

ANALYSIS OF STATE OF LACQUERED LAYER OF METAL SHEET AFTER CORROSION LOAD

Jaroslava Svobodova, Sylvia Kusmierczak

Jan Evangelista Purkyně University in Ústí nad Labem, Czech Republic
svobodova@fvmtm.ujep.cz, kusmierczak@fvmtm.ujep.cz

Abstract. The aim of this paper is to perform a microscopic analysis of the state of the sheet metal after the load in corrosive environment. As an experimental material metal sheets intended for laboratory tests are used, on which to the new surface pre-treatment based on nanotechnology before painting were applied. The sheets will be exposed to corrosive environment in several time periods. The change in the properties of the lacquered layer depending on the time of corrosive action will be monitored. Based on the outcome conclusions and recommendations for manufacturers of coated sheets will be elaborated.

Keywords: lacquered layer, corrosion load, metal sheets, chemical pretreatment, nanotechnology.

Introduction

Surface treatments have substantial influence on the lifetime and the final quality of lacquered products. Each product is exposed during its lifetime to external conditions, which act on its surface. The largest part of the product is exposed to atmospheric conditions. Products and structures are subject to corrosion due to aggressiveness of atmosphere. The main cause of corrosion is the atmospheric humidity and the corrosion rate is dependent on the presence of gaseous impurities or soluble solid impurities. The most aggressive contaminants include SO₂, NaCl, hydrogen sulfide, chlorine, hydrogen chloride, industrial dust, ash, nitrogen oxides, etc. [1].

To achieve the long-term durability of engineering products surface treatments and surface pre-treatments are used. Surface pre-treatments are intended to remove dirt from the surface of the base material and to the creation of suitable surface for applying and good adhesion of the final coating. Surface pre-treatments can be divided into mechanical and chemical. Mechanical pre-treatment used in the area of lacquering is mainly sanding and blasting. Chemical pre-treatments most often are used in degreasing solvents and organic phosphating. Phosphating is a considerably commonly used method, however, at present by legislation on environmental protection pressure is exerted to restrict the use of hexavalent chromium, reduce heavy metals and improve the quality of wastewater discharged from manufacturing companies. Modern chemical surface pre-treatments based on nanotechnology attempt to eliminate these undesirable impacts on the environment. These are nanopassivating layers, which could in the future replace conventional phosphating processes. These nanolayers are able to provide good conditions for adhesion between the coating layer and the base material similar to phosphating, increase productivity and are environmentally friendly.

The bases of these nanopassivating products are highly reactive silanes, which create during the reaction with the surface of the material a chemical bond. These silanes create a highly cross-linked inorganic layer on the surface of material having a thickness of 50-100 nm. Thanks to this layer formed at the surface of the material the barrier effect is increasing the corrosion resistance of the material especially in combination with the subsequent powder coating. Inorganic layer is defined as a highly crosslinked film firmly anchored to the surface material by chemical bonds Si – O – M (M-basic material). The film, which arises on the surface of the material, has a homogeneous structure and a thickness in the range of 50 to 100 nm. Nanopassivating product ZircaSil[®] is multimetallic and therefore can be used for pre-treatment of Fe materials, galvanized materials and aluminum materials. The corrosion resistance of these coatings is comparable with the technology of phosphating [2].

The aim of this paper is to analyze the behavior of the experimental samples after corrosion load, for which a nanopassivating layer was used for the pre-treatment of the surface before applying the powder coating. The samples were burdened in the corrosion chamber for 480, 720 and 1000 hours. After removal from the corrosion chamber the samples were evaluated according to the standards CSN EN ISO below. For samples microstructural analysis was also performed at which the surface quality of basic material of the applied powder coating was evaluated and the surface roughness of the base material was measured before applying the paint. After performing all tests and analyzes conclusions

and recommendations will be elaborated for the use of a new nanopassivating layer ZircaSil® in practice.

Description of the experimental samples

The experiment was carried out using laboratory material Q-Panel Fe. This material is being used for testing of surface coatings. The basic material is supplied by the manufacturer as easily blast. The chemical composition of the material is shown in Table 1.

Table 1

Chemical composition of the of the material Q-Panel Fe

Material	Max. C %	Max. Mn %	P %	S %
Q-panel Fe	0.12	0.60	0.045	0.045

Chemical pretreatment of the base material

The material was pre-treated with alkaline degreasing and subsequently passivated with the product ZircaSil®.

Powder coating

After performing the chemical pretreatment powder coating was applied to the samples. Specifically, the powder coating TIGER Drylac ® Series 29 – light gray color was used. The samples were dried at temperature of 90 to 100 °C per 10 min., temperature and time of paint burning 180°C/20min.

The experimental samples were provided before the corrosion test by cross-cut according to the standard CSN EN ISO 17872 Paints and varnishes – Guidelines for the implementation of cuts throughout coating on metal samples for corrosion tests.

Corrosion load

The experimental samples were corrosion loaded in salt spray of corrosion diagnostic equipment LIEBISCH ®. The working conditions of the corrosion chamber were set according to the standard CSN EN ISO 9227. The set parameters are shown in Table 2.

Table 2

Parameters of corrosion test

Parameters of the test	Neutral salt spray
Temperature	35 °C ± 2 °C
The average rate of the accumulation of spray mist from a horizontal collector area 80cm ²	1.5 ml·h ⁻¹ ± 0.5 ml·h ⁻¹
The concentration of sodium chloride (accumulated in the solution)	50 g·l ⁻¹ ± 5 g·l ⁻¹
pH (accumulated in the solution)	6.5 to 7.2
Corrosion load time	480, 720, 1000 hours

Analysis and evaluation of the samples after corrosion load

The experimental samples were gradually removed from the corrosive environment and the following tests and analyzes were performed:

- CSN EN ISO 4628-8 Paints and varnishes – Evaluation of degradation of coatings – Classification of quantity and size of defects and of intensity of uniform changes in appearance - Part 8: The degree of delamination and corrosion around the cut
- CSN EN ISO 2409 Paints and varnishes – Cross-cut test
- CSN EN ISO 4624 Paints and varnishes – Pull-off adhesion test

- Microstructural evaluation: analysis of the behavior of the surface layer after corrosion load, measurement of the layer thickness, roughness measurements on the samples without powder coating.

In Table 3 designation of the experimental samples is indicated, where the basic material Q-panel Fe (gently blast cleaned) was pretreated with alkaline degreasing and passivated with nanoparticle ZircaSil®.

Table 3

Designation of experimental samples

Corrosion load time				
480 hours	A1-1	A1-2	A1-3	A1-4
720 hours	A2-1	A2-2	A2-3	A2-4
1000 hours	A3-1	A3-2	A3-3	A3-4

Evaluation of experimental samples after corrosion load according to standards CSN

Evaluation of the samples according to the standards CSN listed above is shown in Table 4.

Table 4

Evaluation of samples after corrosion load according to the standards CSN

Sample	The degree of delamination	The degree of corrosion	Cross-cut test	Pull-off adhesion test	Corrosion load time
A1-1	3	Ri 2	0	-	Group A – 480 h
A1-2	5	Ri 2	0	-	
A1-3	4	Ri 2	0	15,37 MPa 0 %	
A1-4	4	Ri 3	0	-	
A2-1	5	Ri 3	0	-	Group B – 720 h
A2-2	5	Ri 2	0	-	
A2-3	5	Ri 3	0	-	
A2-4	5	Ri 4	0	15,50 MPa 0 %	
A3-1	5	Ri 4	0	-	Group C – 1000 h
A3-2	5	Ri 5	0	-	
A3-3	5	Ri 4	0	-	
A3-4	5	Ri 5	0	15,54 MPa 0 %	

The degree of delamination: 1 - very small, 2 - small, 3 - moderate, 4 - high, 5 - very high.

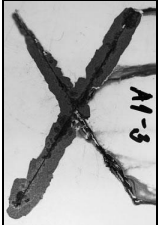
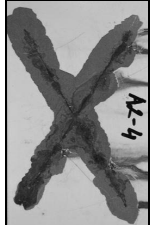
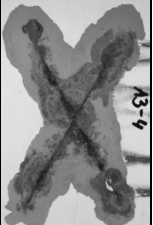
The degree of corrosion: Ri 1 - very small, Ri 2 - small, Ri 3 - moderate Ri 4 - large, Ri 5 - very high.

Cross-cut test: grade 0 - edges of cuts are completely smooth, no grid squares are damaged.

Pull-off adhesion test: pull-off strength in MPa – percentage share of the area and character of the breach of the system under test. The pull-off adhesion test was carried out on three samples that we have chosen as a representative from each group. In Table 5 the samples A1-3 A2-4, A3-4 after corrosion load are illustrated.

Table 5

Samples after corrosion load

Sample	A1-3	A2-4	A3-4
Surface pre-treatment – alkaline degreasing + nanopassivation			

For all samples after corrosive load delamination and corrosion occurred. The degree of delamination and corrosion is dependent on the time of corrosion load and reaches values – for delamination 3-5 (mild-very large) – for corrosion 2-5 (small – very large). The cross-cut test is evaluated for all the samples of level 0. It means that the coated layer on the intact place after corrosion load is perfectly adjacent to the base material. The pull-off test also demonstrated excellent lacquer adhesion to the base material. Although there was on the surface of the samples extensive delamination, we can conclude that the corrosion resistance of the samples in the case of 480 and 720 hours is good.

Microstructural analysis

Microstructural analysis was performed on a confocal laser microscope Olympus LEXT 3100. Within the microstructural analysis we made measurement of the layer thickness, roughness of the sample without powder coating, evaluation of the surface layer after corrosion load.

Measurement of the thickness of the coating

Measurement of the layer thickness was carried out on the samples A1-1, A2-1, A3-1. The measurement results are shown in Table 6.

Table 6

Measuring of the thickness of the coating

The measured thickness of the coating	Sample A1-1	Sample A2-1	Sample A3-1
	Average: 232.8559 μm Max.: 237.5234 μm Min.: 228.0688 μm	Average: 101.5854 μm Max.: 105.6656 μm Min.: 91.8606 μm	Average: 147.1881 μm Max.: 160.5897 μm Min.: 136.239 μm

Roughness measurement of the sample surface

Measuring of the roughness of the sample surface before applying the final powder coating was performed. Roughness was measured on confocal laser microscope Olympus LEXT 3100. The values of the roughness measurements are shown in Table 9.

Table 9

Measurement of the surface roughness

Surface roughness, μm		<i>SRz</i>	<i>SRa</i>
Measured area, μm^2	1224803.12500	144.2872	6.8509
Measured surface, μm^2	11257988.2935		
Line measurement, μm			
<i>Rz</i>		<i>Ra</i>	
Average	48.1141	Average	5.0797
Max.	60.9584	Max.	7.9998
Min.	40.1334	Min.	3.6107

Microstructural evaluation of the lacquered layer

For creating the metallographic sample and evaluation of microstructure we took samples from painted sheet metal after corrosion load. These samples were taken from the place where there was no coating to peel off and from the place of the cut. Microstructural analysis was performed on a confocal laser microscope Olympus LEXT 3100.

- Microstructural analysis of the sample A1-1.

Fig. 1 shows the continuous, unbroken lacquered layer, which was removed from a place where there is no separations from the interlayer of the paint. The average thickness of the lacquered layer is 232.9 microns. The surface material is ragged and its average roughness *Ra* is 5.08 microns. The lacquered layer does not peel and is close fitting to the base material.

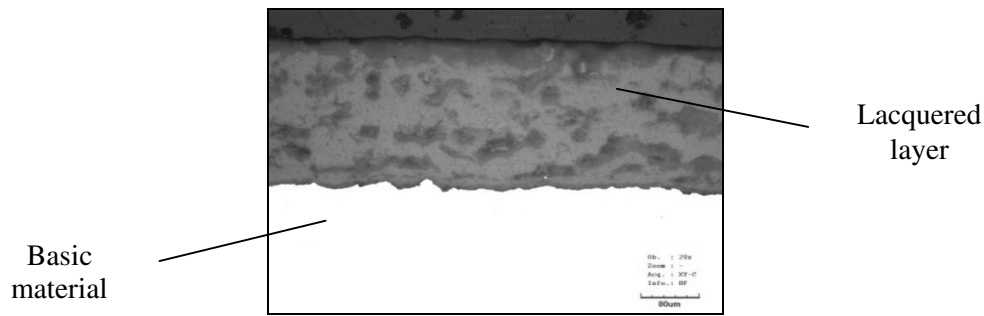


Fig. 1. Lacquered layer A1-1 (a)

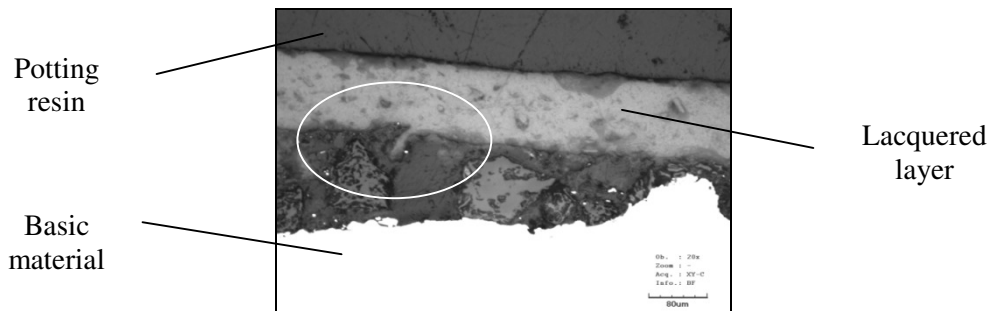


Fig. 2. Lacquered layer after delamination A1-1 (b)

Figure 2 shows a metallographic specimen of the sample taken from the place of the cut. In Figure 2 still separation of the lacquered layer did not occur. As it can be seen from the figure the painted layer was under corroded and due to corrosion its degradation occurred. On the surface of the material corrosion attack is visible. Sample A1-1 was placed in the corrosion chamber for 480 hours.

- Microstructural analysis of the sample A2-1.

By the sample A2-1 occurred after corrosion load 720 hours to the extensive delamination than by the sample A1-1. On the surface of the sample taken from the place of intact coating the painted layer is compact and fits well to the surface of the material. Its average thickness is 101.6 microns. On the sample from the place of the cut there is the surface of the material with no surface layer. Paint is from areas around the cut completely peeled. The surface material is attacked by corrosion.

- Microstructural analysis of the sample A3-1.

Sample A3-1 was placed in the corrosion chamber for 1000 h. On the surface of the sample taken from the place of intact coating there is documented lacquered layer without damage. The layer fits close against the surface of the base material well. The average thickness of the lacquered layer is 147.2 microns. On the sample from the place of the cut it occurred to a very large degradation of the surface. On the surface of the material corrosion products are visible and corrosion reaches to 80 micron under the original surface of the material.

Within the microstructural analysis the following was performed: thickness measurement of the paint, sample surface roughness measurement and microstructural evaluation of the coated layer after corrosion load. The thickness of powder coating on the surface of the material was different for each sample. The greatest thickness of the lacquer was measured for sample A1-1, when the average value was 232.9 µm and the minimum thickness of the lacquer in sample A2-1 with an average thickness of the coated layer of 101.6 µm. On the samples without surface lacquer the surface roughness of the base material was measured.

The average value of line roughness Rz was 48.1 µm and Ra was 5.07 µm. From the previous research we have verified values of roughness of the sheet metal, for which iron phosphating was used. So, we can say that pretreatment of the surface where instead of iron phosphating a new nanoparticle ZircaSil® was used has higher roughness values. This pretreatment therefore provides suitable conditions for anchoring the coating on the surface of the base material. Microstructural analysis was performed on the samples A1-1, A2-1 and A3-1. From all the samples metallographic samples were prepared. The sampling sites for metallographic specimen were chosen in order to

compare the results of the microstructural analysis to the evaluation of the samples according to the CSN standards. The samples were taken from the place where there is no lacquer peel (a) and from the place of cut (b).

The samples taken from the place (a) showed excellent lacquer adhesion to the material surface as demonstrated earlier by the cross-cut test and pull-off adhesion test. The samples taken from the cutting point (b) were attacked by corrosion and its extent is dependent on the time of corrosion load. The samples were attacked by pitting corrosion on the surface of the base material. For a sample of A1-1 the lacquer did not completely peel off after 480 hours of corrosion load. For other samples the surface lacquer from the surface of the sample completely peeled off and the surface corroded. For sample A3-1 in place of the cut corrosion reaches to a depth of 80 micron below the surface of the base material.

Conclusion

The aim of this paper was to analyze the condition of painted sheet metal after corrosion load, on which a new technology nanopassivation has been used. The prepared samples were loaded in the corrosion chamber for 480, 720 and 1000 hours. The samples were gradually removed from corrosive environment and tests were performed according to the CSN standards and after that microstructural analysis was performed.

Based on the evaluation of the experimental samples according to the CSN standard and the microscopic analysis we can make the following conclusions for the use of the new technology of nanopassivation in practice. Undamaged coating exhibits very good adhesion to the base material as demonstrated by the grid test, pull-off adhesion test and microscopic analysis. In the vicinity of the cut after 720 hours extensive separation of the paint layer and corrosion occurred. This degradation can be caused by incorrect choice of the surface finish or poorly applied chemical pretreatment of the surface. Recommendations for improving the life of the painted parts are powder coating applications where it would be appropriate to achieve a uniform coating thickness across the entire surface of painted sheet metal. The new method of nanopassivation ranks among the modern methods of chemical surface pre-treatments. The method is environmentally friendly and economically beneficial. When using this method of surface preparation it is necessary to pay attention to maintain the correct application of the technological process and the subsequent application of powder coating on the pre-treated surface.

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