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Coating *and* Corrosion under Control

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WMV bv.
Lunac 2+ duplex
NBD 10300 (2010) Qualification Test



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1 Introduction

A test cylinder with a diameter of 51 mm with the WMV Lunac 2+ with a duplicate layer. This layer consists of a base and a Cobalt-Nickel layer.

C-Cube is a specialist in corrosion and coating research, and called for the test cylinder to be assessed according to the Department of Public Works Requirements Technical Coatings NBD 10300 (2010).

This report describes the findings, results and evaluation of the coating.



2 Test Setup

According to the Technical Requirements Coatings (NBD10300-2010) applied coatings must meet a galvanostatic test. The full text of the requirements is shown below.

5.2.2. Galvanostatic test

Galvanostatic test should be performed on a carbon steel specimen with an unsealed coating. The diameter of the specimen must be greater than 50 mm.

Note

The test, a destructive galvanostatic qualification test, is to determine whether the coating suitable for the particular conditions. During the test the porosity before and after a simulated period of use is measured.

Note

During the EPQ-test not only the initial porosity, but also the stability of the corrosion behavior of the coating is measured.

The test must be conducted in the following steps:

1. Measuring the porosity of the coating with the EPQ-test according to Section 5.3.2, but with 3.4% NaCl solution in water for at least 100 hours.
2. Determine from the polarization curve of the EPQ test the corrosion current density ICOR according to ASTM G59-97 (2003) and irepass according to ASTM G61-86 (2003).
3. A new surface on the same piece under the same conditions as for the EPQ-test is exposed for 1000 hours galvanostatic test in a positive current density of $10 \times \text{igalvstat ICOR}$, the maximum current density is irepass occurs. ISO 17475 is hereby retained.
4. After the test stated in point 3 the EPQ test is performed, for 100 hours. The measured voltage, current density and appearance shall meet the requirements as stated in section 5.3.2.

From: 5.3.2. corrosion resistance

The measured potential during the entire exhibition may not be less than $-0.35\text{V vs. coll. Ag / AgCl}$. At higher potential is a coating on a carbon steel substrate sufficient final, and at a lower potential lack final. For coatings with a proven passive electrochemical potential of -0.35V lower than potential loss of that criterion.

The polarization curve after the minimum 24 hours exposure, ISO 17475:2005 included. Here the polarized surface from more than 0.2V below the electrochemical potential, with a maximum speed of 1mV / s , to $0\text{ V vs. appl. Ag / AgCl}$. The current density throughout the curve should not exceed $1\mu\text{A}/\text{cm}^2$. At higher current density the coating is too active.

After measuring the polarization curve may have - without cleaning - at a magnification of 10x no visible local corrosion. This should be proven in the report with a photo.

All potentials mentioned in the report relative to saturated silver / silver chloride, expressed in Volts vs. sat. Ag / AgCl.



3 Results

Using a sample of the separate coating, the original potential of the coating determined.

The potential values ranged from -0.38 to -0.32 V.

For the test sample, the potential has been measured in 3.4% NaCl solution for 100 hours from the start of the test, see Figure 1.

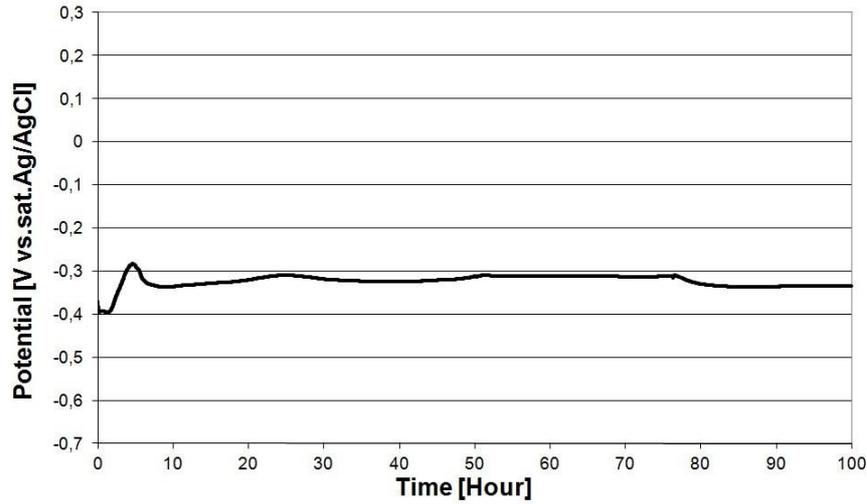


Figure 1: Potential measurement of the Lunac 2+ coating, for 100 hours.

The potential after 100 hours immersion is -0.33V. After this test a polarization curve has been measured, see Figure 2.

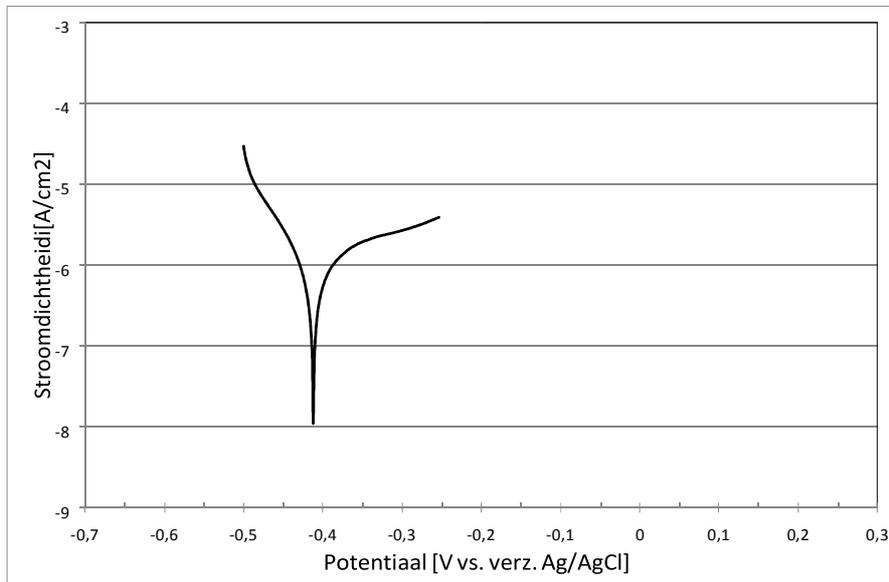


Figure 2: Polarization curve of the Lunac 2+ coating, at 0.5mV/s.

Interestingly, the potential of the polarization curve is equal to the potential at the start of the potential measurements. This indicates that the oxide layer which has built up in 100 hours during the negative polarization in the first part of the polarization curve (left of the V-shape) breaks down locally.



With the polarization resistance, the Tafel gradient and modelling of the curve (ISO 17475), the corrosion current density was derived,

at a level of $I_{corr} = 0.5 \mu A/cm^2$, corresponding to a corrosion rate of 1-4 μm per year. The repassivating potential I_{repass} could not be determined as a result of the uniform corrosion mechanism.

Based on the polarization curve, the current density for the test is determined for the galvanostatic exposure $galvstat = 5 \mu A/cm^2$. For more than 1000 hours, 1400 hours this current is observed, see Figure 3.

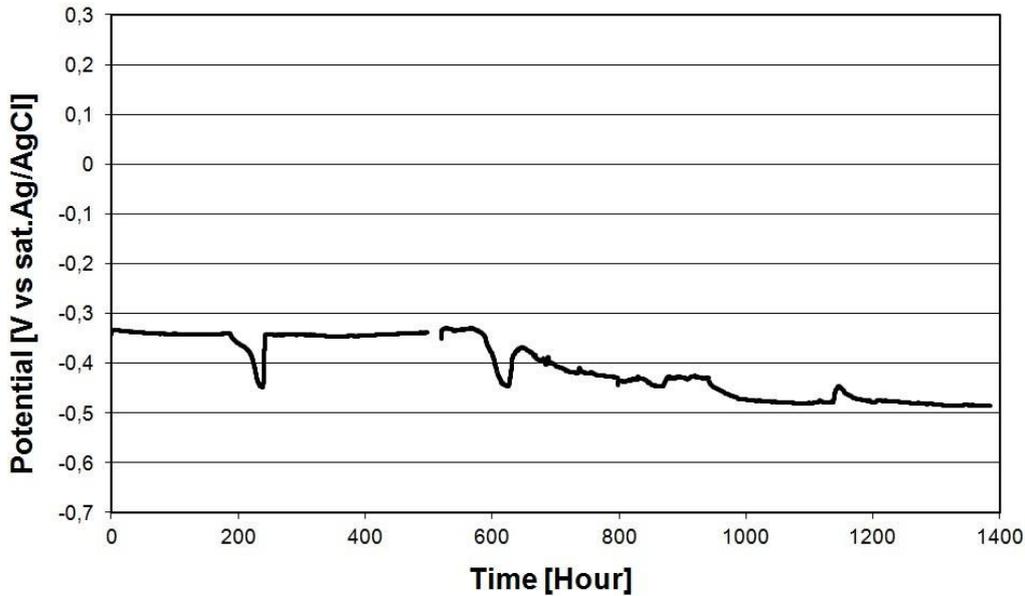


Figure 3: Galvanostatic test, during 1400 uur at $5 \mu A/cm$.

2

From the shape of the graph of the galvanostatic test it can be determined that the coating activates during the test. After the test, the measured potential is: -0.34 V vs. sat. Ag/AgCl. Since this is very stable, the chart has not been included in this report. After the potential measurement of 100 hours a polarization curve has been measured, see Figure 4.

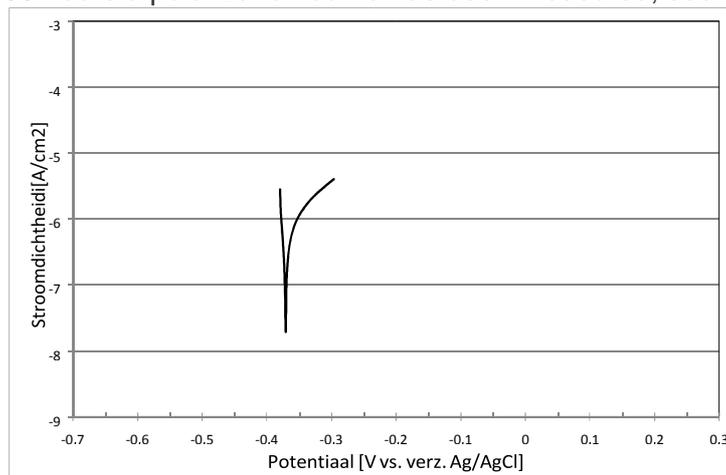


Figure 4: Polarizationcurve after the galvanostatic test.

The potential in the polarization curve is -0.36 V, slightly lower than the potential measurement. The corrosion current density in the curve is $0.6 \mu A/cm^2$, the corrosion rate is almost equal to the corrosion rate before the



test, 1.5 to 4.5 μm / year. The corrosion mechanism is uniform corrosion, which can be seen at the positive right branch. Photographs of the surface are given in Figure 5.

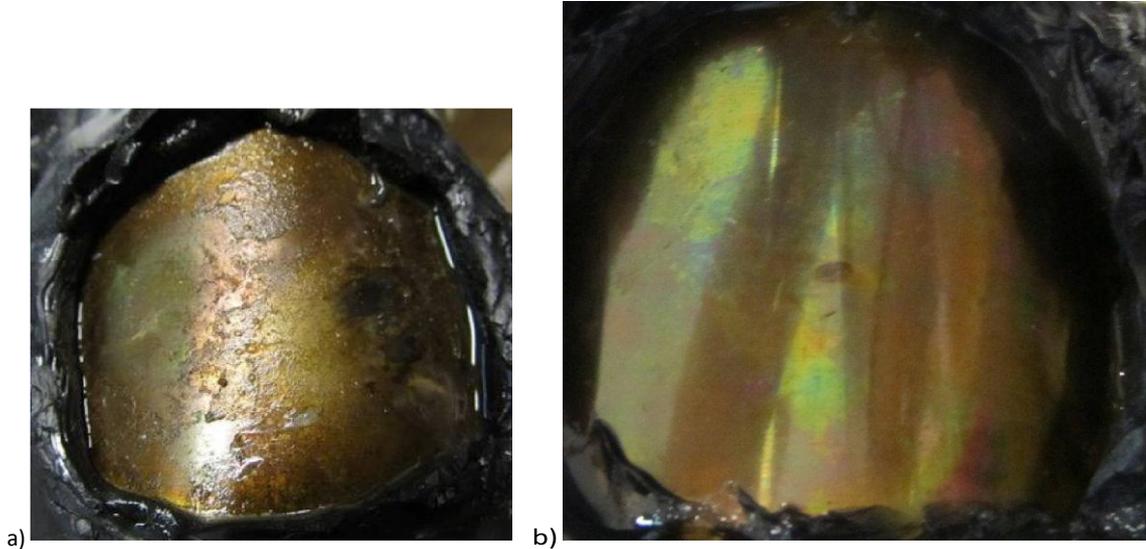


Figure 5: The surface after testing, before (a) and after 9b) removing the debris product with a cloth.

The surface looks stable, in the middle of the surface a small area is present with a different color. There is no visually observable damage to the surface, even in the middle area.

4 Interpretation

The potential of the Lunac2+ duplicate layer is around the criterion of the EPQ test. The Lunac2+ duplicate layer protects itself by means of a visible oxide film. This oxide layer has a constant refresh rate, which indicates a corrosion rate of 1-4 μm /year. It is assumed that the entire surface is metallic, and contributes to corrosion. The presence of ceramic particles in the coating can have an effect, depending on the distribution of the particles. A measurement of the actual decrease during the test would give more insight on this.

During positive polarization, the corrosion rate first increases and then decreases again because a new thicker oxide layer builds up. This can be visualized by recording consecutive polarization curves, see Figure 6.

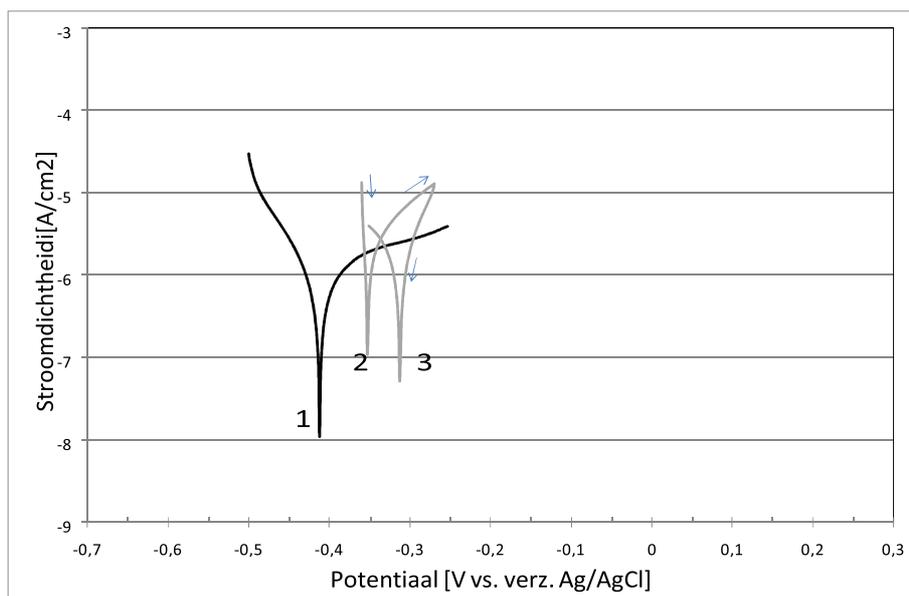




Figure 6: Consecutive polarization curves,, where the corrosion rate is proportional to the height of the V-shape in the graph. The second curve, taken immediately after the first, is higher, and at the retreating measurement the V-shape is at a lower level (= proportional to corrosion rate).

In the design of the coating the refresh level of the oxide layer has been taken into account, which correlates with the corrosion rate of the layer, by applying sufficient coating thickness for a lifetime. Underneath the top layer a nickel layer has been applied. This provides protection against corrosion where the top coating is no longer present.

Table 1 summarizes the results. The interpretation above are taken into account with the conclusions drawn.

Table 1: Overview of the results of the Qualification test according to NBD 10300 (2010) on the Lunac 2+ duplo coating

Onderdeel	Criterium	Resultaat Lunac 2+ duplo	Conclusie
EPQ	Potential >-0.35V	-0.39V to -0.31V [potential -0.38 tot-0.32]	Acceptable
Galvano-static test	Potential >-0.35V	>0.35V	Acceptable
	Stroomdichtheid <1µA/cm² tot 0mV	0.6µA/cm², 1µA/cm² at -0,35V uniform corrosion 1-4µm/jaar	Acceptable, passive sublayer
	Visually no corrosion	Discolouration	Acceptabel



5 Conclusions

The Lunac 2 + coating meets the requirements of the NBD10300 (2010), with the remark:

- The top layer has a corrosion rate of 1-4 μ m per year, the design of the layer has to be taken into account by an adequate thickness of the top layer and an intermediate layer of nickel.

6 Recommendation

There is a dynamic equilibrium in thickness and density of the oxide film that protects the top layer. In practice, the design of the construction is of major importance for the lifetime of the coating. In the case of coupling with a stainless steel under water, the corrosion rate increases, and in the case of coupling with carbon steel corrosion rate will be reduced. It is recommended that this is taken into account in the design.