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RESEARCH ON CORROSION RESISTANCE OF STEEL PLATES FOR SHIPBUILDING

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ABSTRACT

The corrosion of metallic materials is their partial or total destruction through chemical, electrochemical or biochemical reactions, by spontaneous interaction between the surface and the corrosive medium pollution. Generally, corrosion is defined as a medium attack to a material, an attack that leads to a worsening of the properties or destruction. Corrosion is not limited to the destruction of metallic materials; it affects equally plastics, ceramics, concrete and even the environment with which they interact.

KEYWORDS: corrosion resistance, steel plates, shipbuilding

1. Introduction

Most metals in their natural conditions are not thermodynamically stable elementary metallic forms, but a combined state (oxidized or corroded) (Figure 1).

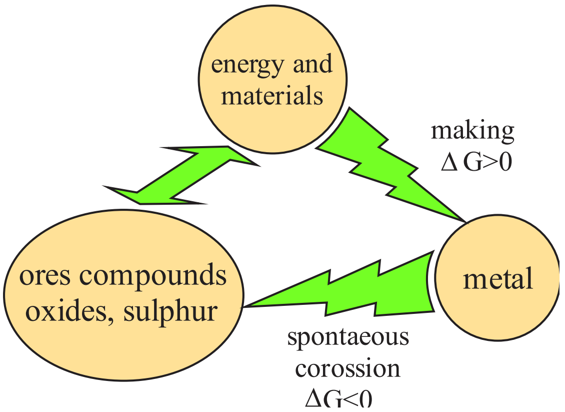


***Fig. 1.** Spontaneous thermodynamic tendency to corrode metals*

In the process of corrosion, material (solid) and environment (liquid or gas) must considered as a place where corrosion processes that occur after the general laws heterogeneous reactions of metal-environment interface (Figure 2).

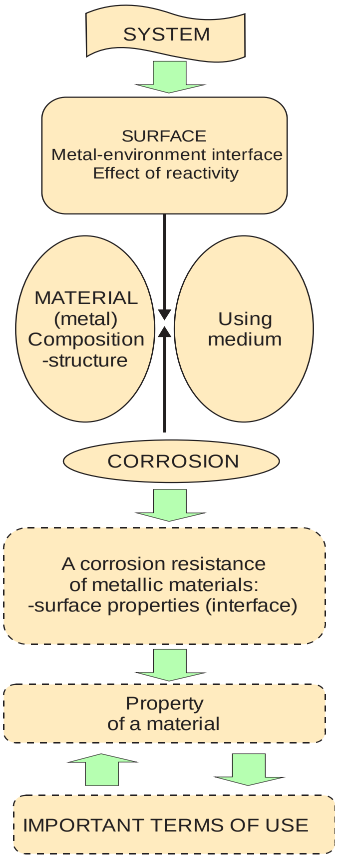


***Fig. 2.** Schematic representation of a corrosion system.*

2. Electrochemical corrosion

Electrochemical corrosion is a process involving the presence of an electrolyte, usually water or an aqueous solution, in contact with a metal. At the interface between the two, electron transfer occurs as a result of the simultaneous deployment of two types of reactions:

- ionization anode reaction (oxidation) of metal, representing its destruction/ corrosion:

$$M + n\,H_2O \xrightarrow{-ze} M^{z+} * n\,H_2O + ze$$

- cathodic reduction reaction of an agent capable of accepting electrons yielded by the metal:

$$X + ze \rightarrow X^{z-}$$

The influence of electrochemical corrosion depends on material factors and external environmental factors.

2.1. Electrochemical corrosion in natural environments

2.1 Underwater Corrosion

Underwater corrosion is primarily dependent on the nature and concentration of solutions, *i.e.* cathodic depolarization of existing agents in water by oxygen. Its concentration varies widely depending on the nature of the water (sweet, salty), its depth and temperature (Table 1). Oxygen dissolved into water acts as a cathode depolarizer; the extent to which that water contains other substances (dissolved salts, in general) increases its conductivity.

With increasing concentration of salts in the water, the corrosion rate of steel by oxygen depolarization increases to a maximum and then decreases due to decreased O_2 concentration. Both the presence and the absence of O_2 in water (increased CO_2 concentration) lead to an increased corrosion rate.

Table 1. *The concentration of O_2 dissolved in freshwater and seawater at different temperatures*

Temperature, (°C)	**Weight of dissolved oxygen**, (pp.m.)			
	Freshwater	**Sea water with chlorine**		
		5000 p.p.m. Cl^-	10000 p.p.m.Cl^-	20000 p.p.m. Cl^-
0	14.62	13.79	12.97	11.32
5	12.80	12.09	11.39	10.01
10	11.33	10.73	10.13	8.98
15	10.15	9.65	9.14	8.14
20	9.17	8,73	8.30	7.42
25	8.38	7.96	7.56	6.74
30	7.63	7.25	6.86	6.13

Assessment criteria corrosion of the vehicles are:

- optical examination - naked eye examination, microscopic examination;
- quantitative criteria: gravimetric index, penetration index;
- depending on the amount of corrosion or penetration rate (estimated by the condition of standard), the extract is shown in Table 2.

Table 2. *General assessment of corrosion condition*

	Assessment groups	**Assessment scale**	**Corrosion rate for metals with ρ< 7500 kg ·m^{-3}**	**Penetration**
			[10^{-3}kg/m^2·day]	[mm/year]
I.	Perfect resistant	1	< 0.021	< 0.001
II.	Very resistant	2 3	0.021...0.10 0.10...0.21	0.001...0.005 0.005...0.01
III.	Resistant	4 5	0.21 ...1 1.....2.1	0.01...0.05 0.05...0.1
IV.	Average resistance*	6 7	2.1...10.5 10.5...21	0.1...0.5 0.5...1
V.	Not resistant	8 9	21...105 105...210	1...5 5...10

* The metal can be used on a case by case

3. Research on salt spray corrosion resistance of steel plates for shipbuilding

The chemical composition of steel plates for shipbuilding is given in Table 3.

The NVA steel sheet was degreased with a solvent and, after blasting, the sheet was blown with air in order to obtain a clean surface.

Table 3. *Chemical composition of steel shipping,* (%)

	NVA								
Chemical composition	C	Mn	Si	P	S	Al	Ni	Cu	Cr
	0.105	0.76	0.25	0.014	0.012	0.035	0.015	0.018	0.028

Then the NVA steel sheet was coated with anticorrosive primer (EGA intergard-269), a second protective layer (interseld ENA-300) and the final layer of gloss (LAC interfin 979). The physical and chemical properties of protective varnishes are shown in Tables 4, 5, 6.

In the next stage the NVA steel sheet was subjected to the salt spray test.

Table 4. *Physical and chemical properties of INTERGARD RED 269*

State	**Liquid**
Color	Red
Ignition temperature (C º)	26
Auto - ignition temperature (Cº)	340
Viscosity	Unspecified
Density	1.29
Weight of solvent (%)	22.95
Vapor density	Heavier than air
PH	0.0
Lower explosion limit (% v / v de aer)	1.1
Solubility in water	Immiscible
Ventilation (air quantity required to reach the lower explosion limit)	87
Odour	Solvent odour

Table 5. *Physical and chemical properties of INTERSHIELD 300 BRONZE*

State	**Liquid**
Color	Dark
Ignition temperature (C º)	28
Auto - ignition temperature (Cº)	340
Viscosity	Unspecified
Density	1.138
Weight of solvent (%)	21.98
Vapor density	Heavier than air
PH	0.0
Lower explosion limit (% v / v de aer)	1.1
Solubility in water	Immiscible
Ventilation (air quantity required to reach the lower explosion limit)	62
Odour	Solvent odour

Table 6. *Physical and chemical properties of INTERFINE 979*

State	**Liquid**
Color	Dark
Ignition temperature (C º)	27
Auto - ignition temperature (Cº)	425
Viscosity	Unspecified
Density	1.19
Weight of solvent (%)	5.00
Vapor density	Heavier than air
PH	Unspecified
Lower explosion limit (% v / v de aer)	2.0
Solubility in water	Immiscible
Ventilation (air quantity required to reach the lower explosion limit)	12.91
Odour	Solvent odour

Accelerated corrosion test in salt spray

The test was conducted according to ISO 9227 in a corrosion chamber (Figure 3).

Fig. 3. *Salt spray chamber used for testing corrosion resistance.*

To carry out the test, sodium chloride solution was prepared by dissolving (conductivity less than or equal to 20 ± 2 µS/cm^2 at 25 ± 2°C) a quantity of sodium chloride in distilled water to obtain a concentration of 50 ± 5 g / L. The relative density of a solution of this concentration is between 1.00255 and 1.0400. The sodium chloride used contains less than 0.001% copper and 0.001% nickel. Also, the sodium iodide content must not exceed 0.1% and the total content of impurities must not be higher than 0.5%.

The pH of the saline solution was adjusted so that the pH of the spray solution collected in the chamber is between 6.5 and 7.2.

For this we used a pH meter HI-991001, produced by "Hanna Instruments", equipped with a temperature indicator. The saline solution supply device comprises a fresh air supply system, a reservoir containing the solution and an aerosol spray. The sprayer with compressed air supply was achieved through a filter which retains any trace of solid material or oil at a pressure of about 100 kPa. To prevent evaporation of water droplets was sprayed with air being moistened before entry into the sprayer, by passing it through a bowl of water. The spray is made of plastic (textolit), inert to corrosive environment. To prevent the direct impact of the solution sprayed samples, they were placed in the direction of the salt spray flow.

The corrosion test was conducted over 168 hours at 35°C. Initially, the samples were degreased with acetone and then weighed on a 0.01 mg precision analytical balance: on the first day, then, after three days, daily until the seventh day. The weighed samples were not placed in closed corrosion, to avoid errors due to removal of corrosion products.

Table 7. *Corrosion speed control and coated samples*

Samples	**Corrosion rate (g/m^2 day) at:**				
	3 days	4 days	5 days	6 days	7 days
Witness samples	3.85	3.02	2.17	1.86	1.79
Covered samples	0.067	0.060	0.054	0.050	0.042

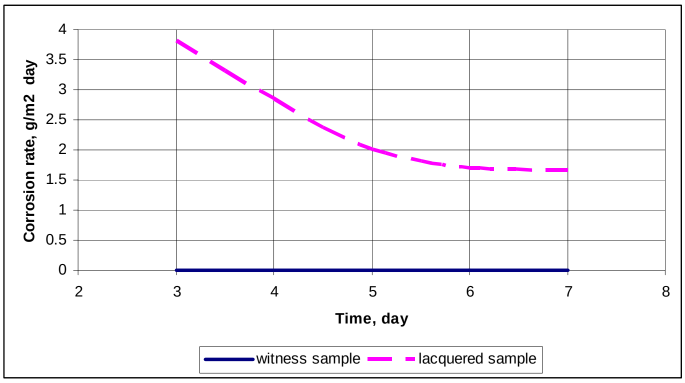


Fig. 4. *Variation of corrosion rate of steel sample.*

At the end of the test, the samples were removed from the room and were allowed to dry for 30 minutes.

To determine mass loss, corrosion products were removed by pickling resulting in 50% hydrochloric acid solution (volumetric concentration); the inhibitor was added to 3.5 g/L hexamethylenetetramine.

After the attack, the samples were well washed, at room temperature, first with water then with acetone until they were dry. Then the samples were weighed again and the mass loss and the corrosion rate were calculated using the relationship:

$$V_C = \frac{\Delta G}{S \cdot t}$$

where: V_C = corrosion rate [g/m^2 day]; ΔG = difference between initial and final sample weight [g]; S = sample area [m^2]; t = time [days].

The results are given in Table 7. The variation of the corrosion rate in time is shown in Figure 4. As shown in the graph, the corrosion resistance of samples coated with varnish is greater than that of the uncoated ones.

The general state of the corrosion rate and of the penetration index values is given in Table 8.

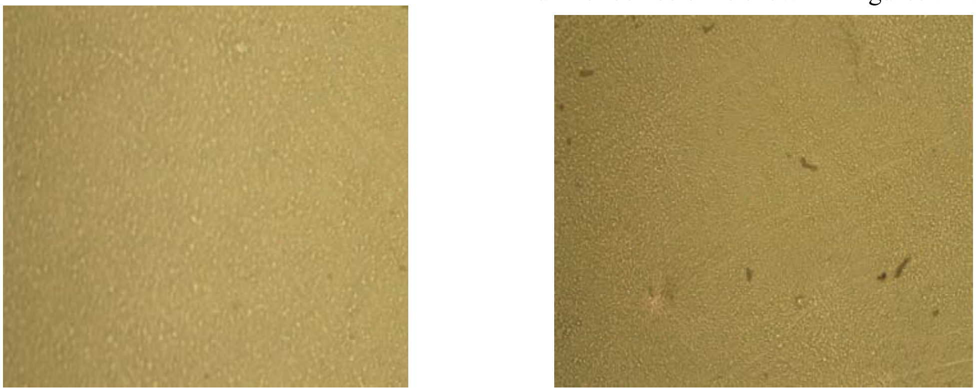
Table 8. *General state of corrosion rate and penetration index values*

Sample code	**Time**	**Weight difference**	**Penetration index**	**Group of resistance**	**Note of appreciation**
	[day]	[g]	[mm/year]		
Witness sample	3	0.0017	0.431	medium resistant	6
	4	0.0018	0.336	medium resistant	6
	5	0.0021	0.241	medium resistant	6
	6	0.0029	0.207	medium resistant	6
	7	0.0033	0.199	medium resistant	6
Lacquer coated sample	3	0.0004	0.08	resistant	5
	4	0.0008	0.18	resistant	5
	5	0.0010	0.22	resistant	5
	6	0.0013	0.29	resistant	5
	7	0.0014	0.37	resistant	5

As shown in Table 8, the penetration index values are much smaller for witness samples than for lacquer coated samples. It also notes that have uncovered evidence of assessment notice and samples coated with varnish resists corrosion better note with appreciation 5.

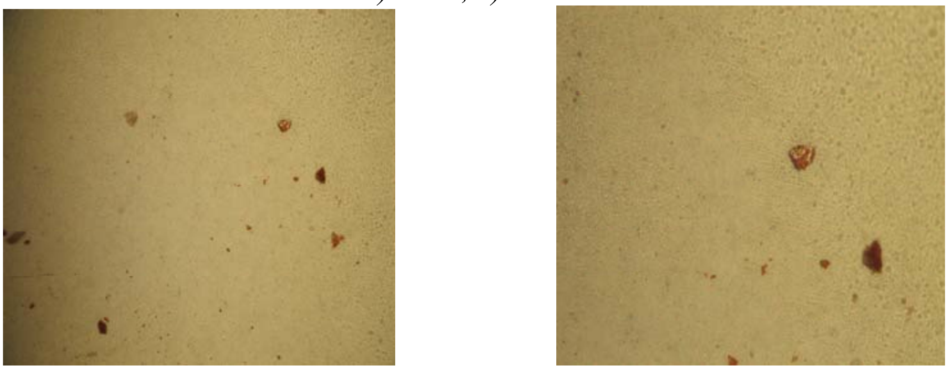
Macro structural analysis

Macro structural analysis of the samples before and after corrosion is shown in Figures 5-10.



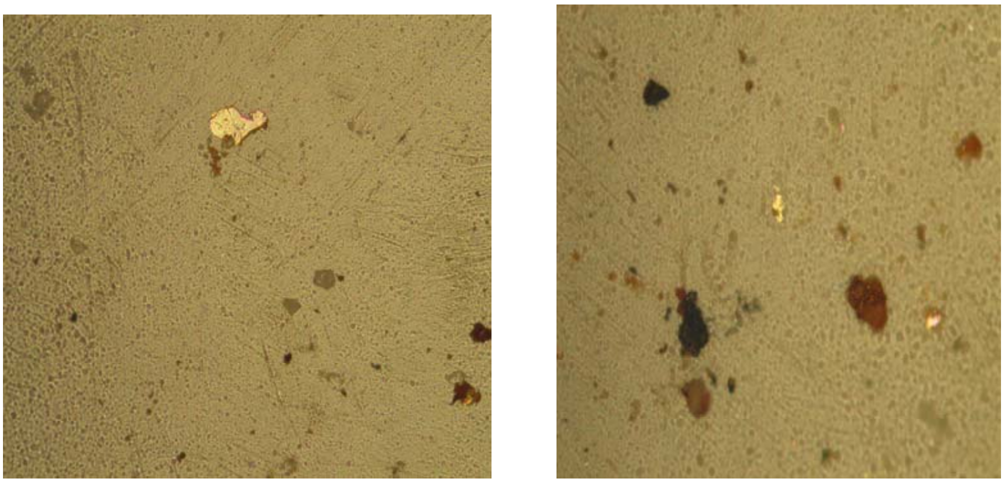
a) *b)*

Fig. 5. *Macrostructure surface: optical aspect of coated samples before corrosion: a) x 200; b) x 400.*



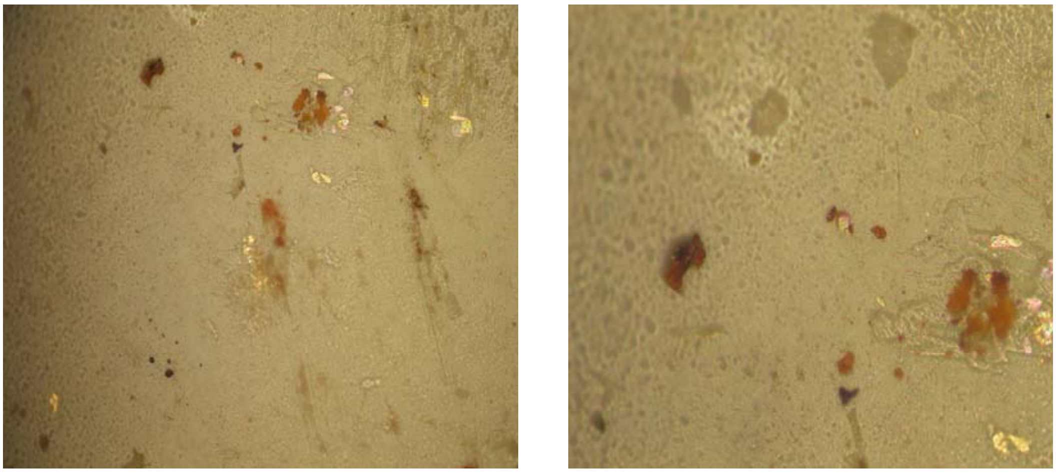
a) *b)*

Fig. 6. *Macrostructure surface: optical aspect of coated samples after 3-day keeping in salt spray: a) x 200; b) x 400.*



a) *b)*

Fig. 7. *Macrostructure surface: optical aspect of coated samples after 4-day keeping in salt spray: a) x 200; b) x 400.*



a) *b)*

Fig. 8. *Macrostructure surface: optical aspect of coated samples after 5-day keeping in salt spray: a) x 200; b) x 400.*

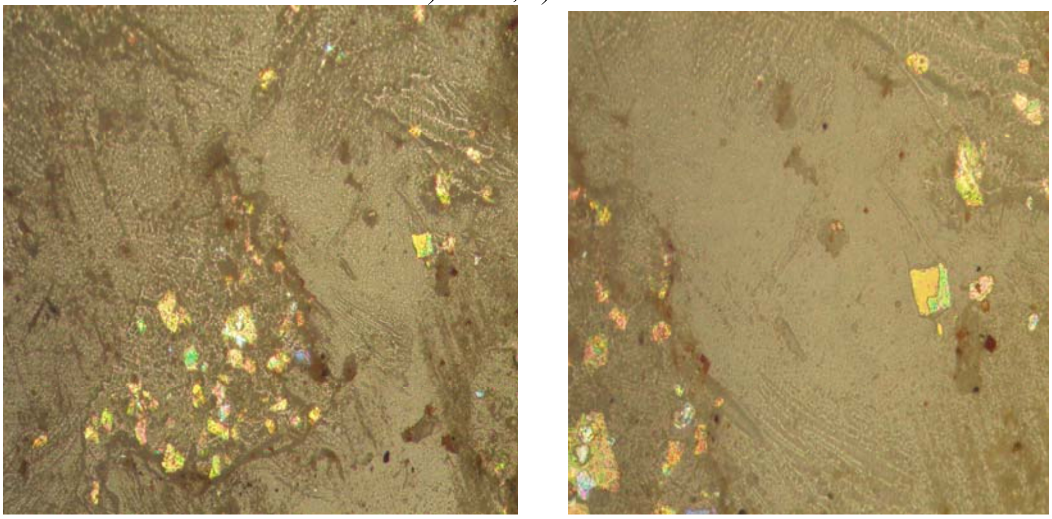


Fig. 9. *Macrostructure surface: optical aspect of coated samples after 6-day keeping in salt spray: a) x 200; b) x 400.*

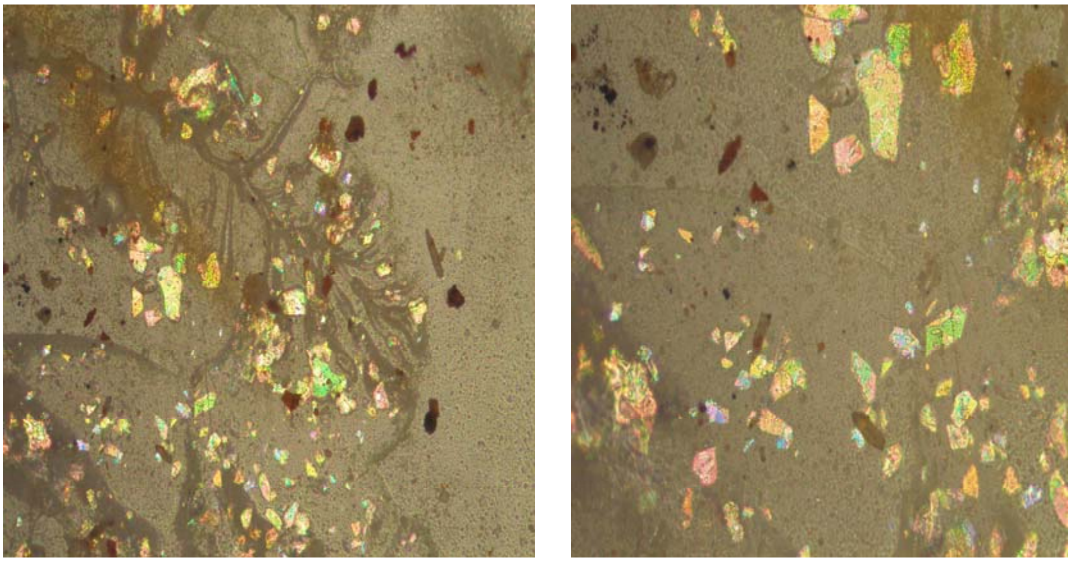


Fig. 10. *Macrostructure surface: optical aspect of coated samples after 7-day keeping in salt spray: a) x 200; b) x 400.*

As shown in Figure 5, after three days, slight traces of corrosion appeared on Interfine 979 and Intershield 300, whereas Intergard 269 was not challenged. In Figures 6 and 7, after four and five days, respectively, we see spots of corrosion, Interfine 979 and Intershield 300 being attacked again while lake Intergard 269 resisted corrosion. After six days (Figure 8), all three coats were corroded, and on the seventh day, corrosion came up at the base, Fig. 9.

4. Conclusions

- The corrosion rate of the varnish coated samples is lower than that of the uncoated samples.
- The penetration index values are much smaller for witness samples than for lacquer coated samples.
- Samples were coated average corrosion resistance, notice of assessment in June and samples are coated with varnish resistant, notice of assessment in May.
- After three days, there were slight traces of corrosion, lakes Intersheild 300 and Interfine 979 having been attacked, while Intergard 269 was not challenged. After four and five days, respectively, spots of corrosion could be observed on Interfine 979 and Intersheild 300, while Intergard 269 resisted corrosion. After six days, all three coats were corroded and on the seventh, it came up at the base.

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