Corrosion Protection with Nanoscale Anticorrosive Pigments in Coatings

Marc Entenmann, Heinz Greisiger, Roman Maurer, Thadeus Schauer

Fraunhofer Institute for Manufacturing Engineering and Automation, Stuttgart, Germany

Fraunhofer IPA

EC European Coatings CONGRESS

European Coatings AWARD

sponsored by
European Coatings JOURNAL

Marc Entenmann
Heinz Greisiger
Roman Maurer
Thadeus Schauer

Fraunhofer Institute for Manufacturing Engineering and Automation et al.

received the European Coatings AWARD 2011
for the best paper, entitled

"Corrosion protection with nanoscale anticorrosive pigments in coatings"

Nuremberg, 28 March 2011

Dr. Sonja Schulte
Managing Editor
European Coatings JOURNAL
Vincentz Network

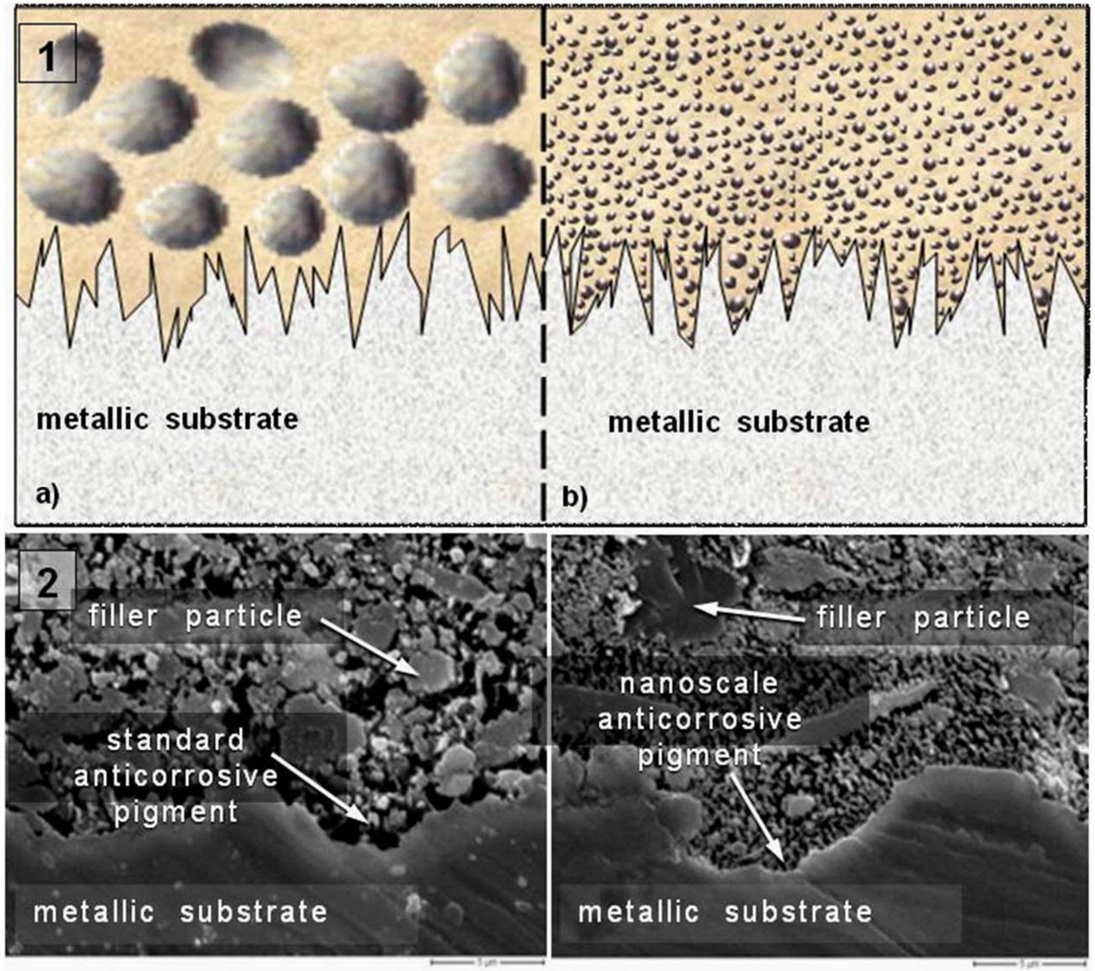
Kirsten Wrede
Editor
European Coatings JOURNAL
Vincentz Network

- **First you will be shocked**
- **Then the coating will be attacked**
- **Finally, if not removed, an irreversible damage and corrosion can proceed**

Corrosion Protection with Anticorrosive Pigments in Primers

- For corrosion protection of metals with primers, the properties of corrosion protection pigments, such as particle size, interaction with binder, barrier effect, as well as release and transport of active species to the metal surface are of great importance.
- A lot of attention was paid to develop new kinds of anticorrosive pigments and to improve barrier effects of coating layers, but less attention was paid to optimize the particle size distribution of corrosion protective pigments.
- Because of the enlarged surface area and their reduced particle size, the release as well as the transport of active species to the metal surface should be improved in case of nanoscale anticorrosive pigments.
- Conventional and nanoscale corrosion protective phosphate derivates have been investigated and compared to clarify the influence of size and surface aspects of pigments on the corrosion protection with primers.

Conventional and Corresponding Nanoscale Pigments - Preparation, Schematic Model and Reality

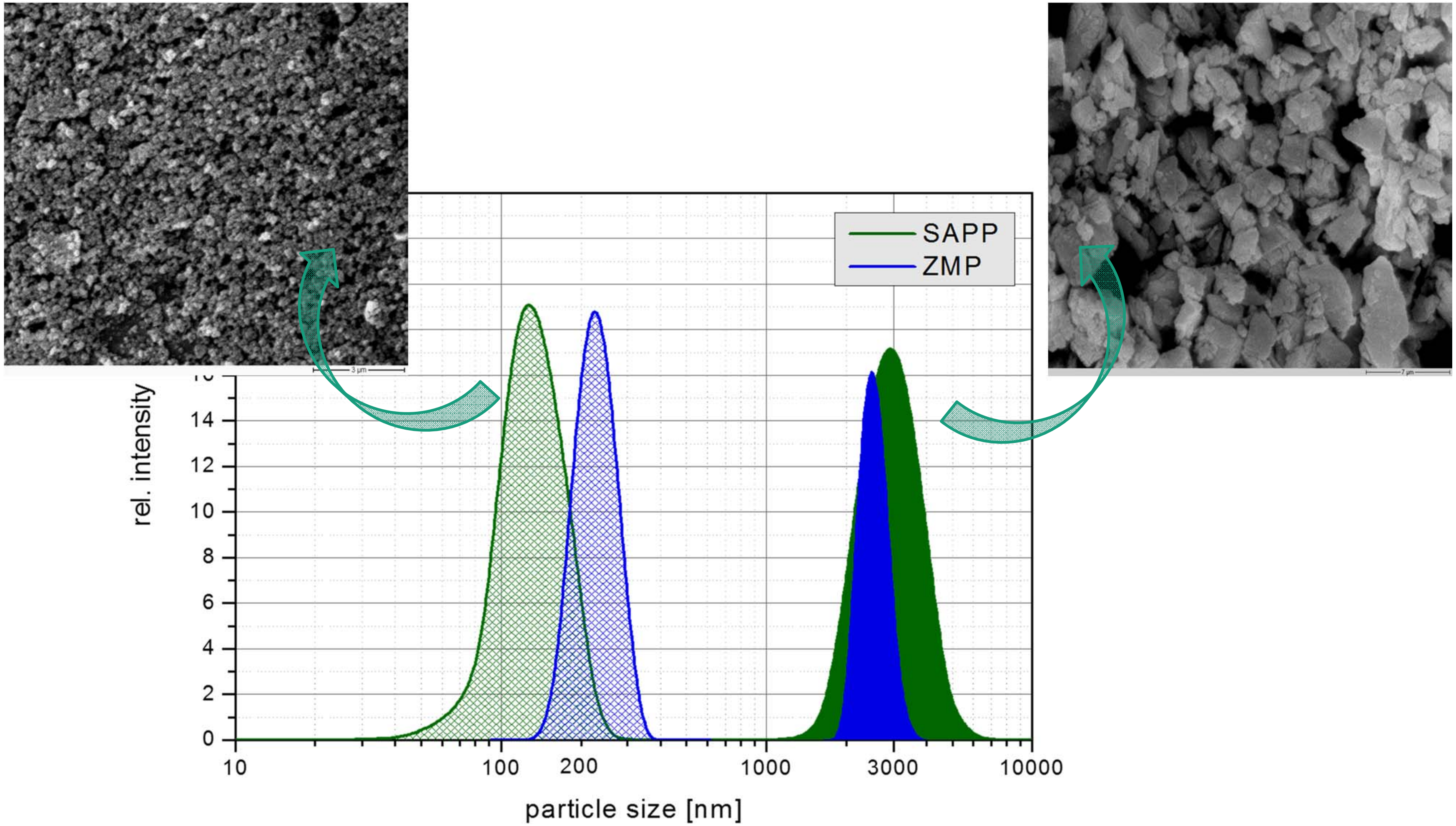


Preparation of nanoscale pigments:

Using a nano-mill equipment as well as wetting and stabilizing agents, the nanoscale corrosion protection pigments were obtained from Heucophos SAPP and ZMP dispersions

The **left picture** represents a schematic model of a pigment distribution in the coating **(1)** and the SEM micrographs **(2)** for a primer coating with standard **(a)** and the obtained nanoscale corrosion protective pigments **(b)**

Characterisation of Corrosion Protection - Pigments with DLLS and SEM



Typical Compositions of a Primer Formulation Including 10 Vol. % of Corrosion Protective Pigment

Component	Amount w. %	Component	Amount w. %
Araldite GZ 7071 X75	18.6	Araldite GZ 7071 X75	17.7
Aradur 423 (60%)	15.3	Aradur 423 (60%)	14.5
Millicarb BG	20.4	Millicarb BG	19.3
Talkum 10M2	6.8	Talkum 10M2	6.4
Heucophos® SAPP	9.7	Heucophos® ZMP	12.7
BYK 052	0.2	BYK 052	0.2
Anti-Terra U	0.5	Anti-Terra U	0.5
Thixatrol ST	1.0	Thixatrol ST	1.0
Xylene	2.0	Xylene	2.0
Solvent mixture	25.6	Solvent mixture	25.6

Barrier Properties of Coatings and Solubility of Standard and Nanoscale Pigments

Anticorrosive pigment	Solubility of Zn [weight %] *	Water permeability of coating film ** [g/(m² *day)]	Oxygen permeability of coating film *** [ml/(m² *day)]
ZMP standard	0.29	11.5	183.6
ZMP nano	0.26	10.2	169.1

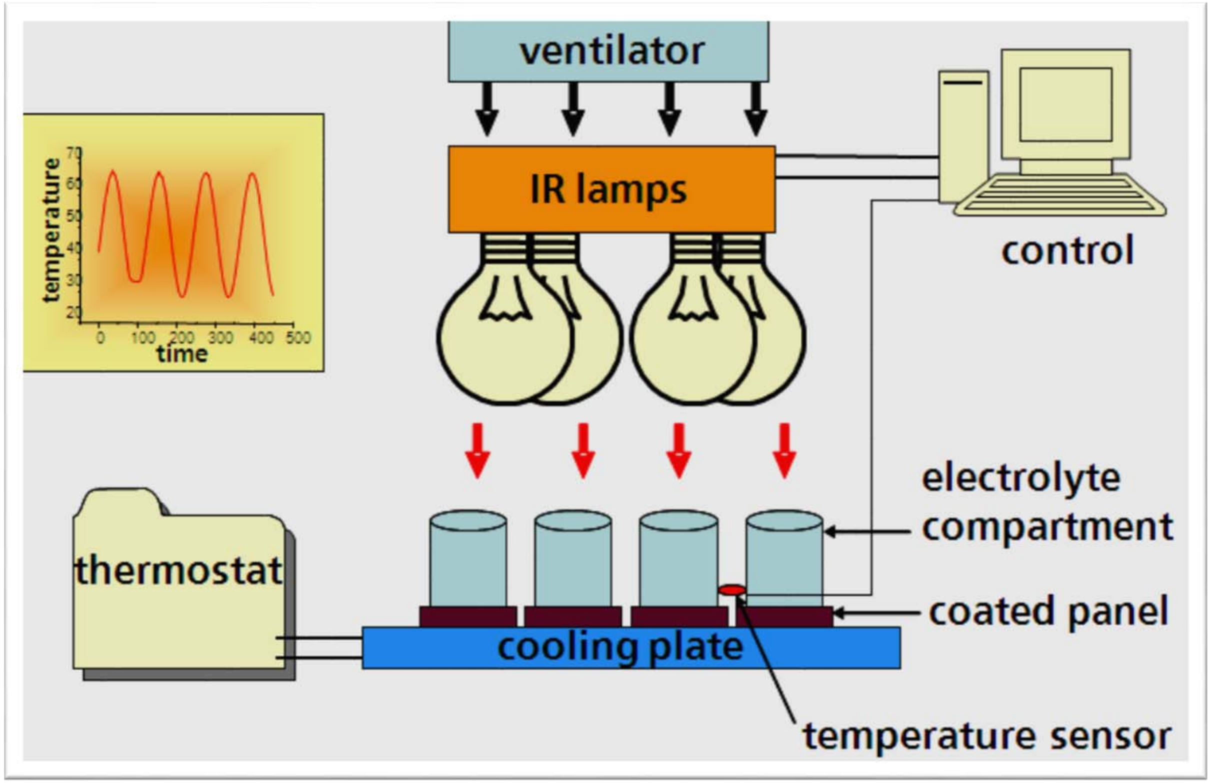
* solubility measurements performed with an inductively coupled plasma optical emission spectrometer ICP-OES

** water permeability measurements performed on free films at 38°C and humidity between 10% to 14% using Lyssy L80-500 from PBI Dansensor

*** oxygen permeability testing performed on free films at 23°C with the oxygen permeability tester Lyssy OPT-5000 from PBI Dansensor

It is obvious that the solubility of the pigment as well as the barrier properties of the coating against water and oxygen permeation were not greatly influenced by the reduction in particle size of the corrosion protective pigment

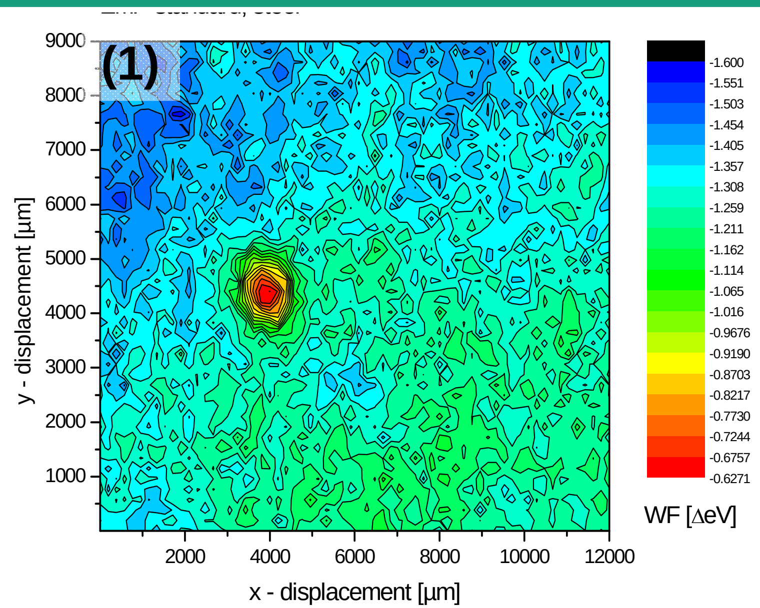
Corrosion Testing - Thermocyclic Electrolytic Loading with FPL Test*

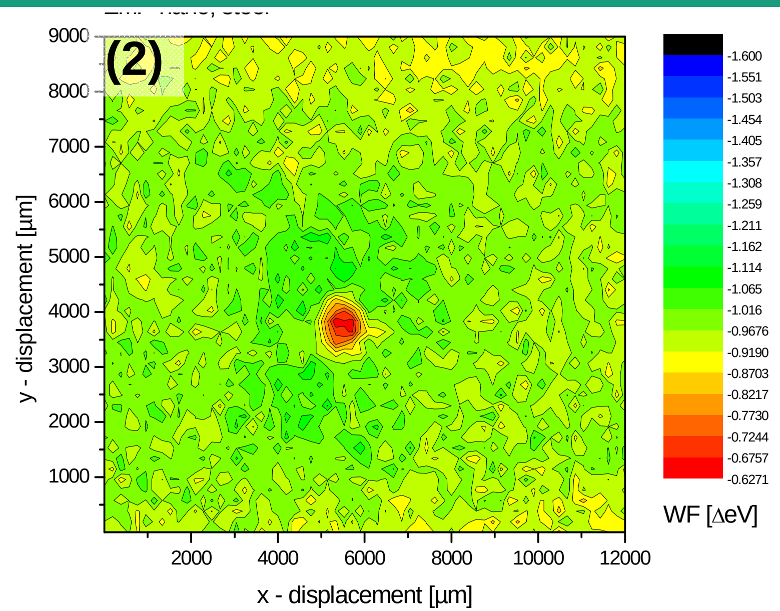


Scanning Kelvin Probe (SKP) and impedance measurements were performed on thermocyclic loaded samples (FPL Test), in contact with Harrison solution, consisting of 35 g/l $(NH_4)_2SO_4$ and 5 g/l NaCl

*Patent Application No. DE 10 2004 027 792

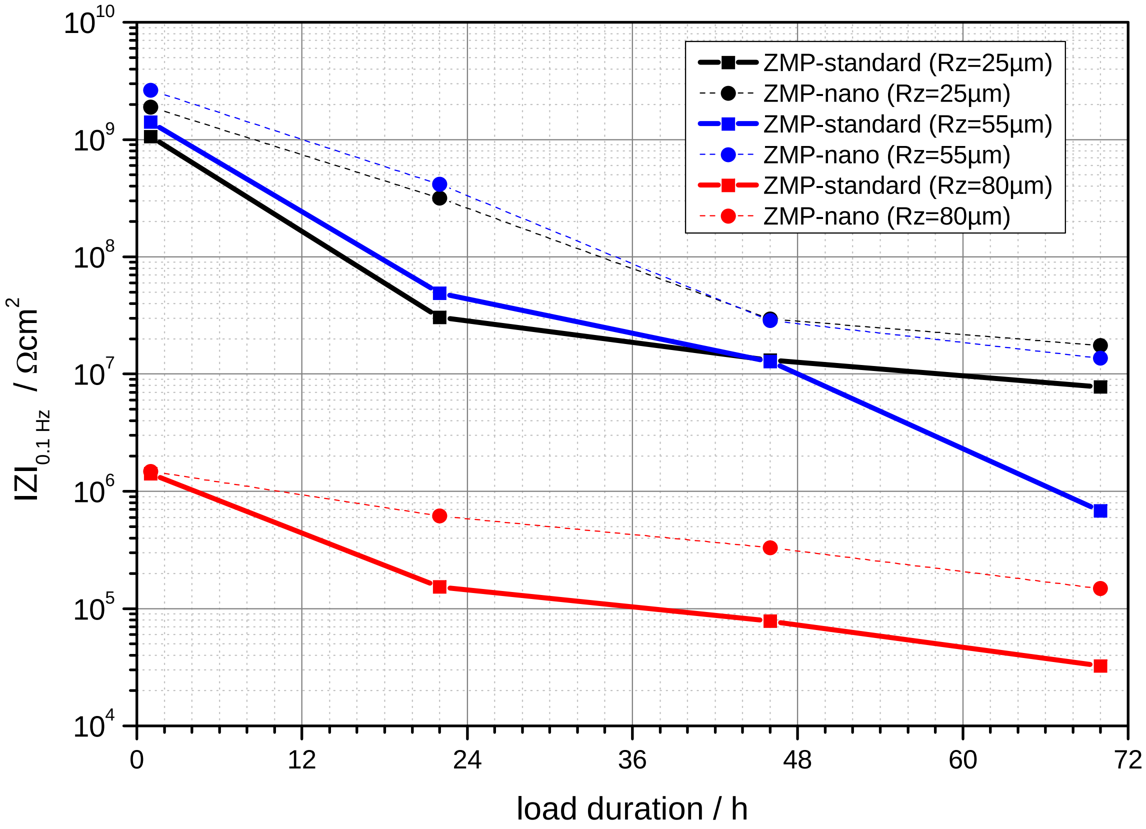
Results of Scanning Kelvin Probe (SKP) Measurements After Thermocyclic Electrolytic Loading Using FPL Test





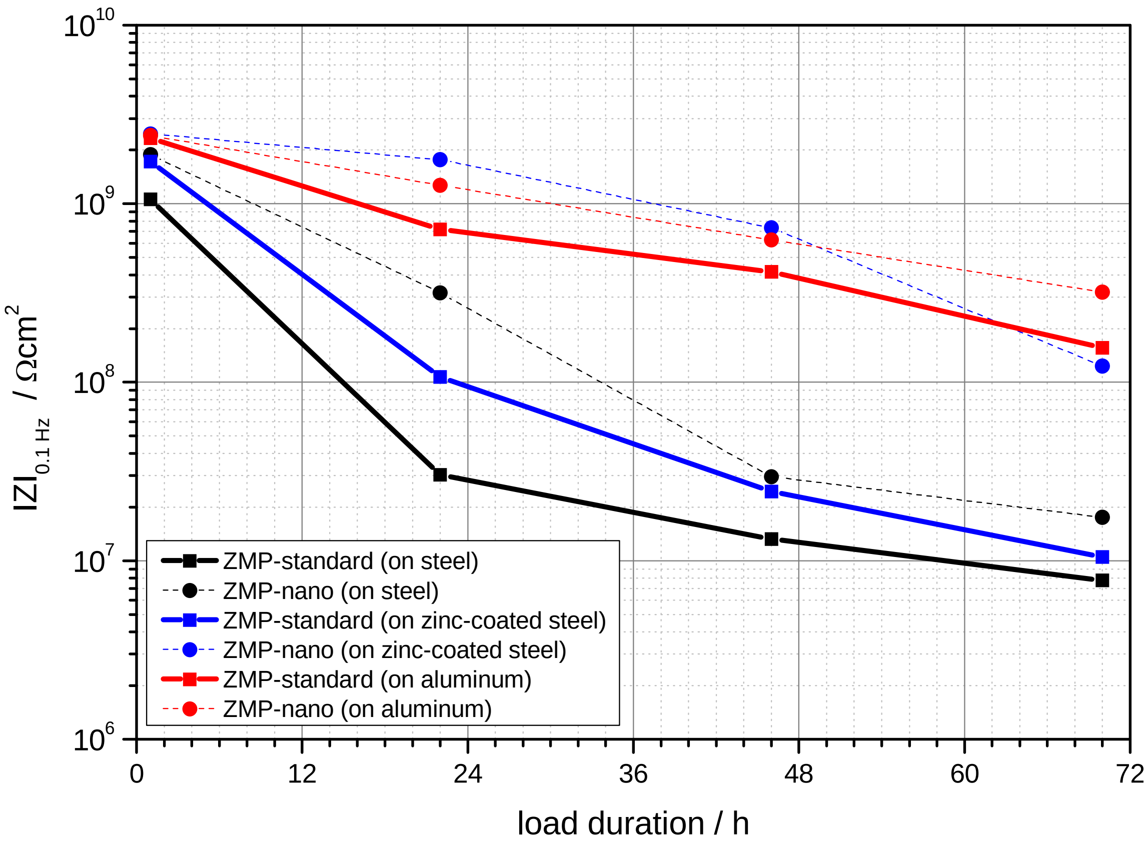
- SKP results for steel panels with medium roughness, coated with a primer containing ZMP standard **(1)** and ZMP nano **(2)** after 70 hours of thermocyclic electrolytic loading (FPL Test)
- The sample with ZMP nano in comparison with ZMP standard shows a more homogeneous work function distribution, with small work function differences and a less active corrosion in the area nearby the defect (Ø 0.1 mm holes)

In Situ Results of Impedance Measurements on Steel Substrates by Thermocyclic Electrolytic Loading



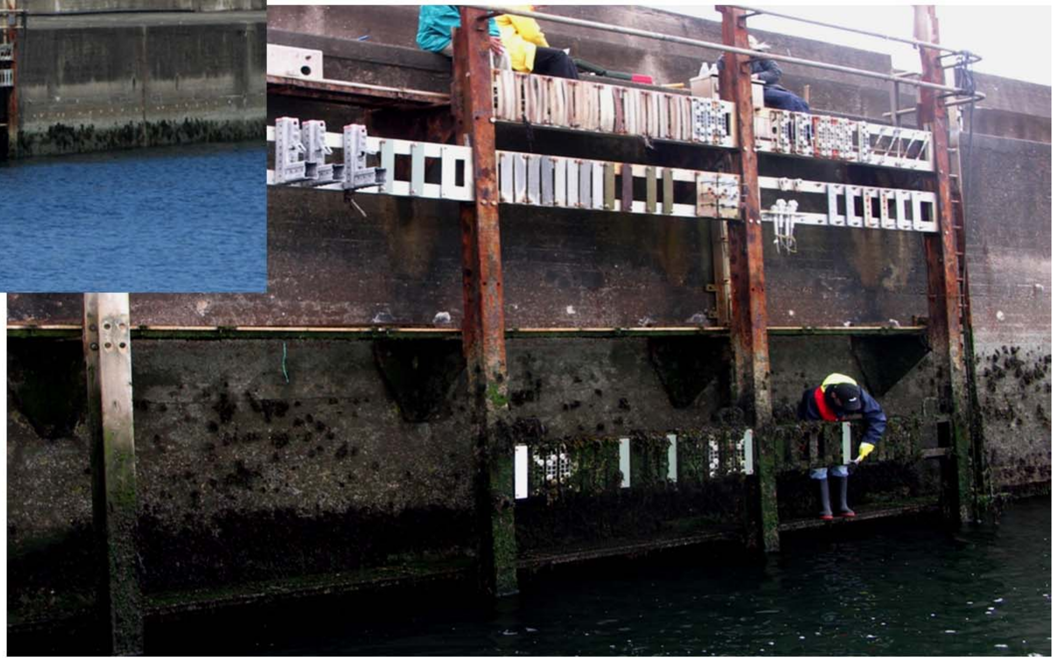
- For characterisation of corrosion stability with impedance measurements mainly the time dependent development of impedance at 0.1 Hz was used
- The difference between nanoscale (dotted line) and standard (solid line) becomes a maximum for steel substrates (DC04B) with medium roughness of Rz = 55 µm (blue line), whereas for higher roughness (Rz = 80 µm; red line) the impedance values are very low. Samples with low surface roughness (Rz = 25 µm; black line) were more stable against corrosion.

In Situ Results of Impedance Measurements on Different Metals by Thermocyclic Electrolytic Loading



- The better corrosion protection properties of the nanoscale corrosion protection pigment (dotted line), in comparison with the corresponding standard pigment (solid line) could also be confirmed for primer coated aluminum (red line) and hot dipped steel (blue line; surface roughness Rz = 20 - 30 µm) substrates

Outdoor Weathering at Helgoland

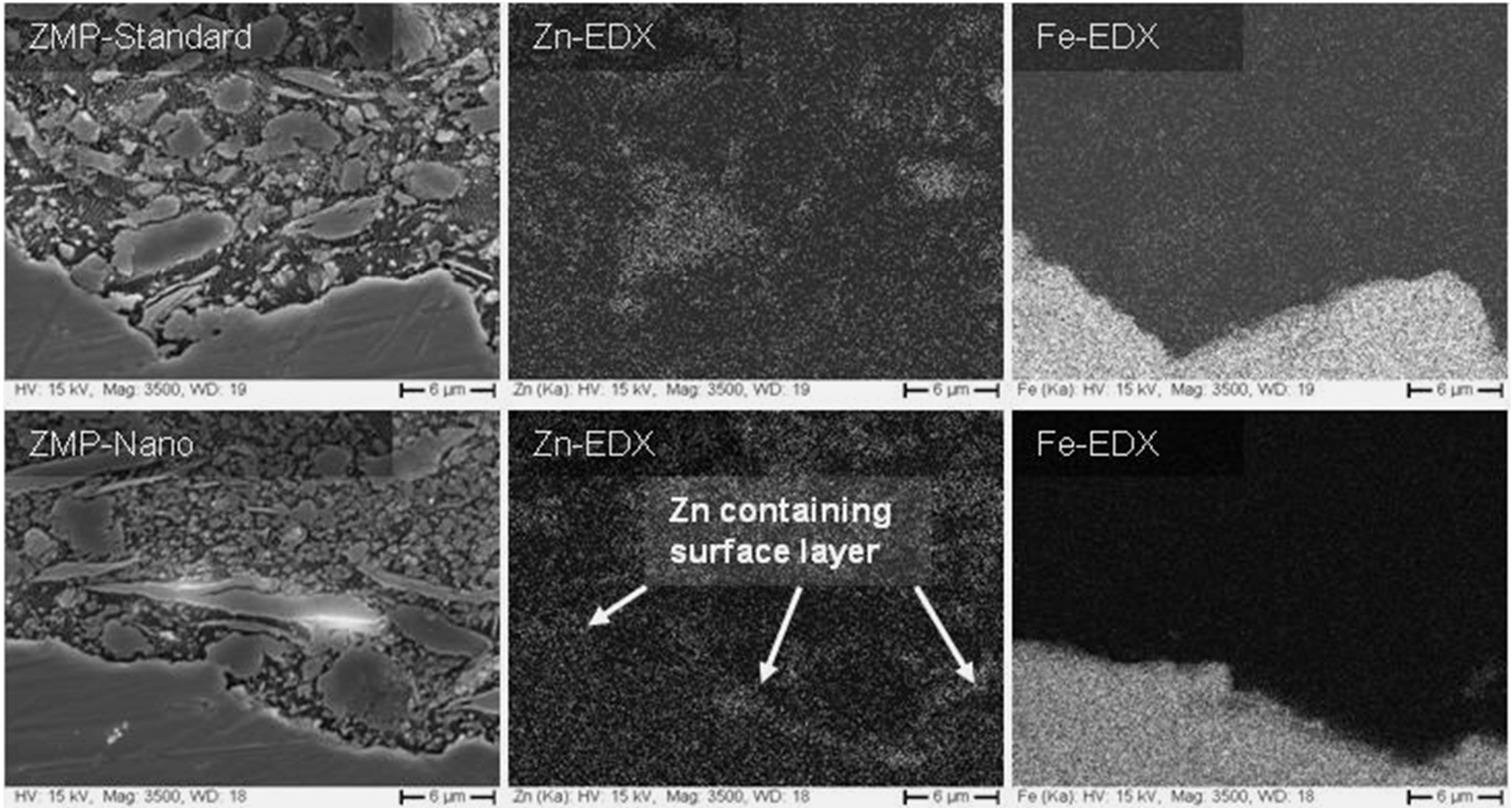


Comparison of Different Corrosion Test Results for Primers on Steel Panels

Corrosion protective pigment	Salt spray test rust grade DIN EN 4628-3	Outdoor weathering rust grade DIN EN 4628-3	Thermocycling, 60 h $\lvert Z \rvert_{0.1\ Hz}$ [Ωcm^2]
Rz ≈ 25 µm			
ZMP standard 10 Vol.%	**2***	**0**	1.0E7
ZMP nano 10 Vol.%	**0***	**0**	**2.3E7**
Rz ≈ 60 µm			
ZMP standard 10 Vol.%	**0**	1	2.5E6
ZMP nano 10 Vol.%	**0**	1	**2.0E7**

• efficient corrosion protection, • less efficient corrosion protection

SEM and EDX Analysis of Primer Coated Steel Samples Exposed to Atmospheric Weathering in Helgoland Clearly Confirm the Better Corrosion Protection of Nanoscale Corrosion Protective Pigments



Conclusions

- Nanoscale corrosion protective pigments of a zinc phosphate type provide a more efficient corrosion protection of steel, aluminium and zinc as standard microscale products.
- The nanoscale pigments can be obtained by milling with proper milling equipment and use of efficient particle stabilizing additives.
- The superior corrosion protection with nanoscale pigments was evidenced by short time thermocycling with impedance and SKP detection, salt spray test and weathering in Helgoland.
- EDX measurements of samples after weathering revealed an enhanced concentration of zinc on the metal surface for primers with nanoscale pigments and more iron for primers with standard pigments. Both results are indicative for a better corrosion protective performance of nanoscale pigments.
- Regarding the protective mechanism, it could be stated that in case of nanoscale pigments a better availability of active species in the close vicinity of the metal surface and their "release on demand" are the reasons for a better corrosion protection.

Acknowledgements

- This project was conducted by Fraunhofer Institute for Manufacturing Engineering and Automation, coordinated by the Research Association of Pigments and Coatings (FPL) and financially funded via AiF by the German Federal Ministry of Economics and Technology within the governmental R&D-support-measure "Industrial cooperative Research".

- Our sincere thanks are given to HEUBACH GmbH, HUNTSMAN Advanced Materials, NANO-X GmbH and EMIL FREI GmbH & Co. KG for supporting the project.

FreiLacke heubach HUNTSMAN Enriching lives through innovation NANO-X

Fraunhofer IPA

Thank you for your Attention …

AiF

Ideen eine Zukunft geben

Gefördert durch das

Bundesministerium
für Wirtschaft
und Technologie

Fraunhofer
IPA

FPL FORSCHUNGSGESELLSCHAFT
FÜR PIGMENTE UND LACKE E.V.

VINCENTZ