrode with system C.
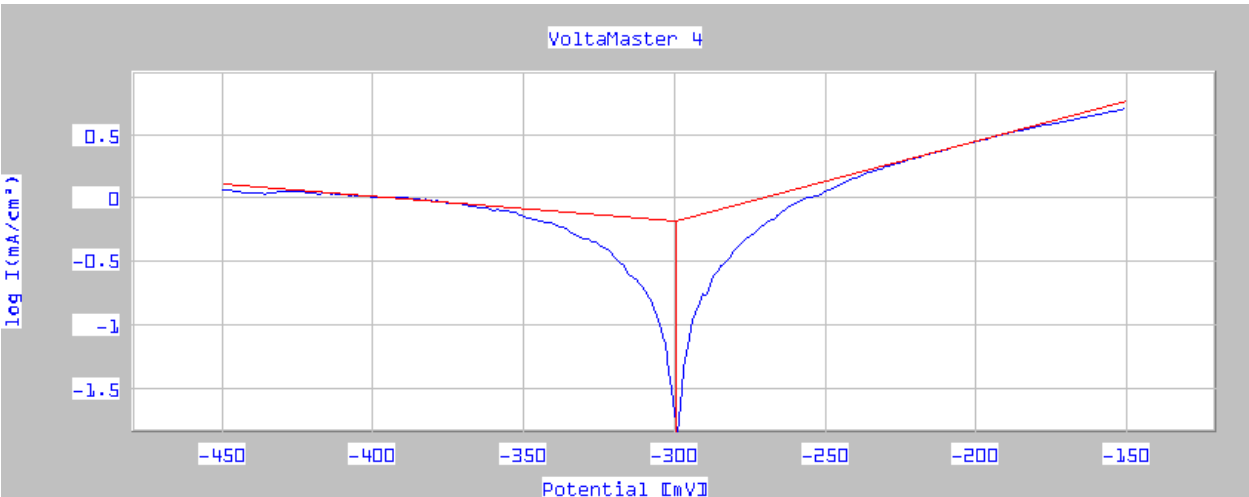
Fig. 4. Tafel tests of coated electrode with system C.
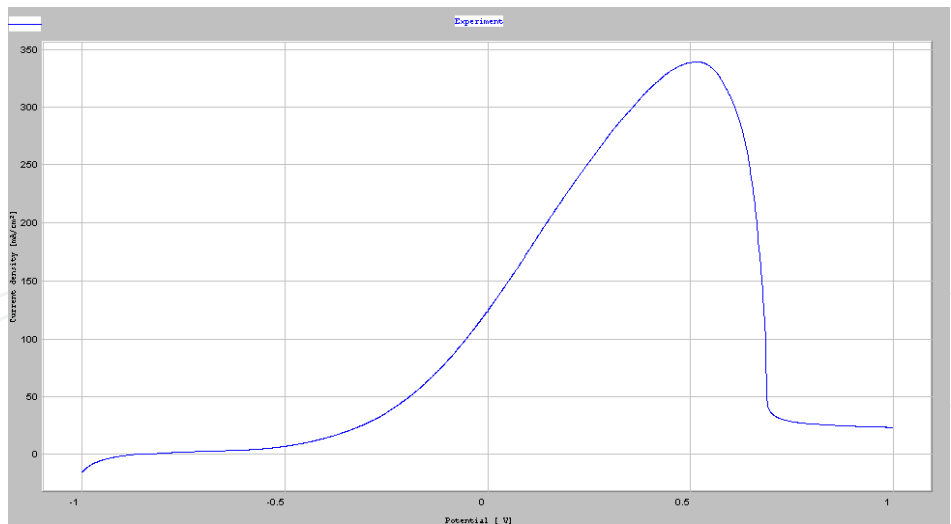
Fig. 5. Cyclic voltammogram of uncoated electrodes.
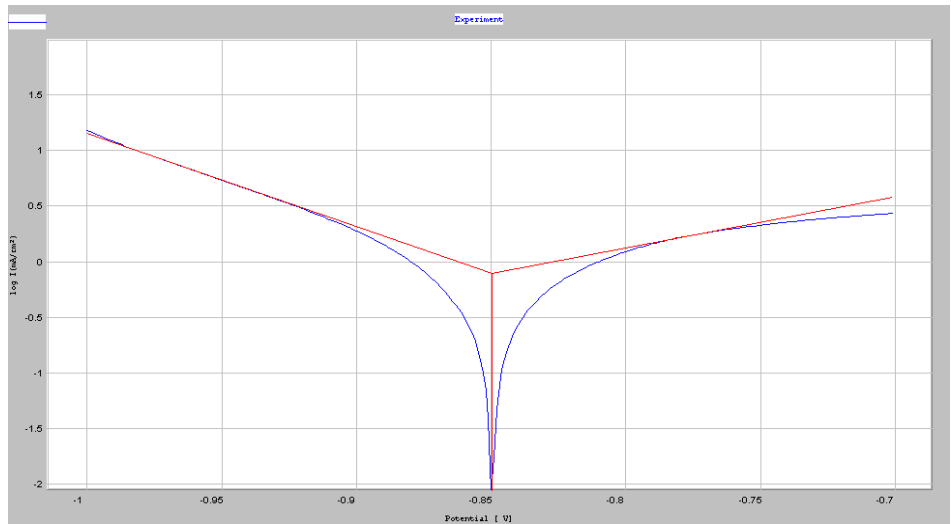
Fig. 6. Tafel tests of uncoated electrodes.
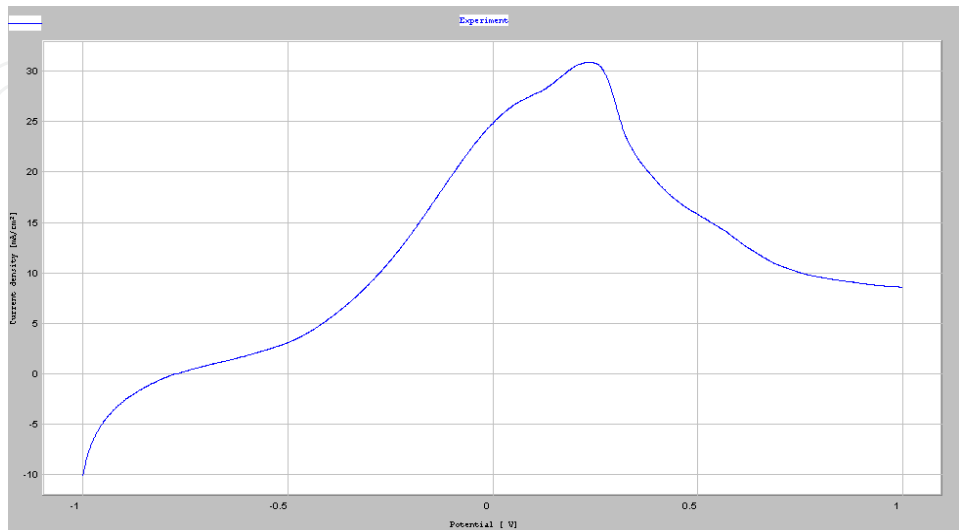
Fig. 7. Cyclic voltammogram of electrodes immersed for 5 minutes in system I.
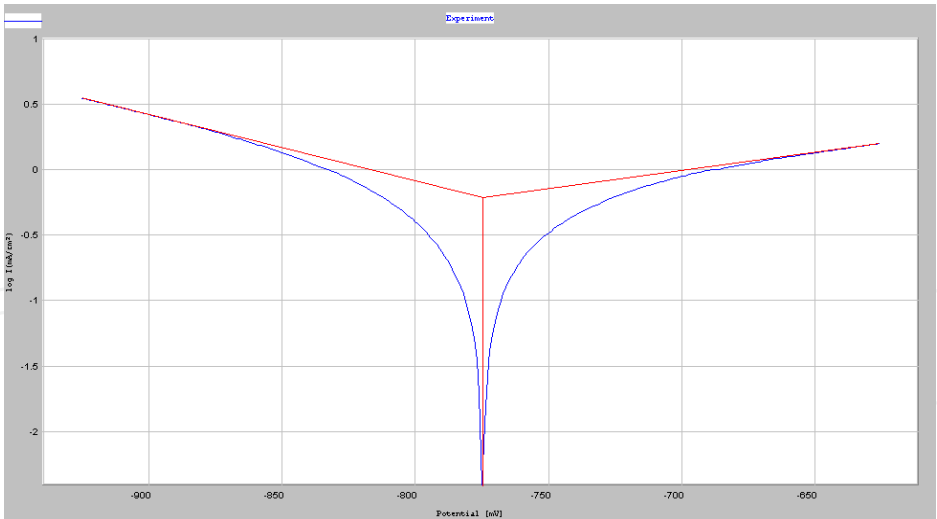
Fig. 8. Tafel tests of electrodes immersed for 5 minutes in system I
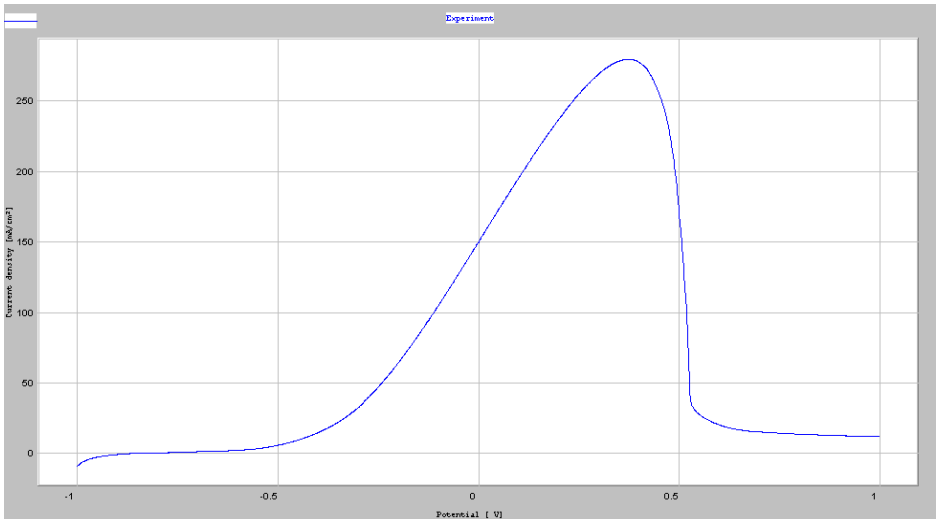
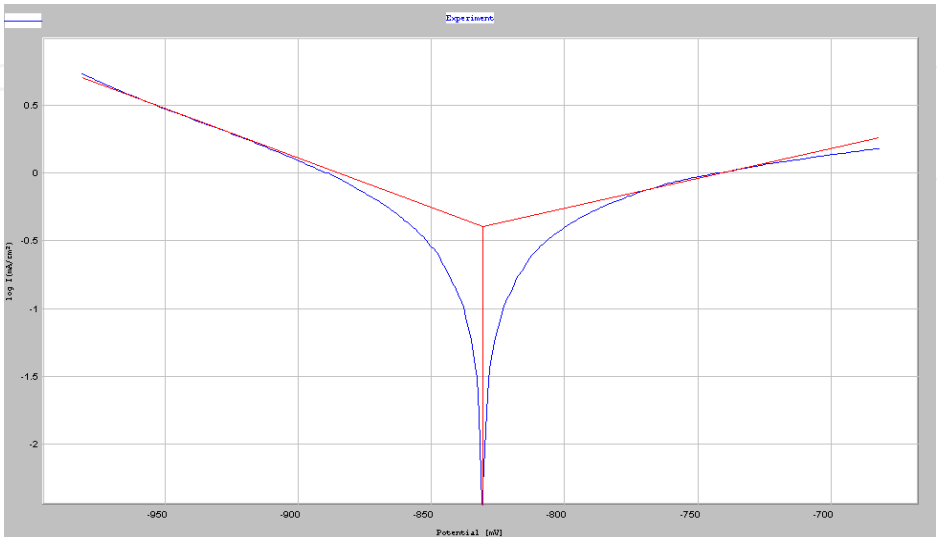Fig. 9. Cyclic voltammogram of electrodes immersed for 5 minutes in system II

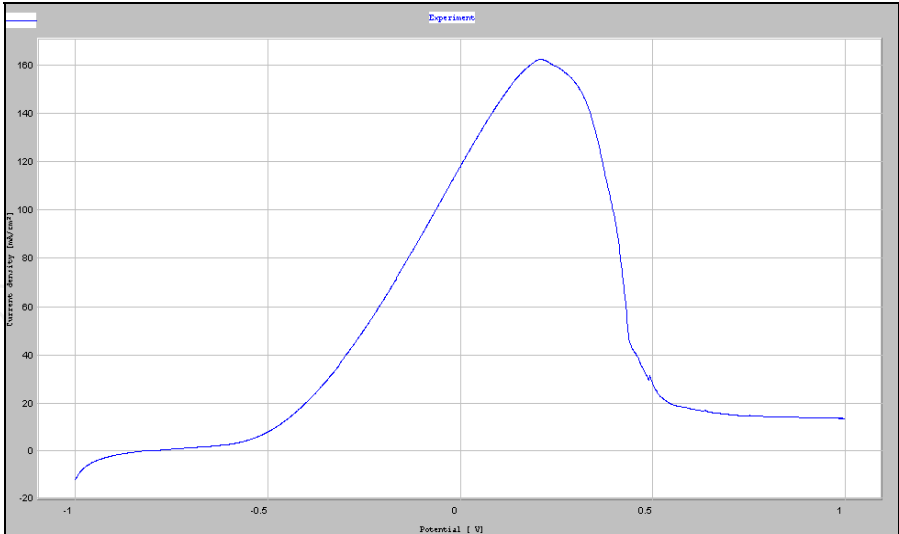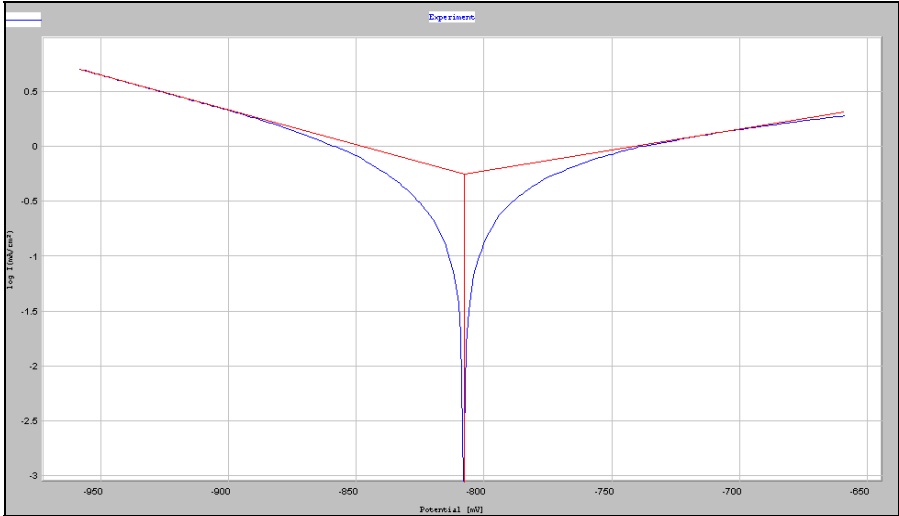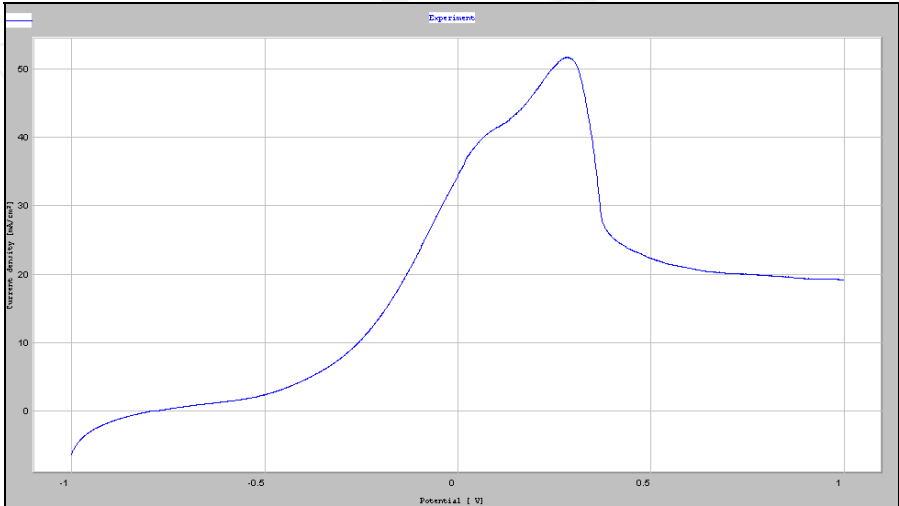Fig. 10. Tafel tests of electrodes immersed for 5 minutes in system II

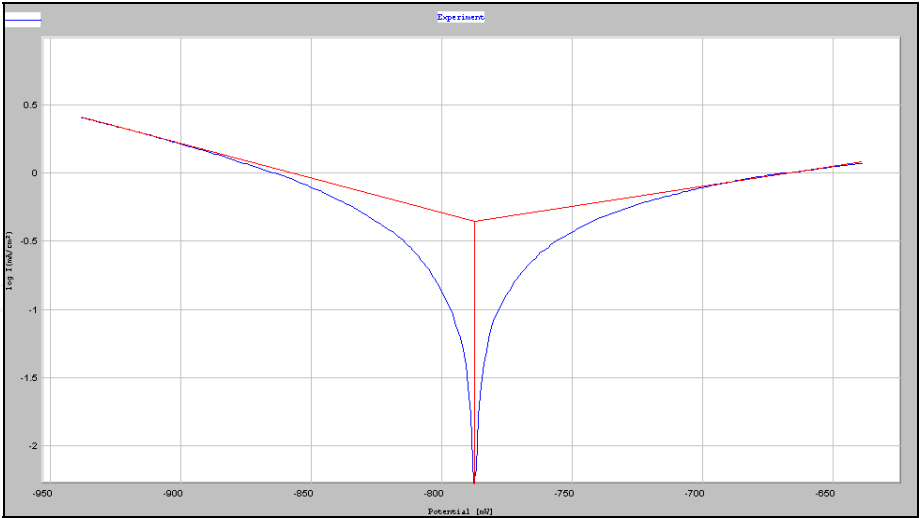Fig. 11. Cyclic voltammogram of electrodes immersed for 60 minutes in system I.

Fig. 12. Tafel tests of electrodes immersed for 60 minutes in system I.

Fig. 13. Cyclic voltammogram of electrodes immersed for 60 minutes in system II.

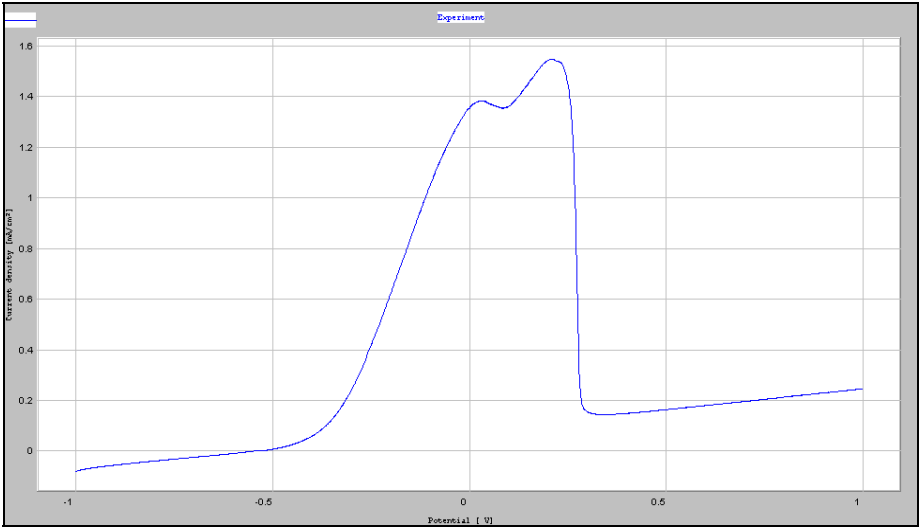Fig. 14. Tafel tests of electrodes immersed for 60 minutes in system II.

Fig. 15. Cyclic voltammogram of electrodes coated with paint.
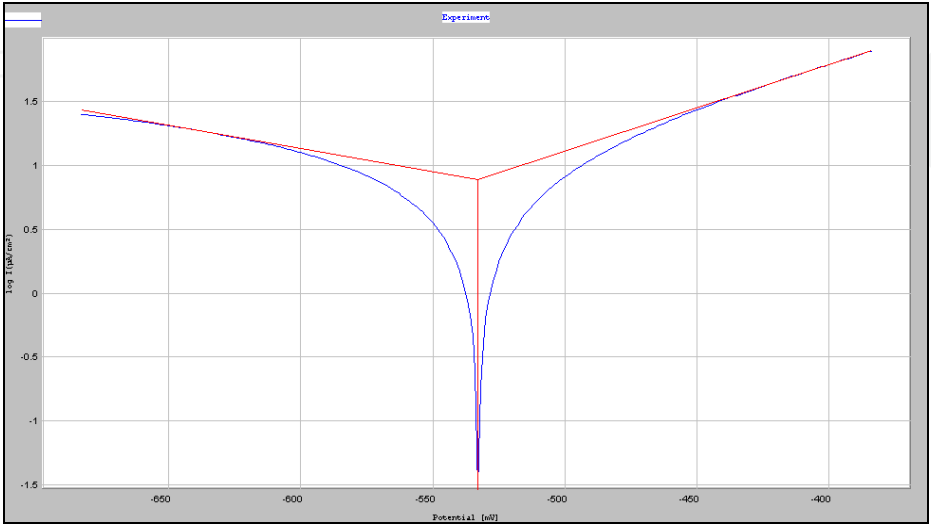

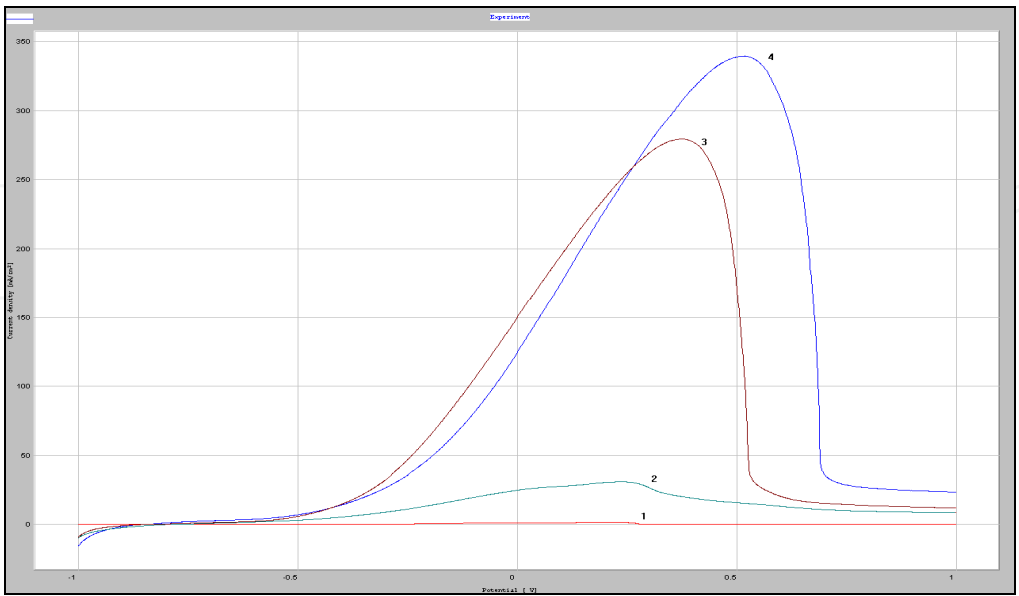Fig. 16. Tafel tests of electrodes coated with paint.

Fig. 17. Cyclic voltammograms of the corrosion process for various electrodes: 1- coated with paint; 2- system I (immersion time 5 minutes); 3- system II (immersion time 5 minute); 4- uncoated.
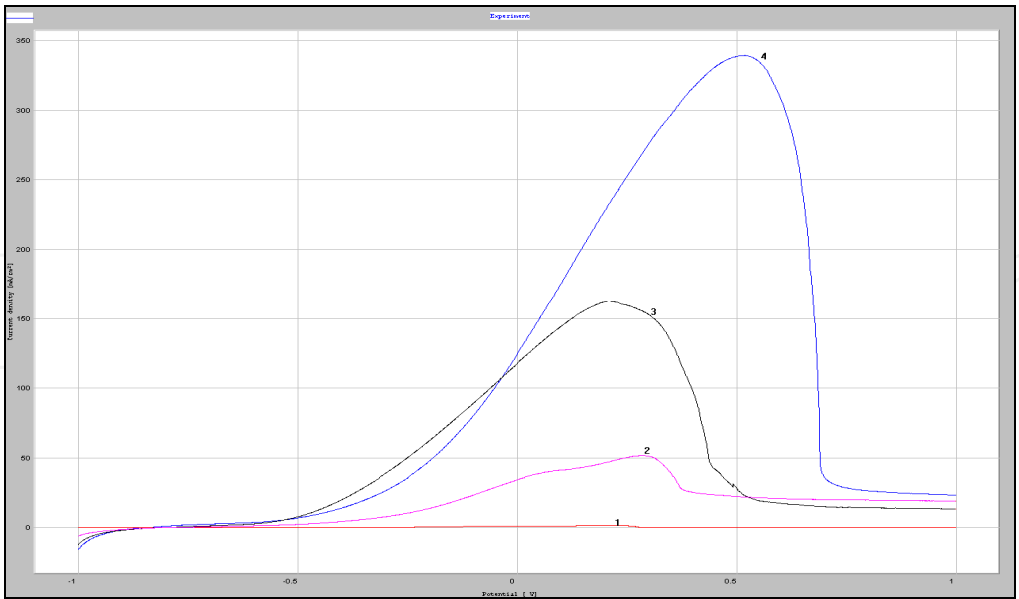

Fig. 18. Cyclic voltammograms of the corrosion process for various electrodes: 1- coated with paint; 2- system I (immersion time 60 minutes); 3- system II (immersion time 60 minute); 4- uncoated.
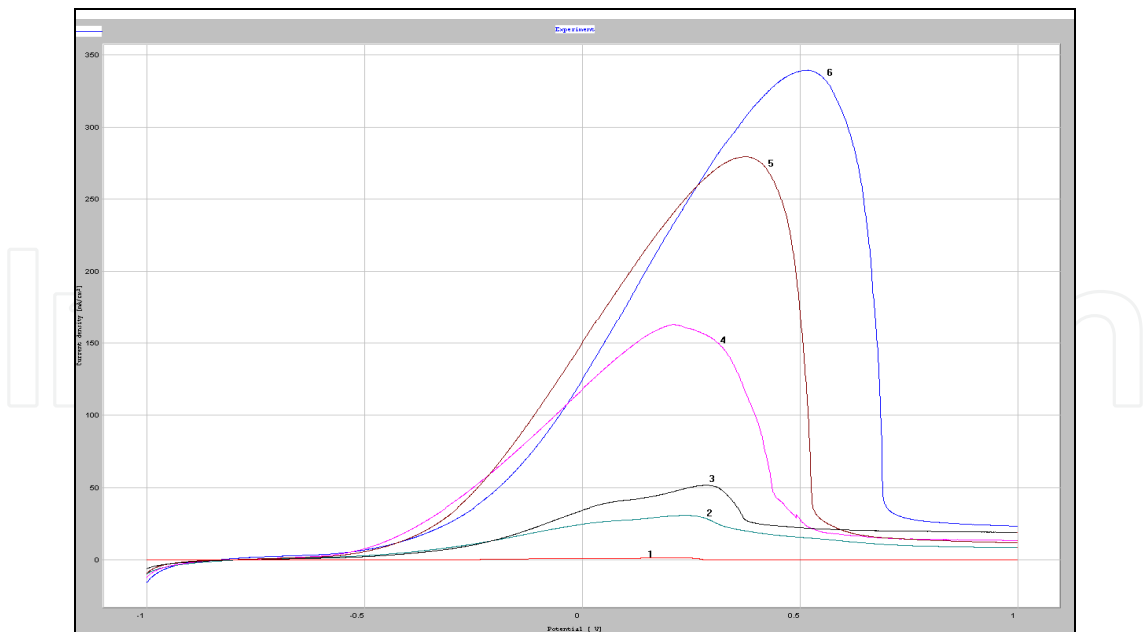
Fig. 19. Cyclic voltammograms of the corrosion process for various electrodes: 1- coated with paint; 2- system I (immersion time 5 minutes); 3- system I (immersion time 60 minute); 4- system II (immersion time 5 minute); 5- system II (immersion time 60 minute); 6- uncoated

Cyclic voltammograms and Tafel tests for 5 minutes and 60 minutes immersion time are presented in Table 3.

Parameters	Electrodes					
	Uncoated	System I		System II		Coated with paint
		Immersion time (5 minutes)	Immersion time (60 minutes)	Immersion time (5 minutes)	Immersion time (60 minutes)	
i_{peak} [mA/cm^2]	337.9	30.68	160.2	279.5	51.67	1.541
ε_{peak} [mV]	0.5178	0.2219	0.2172	0.3747	0.2824	0.21
i_{cor} [mA/cm^2]	0.7791	0.6062	0.5516	0.3983	0.4394	0.7689
v_{cor} [mm/year]	91.37	7.109	6.468	4.670	5.153	9.18
Rp	34.62	68.15	59.81	76.07	93.97	46.42
C	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Table 3. Results obtained from cyclic voltammograms and Tafel tests.

The notations from the table: i_{peak} – peak current density; ε_{peak} – peak potential; i_{cor} – corrosion current density; v_{cor} – corrosion rate; C – correlation coefficient; Rp – polarization resistance

Polarization resistance can be related to the rate of general corrosion for metals at or near their corrosion potential, E_{corr}.

These can be obtained from a *Tafel* plot or estimated from the experimental data.

The polarization resistance or R_P is defined by the following equation:

$$R_P = \left(\frac{\Delta E}{\Delta i} \right)_{\Delta E \to 0}$$

where, ΔE variation of the applied potential around the corrosion potential and Δi is the resulting polarization current.

Polarization resistance, R_P, behaves like a resistor and can be calculated by taking the inverse of the slope of the current potential curve at open circuit or corrosion potential. High R_P of a metal implies high corrosion resistance and low R_P implies low corrosion resistance.

From electrochemical studies it was observed that the electrodes treated with system I in a immersion time of 5 minutes gives better results.

For salt spray chamber tests the electrodes were investigated visually; special attention was given to the appearance of the first corrosion signs and a similar or identical evolution of corrosion rates has resulted.

The electrodes were divided into three categories namely, 3 untreated electrodes, 3 electrodes painted with anti-corrosion paint and 12 electrodes treated according with system I and system II.

These 12 fall into four subcategories, namely:

- 3 treated according to system I, with immersion time of 5 minutes, and respectively other three electrodes with an immersion time of 60 minutes.
- 3 treated according to system II, with immersion time of 5 minutes, and respectively other three electrodes with an immersion time of 60 minutes.

Visual observations:

Untreated electrodes:

• After 24 hours there is a brown coloration on the entire surface of the electrode
• The brown coloration, after 48 hours, intensifies, the electrode's surface becomes more rough
• Specific symptoms appear after 120 hours, that is uniform corrosion throughout the surface of the electrode
• Corrosion progresses, symptoms are increasing after 192 hours. Rust formed is still adherent
• After 264 hours, the rust layer becomes more voluminous
• After 336 no major changes occur.

Painted electrodes:

• After 24 and 48 hours respectively, there are no reported signs of corrosion
• Only after 120 hours, there is loss of the initial gloss paint
• After 192 hours localized corrosion can be seen as brown spots on the surface of the electrodes

- The occurrence of pitting corrosion can be observed after 264 hours; pitting spots occur among previously localized brown spots. At one of the three electrodes, the paint swells.
- After 336 hours, in addition to the initial symptoms, few and very small points of pitting are observed

Electrodes treated as system I:

- no changes can be observed after 24 hours or 48
- After 120 hours the surface of electrodes become more matte
- After 192 hours the surface of electrodes become more rough
- After 264 hours signs of localized corrosion occur
- After 336 hours pitting corrosion occurs; the number of pitting spots is very small

Electrodes treated as system II:

- no changes can be observed after 24 hours or 48
- After 120 hours the surface of electrodes become more matte
- After 192 hours pitting corrosion occurs in several points; on the electrodes with immersion time of 60 minutes the number of pitting points is lower
- After 264 hours no major differences can be observed, the pitting points do not multiply
- After 336 hours uniform corrosion is observed on 2 of the 3 electrodes, with an immersion time of 60 minutes; on the electrodes with an immerse time of 5 minutes, the rust is adhering.

4. Conclusion

In conclusion, from the three types of organic inhibitors studied, it can be said that 5,10,15,20 tetrakis(1-methyl-4pyridyl)21H,23H-porphine,tetra-p-fosylate salt, having the immersion time of 5 minutes was almost similar with the paint used and gives an anticorrosive protection much better than the porphyrin previously tested (H2TPP porphyrin (5,10,15,20 tetrakis 4 phenyl-21H,23H). Similar results can be seen, from the visual observations of the salt spray chamber test.

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Standard practice for operating salt spray (fog) apparatus, B117-02

Corrosion Resistance

Edited by Dr Shih

The book has covered the state-of-the-art technologies, development, and research progress of corrosion studies in a wide range of research and application fields. The authors have contributed their chapters on corrosion characterization and corrosion resistance. The applications of corrosion resistance materials will also bring great values to reader's work at different fields. In addition to traditional corrosion study, the book also contains chapters dealing with energy, fuel cell, daily life materials, corrosion study in green materials, and in semiconductor industry.

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