STUDY OF A NEW POSSIBILITY TO PREDICT THE BEHAVIOR OF HIGH - PERFORMANCE ANTICORROSIVE PROTECTIONS APPLIED ON STEEL AFTER THEIR EXPOSURE IN NATURAL AGGRESSIVE ENVIRONMENTS AND IN LABORATORY ACCELERATED CONDITIONS, RESPECTIVELY

Irina POPA[1], Alexandrina Maria MUREŞANU[2]

[1] Dr. Eng, National Institute for Research and Development in Construction, Urban Planning and Sustainable Spatial Development, URBAN-INCERC, e-mail: irinapopa2006@yahoo.com

[2] Chem., National Institute for Research and Development in Construction, Urban Planning and Sustainable Spatial Development, URBAN-INCERC, e-mail: alexandra.muresanu@yahoo.ro

ABSTRACT

As a result of the global warming, notable changes in the climatic regime of Romania were observed in the last 40-50 years by increasing of the maximum temperatures and decreasing of the minimum temperatures characteristic for each season. This paper makes reference to an experimental research regarding the actual severity of the Romanian climate and its effects toward some performant anticorrosive coatings applied on steel. Such performant anticorrosive protection systems were exposed in situ – marine and alpine environment - and in parallel, aiming to simulate the severe climatic actions through laboratory accelerated environments - neutral salt fog, condensation and temperature variations. The graphical representation and the interpretation of the adhesion to the steel surface by means of the variation of the class into which the paint was framed after performing the cross-cut test during the exposure provided information concerning a new possibility to predict the evolution of the degradation of the paint, by means of this characteristic experimentally determined.

Keywords: anticorrosive; class, adhesion; environment; laboratory.

REZUMAT

Urmare a încălzirii globale, în regimul climatic al României din ultimii 40-50 de ani s-au constatat modificări notabile faţă de regimul termic specific, prin creşterea temperaturilor maxime şi prin scăderea temperaturilor minime caracteristice fiecărui anotimp. Această lucrare face referiri la o serie de cercetări experimentale privind severitatea actuală a solicitărilor climatice specifice României şi efectele acestora asupra unor sisteme peliculogene performante de protecţie anticorozivă aplicate pe oţel. Astfel de sisteme de protecţie anticorozivă au fost expuse in situ - mediul marin, respectiv mediul alpin - şi în paralel, urmărind simularea solicitărilor climatice severe prin condiţii accelerate de laborator, în medii cu ceaţă salină neutră, condensare continuă şi variaţii de temperatură. Reprezentarea grafică şi interpretarea variaţiei aderenţei la suprafaţa de oţel prin variaţia clasei în care este încadrată protecţia la efectuarea încercării de aderenţă prin caroiaj pe parcursul expunerii a furnizat informaţii referitoare la o nouă posibilitate de predicţie a evoluţiei stării de degradare a protecţiei în timp pe baza acestei mărimi determinate experimental.

Cuvinte cheie: anticoroziv; clasă; aderenţă; mediu înconjurător; laborator.

1. INTRODUCTION

World Meteorological Organization (WMO) divides the severe climatic conditions in general severe weather conditions (for example the European storms and phenomena which they accompany, on large geographic areas) and severe localized climate conditions (e.g. tornadoes), with geographical limited action.

The notion of severe climatic conditions differs from that of extreme climatic conditions, the latter describing unusual weather events, located at the extremes of the characteristic parameters for a given area in a long time (8).

Talking last year about global warming, the economist Nicholas Stern, chairman of the Grantham Research Institute on Climate Change and the Environment and also chairman of the Centre for Climate Change Economics and Policy (CCCEP) warned that ”as early as 2035, virtually committing us to a global average temperature rise of over 2°C. In the longer term, there would be more than a 50% chance that the temperature rise would exceed 5°C. This rise would be very dangerous indeed; it is equivalent to the change in average temperatures from the last ice age to today” (7).

In Romania, as a result of global warming, in the last 40-50 years, were found notable changes in the climatic and thermal regime for each season: ”The analyze of the air average temperature strings highlighted a significant warming with about 2°C all over the country during the summer, and in the regions beyond Carpathians, during winter and spring. In autumn was noted a slight cooling trend across the country, however, without being statistically significant” (3).

”In Romania [...], it is expected the same average annual warming as that projected for Europe, namely:
- between 0.5°C and 1.5°C for 2020-2029;
- between 2.0°C and 5.0°C for 2090-2099” (6).

In consonance with the general meteorological predictions issued internationally on global warming, for our country, at least for the next 50 years, weather forecasts indicate an increase in average temperatures by more than four degrees Celsius, especially in the southern area of the country, as set out in the annex to the Decision on Approval of the Government of Romania's National Strategy on Climate Change /SNSC/ 2013-2020 published in the Official Gazette (5).

In this context, it is increasingly clear the need to develop interests referring to extending the knowledge about the impact that climatic changes have towards the built fund, as well as to the actions required to be taken in the sense of reducing this impact.

This paper makes reference to the field of anti-corrosion protections applied on steel surfaces, taking into account the role that this kind of construction materials has to the increase of the sustainability of the built fund, exposed to the action of aggressive environmental factors.

Since temperature and atmospheric humidity represents two of the most important factors that influence the initiation and development of the corrosive phenomena towards the coated steel, it results, not only by means of theoretical issues but also by observing the reality, that the climatic changes mentioned above led already, also on the territory of our country, to an intensification of the atmospheric environment aggressivity, with respect to corrosivity.

In the following, the paper makes reference to an experimental research focused on the first attempt of testing a new way to characterize and to predict the degradation of a high performance anticorrosive system applied on steel and exposed to the current aggressive action of the Romanian atmospheric marine and alpine environments.

2. EXPERIMENTAL RESEARCH. MATERIALS AND METHODS

The types of products and systems for the anticorrosive protection of steel surfaces tested within the framework of the project, citing the ecological characteristics for each product, are presented in table 1.

Table 1. *The anticorrosive products/systems used in the experimental program*

System code	Component product/ number of layers	Ecological characteristics
Systems applied to steel surfaces		
E	"High build" epoxy coating/2 layers	Solid content: 58%
F	Silicate zinc based primer /1 layer	VOC : 26%, in weight
	Aliphatic polyurethane resin coating /2 layers	High solid content: 73%, Low VOC: 13%, in weight
J	High zinc content epoxy primer/ 1 layer	High content of zinc pigment; High solid content: 62%
	Epoxy coating / 2 layers	High solid content: 90%

The systems were applied on steel samples having 100x150x1 mm. It was decided from the very beginning that the samples will be made manually (preparation of the steel surface with a wire brush, cleaning and then applying the products by brush), without aiming to obtain a performant execution, in order to simulate and to test the actual quality of the execution of the anticorrosive systems realized in many cases on the Romanian sites and thus to test the behavior of such systems to the action of different types of stress caused by the climatic changes.

It should be mentioned that, in the technical data sheet, the application by brush is permitted in specific conditions of surface preparation, conditions experimentally fulfilled.

The experimental study consisted in a survey over six advanced systems for corrosion protection coatings having ecological characteristics, in order to compare their behavior during the exposure, in parallel, on different batches, in two natural atmospheric environments (marine and alpine respectively), but also in accelerated laboratory conditions (neutral saline fog, condensation, temperature variations).

Laboratory environments were selected in order to simulate severe environmental conditions that are characterized by at least one important feature of the Romanian climate: temperature, atmospheric humidity, and significant differences between day and night temperatures.

The element used to analyze the behavior of the systems exposed in the aggressive environments was the class in which each system was framed after completing the test that assesses the adhesion of the coating to the support (by the cross-cut test, according to SR EN ISO 2409:2013), during the entire exposure period. The choice was made taking into account that:

a) this feature was determined anyway during the experimental part of the project, in order to assess the evolution of adherence to the surface support;

b) this is one of the characteristics officially and frequently declared in the data sheets of the anti-corrosion products.

A new possibility of characterizing and predicting the behavior of high-performance anticorrosive protection having eco-friendly features was studied through the analysis of graphs generated based on the experimental results obtained during the exposure to aggressive environments. For each system, the graph was done putting on the abscissa the number of cycles of exposure in each environment, and on the ordinates, the class in which was framed each of the three systems of protection in each of the exposure environment.

At international level, life prediction of an anti-corrosive coating is determined through many other methods (1), (2), (4).

In this experimental research, life prediction of the coating was chosen to be done using, as a study element, the class in which each system of protection is framed during exposure, according to SR EN ISO 2409:2013. Our choice is also sustained by the fact that even if the above mentioned class is not considered as a measure of the adherence of the coating to the substrate, the cross-cut test is accepted to be done also on the field.

2.1. Experimental researches "in situ"

Because INCERC Bucharest Branch offers exposure sites in locations having different types of atmospheric aggressiveness, „in situ" experimental researches were conducted in the following conditions:

- **Exposure in natural marine environment** – the site is placed on the ground, at the „Marine Corrosion Test Site" in Constanța, at about 1 km distance from the Black See Romanian shore;
- **Exposure in natural alpine environment** – at 1604 m altitude, at „Postavaru Cottage", near Poiana Braşov.

It was considered that one exposure cycle consists in a 24 hours exposure in each of the "in situ" environments.

2.2. Experimental research in accelerated laboratory conditions

The exposure in accelerated laboratory conditions consisted in:

- ***Exposure to temperature variations*** – according to SR EN 60068-2-14:2010, "Environmental testing - Part 2-14: Tests - Test N: Change of temperature" - Na test. One cycle of exposure was 24 hours long:
  - 7 hours at T = + (40 ±3)°C,
  - 17 hours la T = – (20±3)°C;
- ***Exposure to continuous condensation*** – according to SR EN ISO 6270-1:2002. "Determination of resistance to humidity. Part 1: Continuous condensation". The temperature in the test chamber: (38±2) °C, air relative humidity U_r air = 100%;
- ***Exposure to neutral salt fog*** – according to SR EN ISO 9227:2012. "Corrosion tests in artificial atmospheres - Salt spray tests". The temperature in the test chamber: (35±2) ^{0}C, salt air relative humidity U_r = 100%.

3. EXPERIMENTAL RESULTS

Tables 2-4 show the experimental results concerning the assessment of the adherence to the support for the anti-corrosion coating systems exposed in each environment created under accelerated conditions. The results were expressed by the class in which the systems applied on steel surfaces were framed, according to SR EN ISO 2409:2013.

The experimental results presented in tables 2 – 6 are displayed graphically in Figures 1 – 5, both through points (the curve line) and between points (straight line).

Table 2. *Temperatures variations. Experimental results*

Period of exposure	Corrosion protection systems applied on steel surface		
	E	F	J
	Class - Classification of test results		
Initial (0 cycles)	1	1	1
210 cycles	1	1	1
340 cycles	1	5	1

Table 3. *Continuous condensation. Experimental results*

Period of exposure	Corrosion protection systems applied on steel surface		
	E	F	J
	Class - Classification of test results		
Initial (0 cycles)	1	1	1
53 cycles	1	1	3
88 cycles	2	5	4

Table 4. *Neutral salt fog. Experimental results*

Period of exposure	Corrosion protection systems applied on steel surface		
	E	F	J
	Class - Classification of test results		
Initial (0 cycles)	1	1	1
224 cycles	1	2	4
362 cycles	5	5	5

Tables 5 and 6 show the experimental results concerning the adherence to the support of the anti-corrosion protection systems after exposure in each of the "in situ" environment. Again, the results were expressed by the class in which the systems applied on steel surfaces were categorized.

Table 5. *Natural marine environment. Experimental results. Continuous exposure*

Period of exposure	Corrosion protection systems applied on steel surface		
	E	F	J
	Class - Classification of test results		
Initial (0 cycles)	1	1	1
365 cycles	1	2	1
610 cycles	1	5	1

Table 6. *Natural alpine environment. Experimental results. Continuous exposure*

Period of exposure	Corrosion protection systems applied on steel surface		
	E	F	J
	Class - Classification of test results		
Initial (0 cycles)	1	1	1
365 cycles	1	1	2
610 cycles	1	3	2

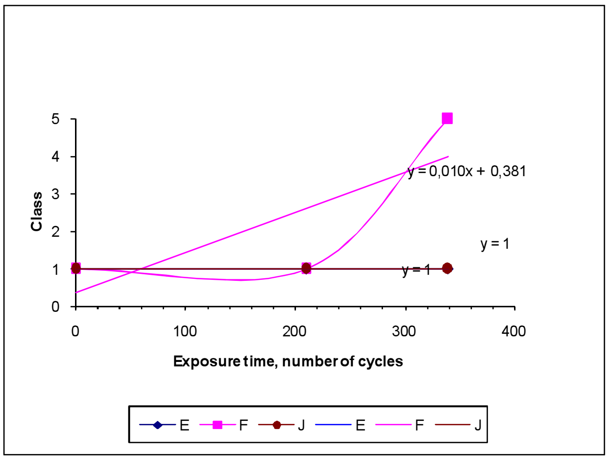

Fig. 1 Exposure in laboratory accelerated conditions. Temperature variations

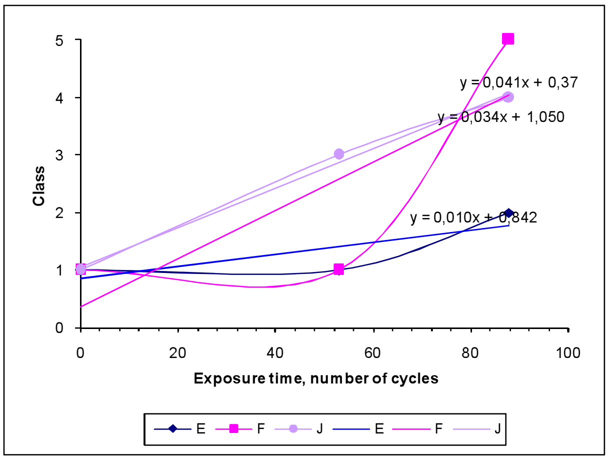

Fig. 2 Exposure in laboratory accelerated conditions. Continuous condensation

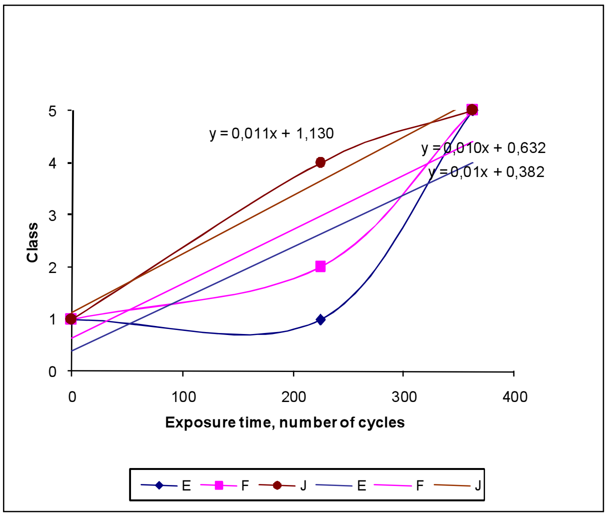

Fig. 3 Exposure in laboratory accelerated conditions. Neutral salt fog

The equations of the plotted straight lines are presented in Tables 7 and 8.

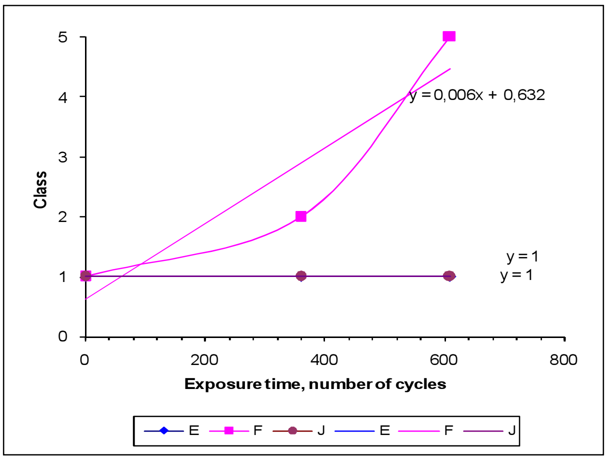

Fig. 4 Exposure to the action of the natural marine environment

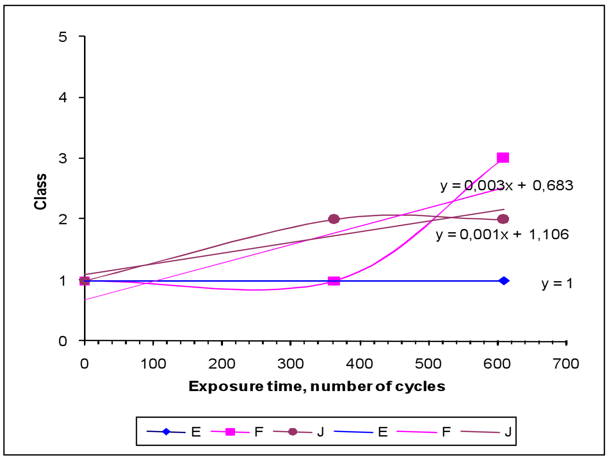

Fig. 5 Exposure to the action of the natural alpine environment

Tables 9-18 show the classes that were experimentally determined and those calculated by means of graphs, for the corrosion protection systems exposed in each of the aggressive environments. The tables also include the calculated predictions regarding the evolution of the class to the value 5, for those anti-corrosion protections which experimentally attained smaller values of the class during their exposure.

The initial class remained unchanged during the entire exposure (y = 1) for:

- Systems E and J exposed to temperature variations;
- Systems E and J exposed to the marine environment;
- System E exposed to the alpine environment.

Table 7. *Exposure in accelerated laboratory conditions. The equations of the straight lines of regression*

The exposure environment / The protection system	Temperature variations	Continuous condensation	Neutral salt fog
E	y = 1	y = 0,0104x + 0,8425	y = 0,0100x + 0,3826
F	y = 0,0106x + 0,3817	y = 0,0418x + 0,37	y = 0,0104x + 0,6320
J	y = 1	y = 0,0344x + 1,0505	y = 0,0113x + 1,2309

Table 8. „In situ" exposure, in natural environments. The equations of the straight lines of regression

The exposure environment / The protection system	Marine environment	Alpine environment
E	y = 1	y = 1
F	y = 0,0063x + 0,6322	y = 0,0030x + 0,6836
J	y = 1	y = 0,0017x + 1,1062

Table 9. *Calculation of the classes. System F (y = 0,0106x + 0,3817). Temperature variations.*

Number of cycles, x	Experimental			Calculated					
	0	210	340	0	100	150	210	340	400
Class, y	1	1	1	0	1 (1,4417)	2 (1,9717)	3 (2,6077)	4 (3,9857)	5 (4,6217)

Table 10. *Calculation of the classes. System E (y = 0,0104x + 0,8425). Continuous condensation*

Number of cycles, x	Experimental			Calculated					
	0	53	88	0	53	88	170	260	360
Class, y	1	1	2	1 (0,8425)	1 (1,3037)	2 (1,7577)	3 (2,6105)	4 (3,5465)	5 (4,5865)

Table 11. *Calculation of the classes. System F (y = 0,0418x + 0,37). Continuous condensation*

Number of cycles, x	Experimental			Calculated					
	0	53	88	0	25	45	53	83	100
Class, y	1	1	5	0 (0,3700)	1 (1,4150)	2 (2,2510)	3 (2,5854)	4 (3,8394)	5 (4,5500)

Table 12. *Calculation of the classes. System J (y = 0,0344x + 1,0505). Continuous condensation*

Number of cycles, x	Experimental			Calculated				
	0	53	88	0	25	53	83	100
Class, y	1	3	4	1 (1,0505)	2 (1,9105)	3 (2,8737)	4 (3,9057)	5 (4,4905)

Table 13. *Calculation of the classes. System E (y = 0,0100x + 0,3826). Neutral salt fog*

Number of cycles, x	Experimental			Calculated					
	0	224	362	0	100	200	224	362	420
Class, y	1	1	5	0 (0,3826)	1 (1, 3826)	2 (2,3800)	3 (2,6200)	4 (4,0000)	5 (4,5800)

Table 14. *Calculation of the classes. System F (y = 0,0104x + 0,6320). Neutral salt fog*

Number of cycles, x	Experimental			Calculated				
	0	224	362	0	100	224	362	400
Class, y	1	2	5	1 (0,6320)	2 (1,672)	3 (2,9596)	4 (4,3960)	5 (4,7900)

Table 15. *Calculation of the classes. System J (y = 0,0113x + 1,2309). Neutral salt fog*

Number of cycles, x	Experimental			Calculated				
	0	224	362	0	100	150	224	362
Class, y	1	4	5	1 (1,2309)	2 (2,3609)	3 (2,9259)	4 (3,7613)	5 (5, 3215)

Table 16. *Calculation of the classes. System F (y = 0,0063x + 0,6322). Marine environment*

Number of cycles, x	Experimental			Calculated				
	0	365	610	0	150	365	500	610
Class, y	1	2	5	1 (0,6322)	2 (1,5772)	3 (2,9322)	4 (3,7822)	5 (4,4752)

Table 17. *Calculation of the classes. System F (y = 0,0030x + 0,6836). Alpine environment*

Number of cycles, x	Experimental			Calculated				
	0	365	610	0	365	610	950	1400
Class, y	1	1	3	1 (0,6836)	2 (1,7786)	3 (2,5136)	4 (3,5336)	5 (4,8836)

Table 18. *Calculation of the classes. System J (y = 0,0017x + 1,1062). Alpine environment*

Number of cycles, x	Experimental			Calculated				
	0	365	610	0	365	850	1500	2000
Class, y	1	2	2	1 (1,1062)	2 (1,7267)	3 (2,5512)	4 (3,6562)	5 (4,5062)

4. DISCUSSION

Referring to the experimental research, the following discussion can be done:

- The experimental part of the study was conceived in order to get maximum information on the behavior of three of the main types of advanced systems for corrosion protection of steel currently available on the Romanian market, systems subjected to the action of the specific climatic conditions of Romanian marine/ alpine environment. The protections were manually executed (surface preparation of the substrate and application of the protection products).

Thus, there were simulated unfavorable cases through which the durability of the coatings is affected from the very beginning, common situations for Romanian sites that use unskilled work force.

- Tracing the regression lines and studying the variation of the class/adhesion to the substrate with exposure time for each protection, provided information about the possibility of predicting the state of degradation for the coating by means of adhesion/class, a characteristic determined from graphs, where possible.
- The study of the graphs was done in two steps:

a) Determining the evolution of the degradation for each system applied on steel, on the base of the regression line equation (y = ax + b). The abscissa (x) is the time of exposure expressed through the number of cycles and the ordinate (y) is the adherence to the substrate, respectively the class in which the protection is framed during its real exposure in each of the aggressive environments;

b) Predicting the degradation of the anti-corrosive system by calculating his adhesion/class, for an exposure period longer than the experimental one. In this way, the prediction was made for those systems where, up to the end of the exposure, the class was lower than 5.

According to SR EN ISO 2409:2013, it is class 5 when "any degree of flaking cannot even be classified by classification 4" and it is class 4 when "the coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35% but not greater than 65%, is affected".

As noted, in the analysis were taken into account the differences and errors intentionally or unintentionally introduced in the experimental part (surface preparation of the steel substrate and application method of the products).

With all the practical importance of this kind of study, the wished or unwished errors of the experimental program generated in their turn partial or total errors when verifying the research method. With respect to this, a partial error is named the situation when only a part of the experimental data (number of exposure cycles and the corresponding class) was verified by means of the calculations, and a total error is named the situation when no experimental data could be verified through calculation, even if the differences were not consistent.

Even if there were partial or total errors, there also were plenty of cases when the method was verified, for example system E exposed to continuous condensation or system J exposed in continuous condensation, neutral salt fog or alpine environment.

Thus, we conclude that this last aspect promotes the method to be taken into consideration as a possible way to predict the behavior of an anticorrosion coating applied on steel after being exposed to an aggressive environment.

A limitation of the method is that the class cannot be determined from graphs if the initial class of the coating is not changing during the exposure.

Errors and other possible limitations of the method are going to be studied further in a future research.

5. CONCLUSIONS

The main conclusions of this experimental research are:

1. This study on the behavior of anticorrosive systems applied on steel and subjected to the action of various kinds of corrosive environments brought an element of novelty because it was done through the analyze of the class in which the system was framed after the cross-cutting test, according to SR EN ISO 2409:2013.
2. The method used in this research on anti-corrosion protections applied on steel could represent a possibility for determining the evolution of the adherence during exposure/exploitation until a certain moment.
3. Although because of the small number of test dates for each system in each environment of exposure and through the manual execution of the protections were introduced some errors in the analysis, it results that the study of adherence, expressed by means of the class in which the protection was framed during exposure, represents a first step in the research carried out for establishing a new way for characterizing the degradation of the protection.
4. Tracing the regression lines and studying the variation of the class/adhesion to the substrate with exposure time for each protection, is a very first step developed in order to establish a new prediction way of

the deterioration stage for an anticorrosive protection applied on steel.

5. Other similar studies, without the errors mentioned above, will aim to verify and improve the results obtained and by that means, to obtain a new research method for characterizing and predicting the degradation of an anticorrosive protection applied on steel while is exposed to an aggressive environment.

REFERENCES

1. Bierwagen, G., Tallman, D., Farden, D., Croll, S., Urban, M.W., ”Corrosion testing, life prediction and corrosion sensor development for coated aircraft systems – Emphasis on environmentally compliant practices”, DTIC News Wire, 2001;

2. Boss, T. - Prediction of coating durability. Early detection using electrochemical methods - repository.tudelft.nl/.../bos_20080311.pdf.

3. Busuioc, A., Caian, M., Bojariu, R., Boroneanţ, C., Cheval, S., Baiu, M., Dumitrescu, Al., ”Scenarii de schimbare a regimului climatic în România în perioada 2001-2030”- Administraţia Naţională de Meteorologie, 2012;

4. Hinderliter, B.R. and Croll, S.G. - Predicting coating failure using the Central Limit Theorem and Physical Modelling - ECS Transaction, shttp://ecst.ecsdl.org/content/24/1/1.full.pdf;

5. Ministerul Mediului şi Pădurilor – ”Strategia Naţională a României privind Schimbările Climatice 2013 – 2020”, Monitorul Oficial al României, Partea I, nr. 536 bis;

6. Sandu, I., ”Evoluţia regimului climatic în România” - Administraţia Naţională de Meteorologie, 2009;

7. Stern, N., ”The Economics of Climate Change: The Stern Review”, Cambridge University Press, 978-0-521-70080-1;

8. World Meteorological Organization, "Workshop On Severe and Extreme Events Forecasting", 2004.