# A finer level of defence

## Corrosion protection with nanoscale anticorrosive pigments in coatings

* **Corresponding author:**
Dr. Marc Entenmann
Fraunhofer Institute for Manufacturing, Engineering and Automation (IPA)
T +49 711 68780-49
marc.entenmann@ipa.fraunhofer.de

Marc Entenmann*
Heinz Greisiger
Roman Maurer
Thadeus Schauer

**The effects of milling standard phosphate-based anticorrosive pigments to nanoparticle size have been investigated. Notably, the finer particles were able to approach the metal surface more closely when formulated into a primer. Several different tests in an epoxy primer confirmed that the nanoparticles gave better corrosion resistance than the standard form of the same pigment.**

For efficient corrosion protection of metals and alloys with primers as well as for self-healing effects, the properties of anticorrosive pigments such as particle size, interaction with the binder, barrier effect, release of active species and their transport to the metal surface are all of great importance.

Conventional and nanoscale corrosion protective phosphate derivatives have been investigated to clarify their influence on all these factors and ultimately on the efficiency of the corrosion protection of metallic substrates. The chosen pigments were incorporated into a solvent-based epoxy primer and tested on steel, galvanised steel and aluminium substrates with short time tests, electrochemical methods and atmospheric weathering.

SEM images of paint cross-sections were also taken to reveal the pigment particle distributions. Advantages of nanoscale pigments such as efficient corrosion protection, good self-healing and barrier properties have been noted. Some influence of the metal surface roughness on these properties was also observed.

| Component | Primer 1 [wt. %] | Primer 2 [wt. %] |
|---|---|---|
| Araldite GZ 7071 X75 | 18.6 | 17.7 |
| Aradur 423 (60 %) | 15.3 | 14.5 |
| Millicarb BG | 20.4 | 19.3 |
| Talkum 10M2 | 6.8 | 6.4 |
| Heucophos SAPP | 9.7 | -- |
| Heucophos ZMP | -- | 12.7 |
| BYK 052 | 0.2 | 0.2 |
| Anti-Terra U | 0.5 | 0.5 |
| Thixatrol ST | 1.0 | 1.0 |
| Xylene | 2.0 | 2.0 |
| Solvent mixture | 25.6 | 25.6 |
| Total | 100.1 | 99.9 |

*Table 1: Compositions of a primer formulation with 10 vol. % of corrosion protective pigment*

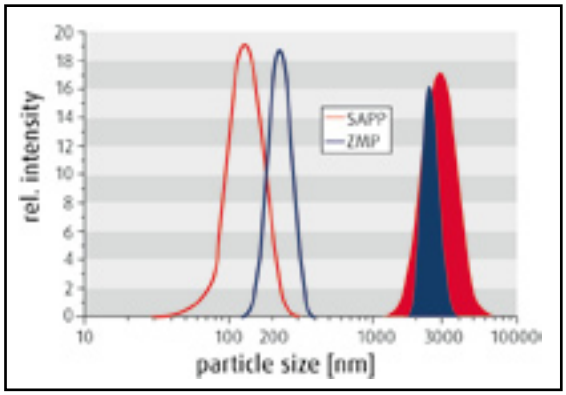


*Figure 1: Particle size distributions of the original and milled anticorrosive pigments according to a DLLS test procedure*

### Milling and application procedures

Nano-mill equipment was used for the milling experiments with the conventional corrosion protective pigments "Heucophos SAPP" and "Heucophos ZMP". With the use of wetting and dispersion agents, the best results after three hours of milling were obtained for a 25 wt.% pigment dispersion in isobutanol.

These nanoscale anticorrosive pigment pastes were added to a conventional epoxy primer formulation consisting of "Araldite GZ 7071X75" and "Aradur 423". "Millicarb BG" and "Talkum 10M2" were added to the formulation as fillers. Typical compositions of a primer formulation with 10 vol.% of standard and nanoscale corrosion protective pigment are given in *Table 1* for both anticorrosive pigments.

After spray application of the primer formulations with a dry layer thickness of 60 µm on typical construction materials like on steel (DC04B) with different surface roughness, on hot dipped steel (surface roughness Rz = 20-30 µm) and aluminium panels (Rz = 20-30 µm), the samples were stored for seven days at 23 °C before they were finally dried in an oven for 30 minutes at 80 °C. For steel panels a fine (Rz = 20-30 µm), medium (Rz = 50-60 µm) and rough surface (Rz = 80-100 µm) were obtained using sandblasting devices.

### Test procedures summarised

The particle size distribution was characterised with a "Nanosizer ZS" from Malvern Instruments, utilising dynamic laser light scattering (DLLS).

The barrier properties of the primer layers were determined on free coating films with permeability testers from PBI Dansensor. For the water permeability meas-

urements, the permeability tester "Lyssy L80-500" was used at a relative humidity of 10 % to 14 % and a temperature of 38 °C. The oxygen permeability testing was performed at 23 °C using the oxygen permeability tester "Lyssy OPT-5000".

The pigment solubility of ZMP was determined by means of zinc dissolution, using an inductively coupled plasma optical emission spectrometry (ICP-OES) device. For the analysis, 1 g of pigment was dispersed in 400 g distilled water and dialysis in distilled water was performed for a duration of four weeks. The solubility obtained was calculated in wt. % with respect to the original pigment.

Corrosion testing was carried out by applying scanning Kelvin probe (SKP) and impedance measurements. Both measurements were performed after a thermal cycling loading for 70 h on samples additionally charged with a Harrison solution, consisting of 35 g/l $(NH_4)_2SO_4$ and 5 g/l NaCl. In contrast to impedance measurements, for the SKP measurements 0.1 mm holes were drilled through the coating layer of the samples before charging the sample with Harrison solution and thermal cycle loading.

To characterise the corrosion stability with impedance measurements, the time-dependent development of the impedance at 0.1 Hz was mainly used. The results obtained were compared with atmospheric weathering evaluations of samples exposed in Helgoland (off the north German coast) and also with salt spray test according to DIN EN ISO 9227 using a rust grade evaluation according to DIN EN 4628-3.

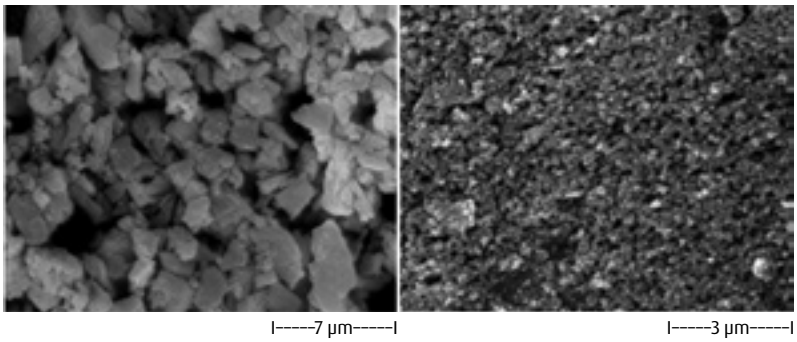


*Figure 2: SEM micrographs for the original (left) and milled (right) anticorrosive pigment*

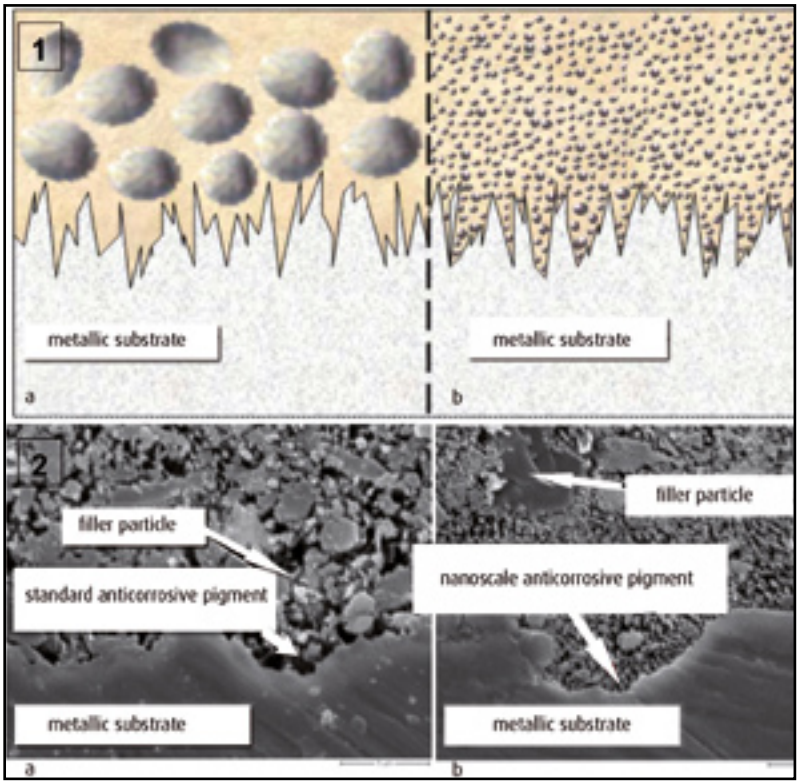


*Figure 3: Schematic model of a pigment distribution in the coating (1) and the SEM micrographs (2) for the primer with a standard (a) and a nanoscale anticorrosive pigment (b)*

## Results at a glance

»› The effects of milling standard phosphate-based anticorrosive pigments to nanoparticle size have been investigated. Particle size was reduced from the standard 3 µm to approximately 200 nm.

»› It was confirmed by SEM that a stable nanodispersion had been obtained, and that (in accordance with theory) the finer particles were able to approach more closely to the metal surface when formulated into an epoxy primer coating.

»› Tests were based on natural weathering, scanning Kelvin probe evaluation of the work function, impedance measurements and salt spray. All methods confirmed that the nano form of the pigment "Heucophos ZMP" gave better corrosion protection than the standard.

»› On the other hand, tests of zinc solubility, water permeability and oxygen permeability of the test coating showed only minor differences between the standard and nanoparticulate pigments.

## How particle size reduction modifies performance

For both commercially available anticorrosive pigments, after milling the original d50 values of approx. 3 µm were reduced to values between 100 and 200 nm, as shown in *Figure 1*. In *Figure 2*, SEM micrographs for the original and milled anticorrosive pigment are presented. From both

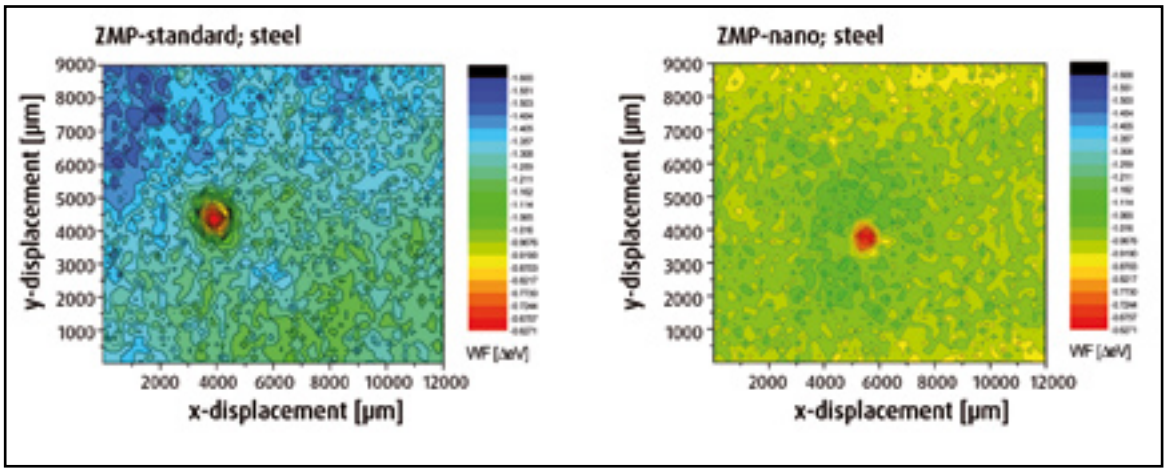


*Figure 4: Differences in work function WF (ΔeV) obtained by SKP measurements for primers with "ZMP" standard (left scan) and the nano form (right scan) after thermal cyclic loading*

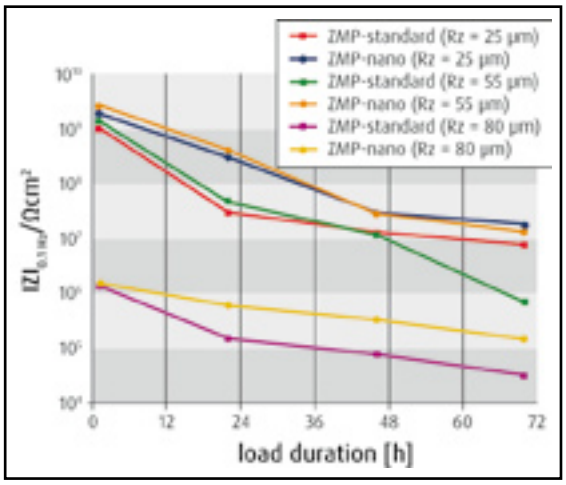


*Figure 5: Impedance data at 0.1 Hz for primers with "ZMP" standard and nano on steel substrates with different surface roughness, under combined thermal cycle and Harrison solution loading*

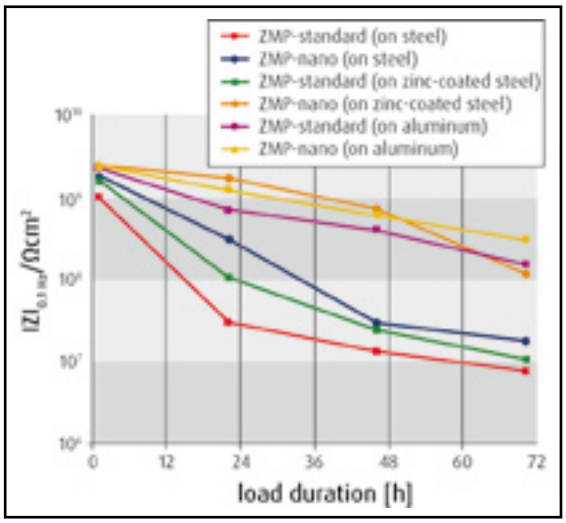


*Figure 6: Impedance data for primer layers with "ZMP" standard and nano on steel, zinc coated steel and aluminium substrates under combined thermal cycle and Harrison solution loading*

figures it can be concluded that nanoscale anticorrosive pigments can be obtained by milling with suitable equipment and appropriate stabilisation of particles.

Because of the nanoscale character and relatively large surface area, the availability of anticorrosive active species for corrosion inhibition of the metallic surface should be improved with nanomilled pigments. The potential to approach closely to the metal surface, despite any roughness hindrance, should also be better for nanoparticulate pigments. Both the smaller surface distance as well as the increased availability of corrosion inhibitive species should lead to better corrosion protection of a metal substrate.

In *Figure 3* a proposed schematic model for the distribution of pigment particles in a coating is compared with real SEM micrographs, obtained for primers with standard and nanoscale corrosion protective pigments. With these micrographs the closer approach of nanoscale pigment particles to the metallic surface is confirmed.

The influence of a nanoscale character of ZMP on the barrier properties of the coating and pigment solubility were also tested. *Table 2* summarises the results obtained. It is obvious that both characteristics, 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.

## Laboratory tests show improved corrosion protection

The corrosion testing of samples was performed by SKP and impedance measurements. With SKP measurements, the differences in a work function were determined after conducting a thermal cycle loading for 70 hours on samples which were additionally charged with a Harrison solution.

In *Figure 4* the SKP data for steel panels with medium roughness, coated with primers containing standard and nano "ZMP" are shown after thermal cycling. It is

obvious that the sample with the nano pigment in comparison with "ZMP" standard shows a more homogeneous work function distribution, with small work function differences and less active corrosion in the area near the defect.

The improved anticorrosive action of nanoscale anticorrosive pigments could also be confirmed by impedance measurements for primers on steel substrates with a different surface roughness (*Figure 5*) and for other metal surfaces such as hot dipped steel and aluminium (*Figure 6*), loaded by thermal cycling and Harrison solution.

In *Figure 5* it can be seen that the difference in impedance between nanoscale and standard pigmented coatings becomes maximal for steel substrates with a medium roughness of Rz = 55 µm, whereas for substrates with a higher roughness (Rz = 80 µm) the impedance values are very low from the very beginning of measurements.

In each case, the samples with low surface roughness were more stable against corrosion, so the difference in the corrosion protection between the samples with the nanoscale and the standard pigments was also less pronounced. These findings were confirmed by the results of the atmospheric weathering of samples.

The same positive effect is found for nanoscale corrosion protective pigments in a primer on different me-

*Table 2: Barrier properties of coatings and solubility of standard and nanoparticulate pigments*

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

*Table 3: Data from different corrosion tests 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 | Thermal cycling, 60 h \|Z\| 0.1 Hz [Ωcm²] |
|---|---|---|---|
| **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/less efficient corrosion protection)

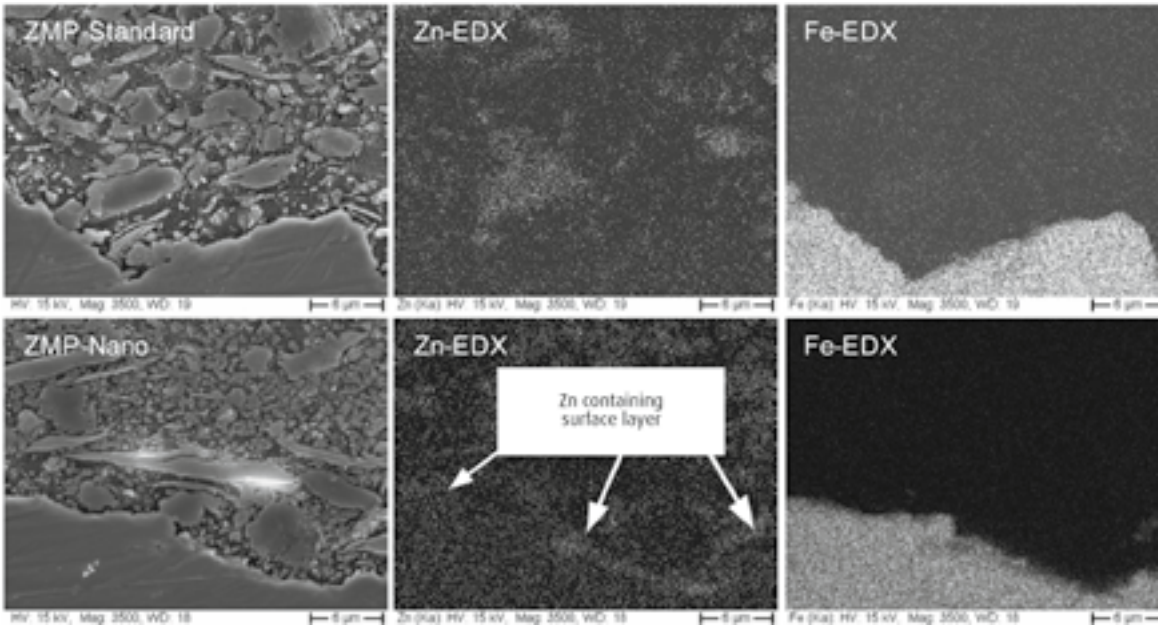


*Figure 7: SEM micrographs and EDX data for primers with "ZMP" standard and nano after weathering in Helgoland*

tallic substrates, as evidenced by the smaller decrease of impedance by thermal cycle loading for the samples with "ZMP" nano in comparison with the standard form (*Figure 6*).

## Natural exposure confirms improved performance

In *Table 3* the impedance data for primers on steel panels with Rz = 25 µm are compared with results of the atmospheric weathering performed in Helgoland and results of the salt spray test, according to DIN EN ISO 9227 with a rust grade evaluation according to DIN EN 4628-3. The data for the tested samples are benchmarked for their efficient (green) and less efficient (red) corrosion protective action.

SEM and EDX analysis of samples exposed to atmospheric weathering in Helgoland clearly confirmed the better corrosion protection with ZMP nano (*Figure 7*). For weathered samples with the nanoscale anticorrosion pigment, zinc was detected on the steel surface, whereas no zinc was found on the surface of samples with ZMP standard pigmented primer. Additionally, more iron was detected within the primer with ZMP standard pigment, which indicates a more intense corrosion of the steel substrate.

## Benefits of finer particles summarised

Nanoscale corrosion protective pigments of a zinc phosphate type provide a more efficient corrosion protection of steel, aluminium and zinc than standard micrometre-sized products. The nanoscale pigments can be obtained by milling the standard products with proper milling equipment and using efficient particle stabilising additives.

The superior corrosion protection with nanoscale pigments was evidenced by short time thermal cycling with impedance and SKP detection, salt spray test and weathering in Helgoland.

EDX measurements on samples after weathering revealed an enhanced concentration of Zn on the metal surface for primers with nanoscale pigments and more Fe for primers with standard pigments. Both results are indicative of a better corrosion protective performance of nanoscale pigments.

Regarding the mechanism of action, it could be stated that in case of nanoscale pigments a better availability of active species in the close vicinity of a metal surface and the action according to the "release on demand" principle explains the improved corrosion protection.

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