

NEW APPROACH TO THE FURTHER DEVELOPMENT OF ZINC PRIMERS

Abstract

- The best corrosion protection is obtained with systems containing a high percentage of spherical Zn pigments.
- A partial replacement of the zinc by conductivity additives is possible; though the optimal composition must be determined individually.
- The system can be held longer within the range of a transitional phase by means of a suitable surface treatment of the zinc pigments. The current results of outdoor exposure prove that this at least does not lead to a decrease of the resistance. Long-term outdoor exposure will show to what extent zinc pigments with surface treatment lead to an increased resistance.
- The results of the standardized and the electrochemical tests broadly confirm each other.
- The electrochemical tests reveal strong indications for the actual existence of a two phase protective effect mechanism in zinc primers. The formation of a protective effect plateau when exceeding the transitional phase (-0.70 V vs. calomel) proves that the zinc corrosion products developing in the electrochemical active phase of the zinc significantly contribute to the barrier effect of the system.

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Table 1: Composition of the zinc primers; the additives were appointed to increase conductivity

| Probe name | Zinc sphere content/Vol. % | Additive content/Vol. % | Talc content/Vol. % | PVK/Vol. % |
|--------------------------|----------------------------|-------------------------|---------------------|------------|
| VS50 ¹⁾ | 50 | - | 8 | 58 |
| VS40-VMi10 ²⁾ | 40 | 10 | 8 | 58 |
| VS40-VMi3 | 40 | 3 | 15 | 58 |
| VS40-VRu3 ³⁾ | 40 | 3 | 15 | 58 |
| VS40-VBa3 ⁴⁾ | 40 | 3 | 15 | 58 |
| VS25-VMi10 | 25 | 10 | 19 | 54 |
| VS35 | 35 | - | 19 | 54 |
| VS50beh1 | 50 | - | 8 | 58 |
| VS50beh2 | 50 | - | 8 | 58 |

1 S: Zinc dust Superfine 620 (Conmet)

2 Mi: Minatec 31CM Transparent (Merck)

3 Ru: Carbon black Special black 100 (Evonik)

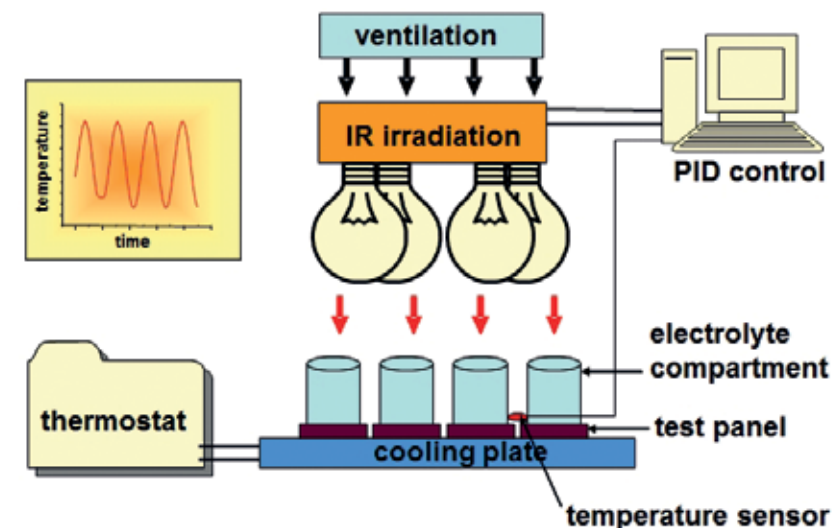
4 Ba: Barium ferrite (Sigma-Aldrich)

Goals of the Analysis

The scope of this analysis is intended to determine that

- in zinc corrosion protection primers, variation, type and amount of the zinc proportion, furthermore surface treatment of the particles as well as partial substitution with conductible additives can achieve an improvement of corrosion protection properties.

- the dual effect mechanism discussed in literature actually exists (phase 1: cathodic corrosion protection, phase 2: barrier).



Device for conducting the thermocyclic-electrolytic loading

Sample Preparation and Conduct of the Analysis

Table 1 shows the basic composition of the produced zinc primers that were applied on sheet steel (Co. Krüppel) by spraying. A week earlier, these steel sheets were sandblasted with grit (Sa2.5 medium(G) RZ 66-70 µm, Co. Raga). With spray application employing the two-part epoxy system, the one layer thickness of the dry layer resulted 80 µm. On the sheet steel intended for atmospheric exposure on Helgoland, the left side was applied in one layer, the right side in two layers (dry layer thickness 120 µm). The layer thicknesses on the substrates that were used for standard laboratory atmospheres and electro chemical measurements were applied on the two layer dry layer thicknesses (120 µm). All listed systems were also produced in the version with a finishing coat, for which the mentioned two-part epoxy system was employed (without corrosion protection pigmentation). The samples were stored for at least ten days at 23°C/50% RH after the application.

The exposures were conducted for electrochemical analysis and realized via the FPL test, which generates an accelerated aging of the coating due to thermo-cyclic induced internal stress. Here a 3% NaCl solution continuously acts in a sinus form temperature cycle from 20°C to 70°C upon the coating surface (period length: 1 h). To determine the electrochemical character, the sample steel platens were removed approx. Every 36 hours from their exposure and characterized in terms of their electrochemical potential as well as of their impedance spectroscopic data. Both were carried out via a Gamry Reference 600 Potenziostat/Galvanostat/ZRA combined device. The impedance spectroscopic characterization was carried out in a two electrode configuration with a modulation amplitude of 15 mV. The capacitances correlating with the water absorption were determined from the high frequency impedance modules $|Z|_{HF}$ ($f = 100$ kHz) as per

$$C = (2\pi f|Z|_{HF})^{-1}$$

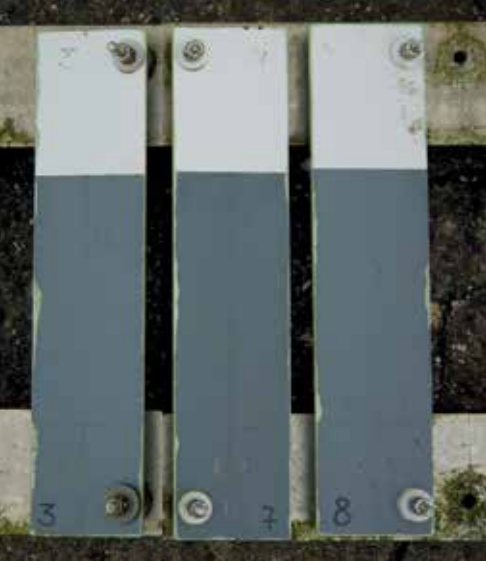
The quantity correlating with the barrier effect is the low frequency impedance module $|Z|_{LF}$, that is read at 0.1 Hz. A calomel electrode was employed for absorption of the

electrochemical potentials; the values of the potentials were read after the plateau phase was reached. The Helgoland atmospheric exposure was carried out after a 14-day-minimum period of standard climate conditioning. The selected dedicated systems were vertically located in the spray water zone within the breakwater in calendar week 24 of 2012, and inspected in calendar week 47 of 2012. The salt spray test was carried out in compliance with DIN EN ISO 9227, the condense water test in compliance with DIN EN ISO 6270-1.

Results

The potential profiles registered during the thermo-cyclic electrolyte exposures for the zinc primers described in table 1 are displayed in figs. 1 and 2.

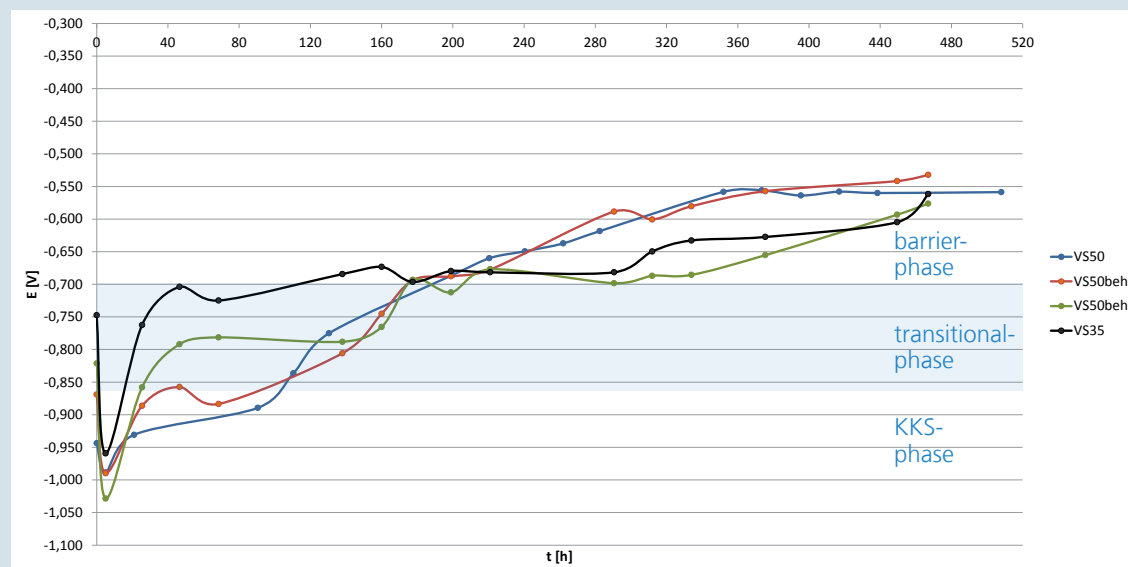
The corrosion potential of iron is -0.86 V. As long as lower potentials are registered, oxidative processes will solely take place on the zinc. With reference to literature, this phase is denominated as the phase of cathodic corrosion protection (KKS). In the potential range of up to approx. -0.70 V the percentage of the already oxidized zinc increases, however, the remaining active zinc effectively continues to prevent corrosion of the iron (transitional phase). Pertaining to potentials above -0.70 V, the electrochemical contribution of the zinc is significantly less; instead the barrier effect resulting from the emerged zinc corrosion products moves in the foreground. These corrosion products block the diffusion paths through the coating and block further access of corrosive media to the substrate.



An exposition to outdoor weathering for a duration of six months of the systems VS50 (3, left), VS40-VMi10 (7, middle) and VS50beh1 (8, right) in the splash zone on Helgoland proves the excellent anti-corrosion effectiveness.

„THE FRAUNHOFER IPA CHOSE AN INNOVATIVE APPROACH FOR THE ASSESSMENT OF ZINC DUST PRIMING COATS AND IMPLEMENTED THIS APPROACH INTO IMPRESSIVE NEW INSIGHTS. WE WOULD LIKE TO THANK THE FRAUNHOFER IPA FOR THEIR ENORMOUS COOPERATION.“
DR. RALF GORNY, CONMET GMBH

Fig. 1: Potential profile (vs. calomel) of the four primers without conductible additives during the thermo-cyclic electrolyte exposure.



The comparison of the potential profiles in figs. 1 and 2 with the evaluated impedance data exemplary for VS50 in terms of water absorption and barrier effect (fig. 3) shows that the time of entry in the barrier phase coincides with the creation of a plateau situation correlating with the water absorption and barrier effect high frequency capacitances and low frequency impedance modules ($t = 190$ h). The coincidence shown here is a phenomenon almost continuously occurring, at least in terms of correlation between entering the barrier phase and appearance of a plateau with low frequency modules.

Fig. 2: Potential profiles (vs. calomel) of the five primers with conductible additives during the thermo-cyclic electrolyte exposure.

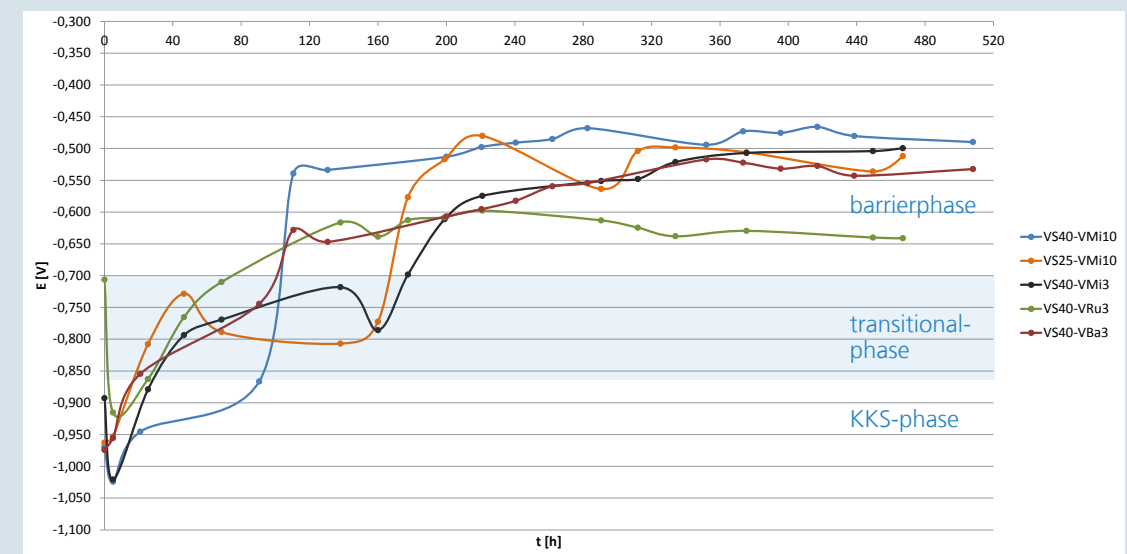


Fig. 3: High frequency capacitances (blue) and low frequency modules (red) absorbed by the primer system VS50 during thermo-cyclic electrolyte exposure.



**„THE FRAUNHOFER IPA WOULD LIKE TO THANK CONMET
FOR THE CONSTRUCTIVE COOPERATION AND THE
GENEROUS SUPPORT OF OUR RESEARCH ACTIVITIES.“**
DR. MATTHIAS WANNER, FRAUNHOFER IPA

Table 2: Data characterizing the potential profiles shown in figs. 1 and 2

| Probe denomination | Durance KKS/h | Entry in the barrier phase/h | E(0h)/V vs. calomel | E(Plateau)/V vs. calomel |
|--------------------|---------------|------------------------------|---------------------|--------------------------|
| VS50 | 109 | 190 | -0,94 | -0,56 |
| VS40-VMi10 | 91 | 105 | -0,97 | -0,47 |
| VS40-VMi3 | 32 | 180 | -0,89 | -0,55 |
| VS40-VRu3 | 27 | 73 | -0,70 | -0,62 |
| VS40-VBa3 | 20 | 103 | -0,97 | -0,52 |
| VS25-VMi10 | 20 | 170 | -0,96 | -0,52 |
| VS35 | 19 | 120 | -0,75 | -0,66 |
| VS50beh1 | 98 | 172 | -0,87 | -0,60 |
| VS50beh2 | 27 | 172..340 | -0,82 | n/a |

Table 2 shows the concluded data of the potential measurements directly accessible at the primers that potentially can be seen in relation with the two phase corrosion protection mechanisms.

Concluded from the potential profiles, the parameter „Durance KKS“ represents the duration until the corrosion potential of the iron is reached (-0.86 V vs. calomel). The parameter „Entry in the Barrier Phase“ represents the duration when the potential of -0.70 V is exceeded. Furthermore, the differences between E(0h) and E(plateau) document the difference between the initially detected potential and the potential that in the barrier phase may be seen as mostly consistent.

The phenomenon of the coincidence between the entry in the barrier phase and the creation of a plateau situation with the low frequency impedance modules meets expectations, since at entry in the barrier phase the barrier effect indeed should be conserved as far as possible due to diffusion restraint induced by the zinc oxide formation. Consequently, the impedance spectroscopic data and the results of the potential are mutually supportive. However, from the high frequency capacitance

diagrams the moment of transition in the barrier phase only in exceptional cases can be read precisely. This is most probably due to the fact that the capacitance of the probes impacted by electrolyte exposure is influenced by the water ingress as well as by the formation of zinc oxide. While the water ingress with its high dielectric constant ($\epsilon_r \approx 80$) highly enhances the capacitance, the increased formation of zinc oxide ($\epsilon_r \approx 8$) altogether contributes to a decrease in capacitance. These two effects superpose each other and thus typically do not lead to a spontaneous formation of a plateau situation in the capacitance figures.

In particular, the data contained in Table 2 may be discussed in the following manner:

- For the primers VS50 and VS35 provided with purely spherical zinc pigments it is valid that a decrease of their concentration leads to an over proportional decrease of the duration for entering the barrier phase; the potentials are highly influenced by variation in concentration.
- Primers with treated (beh) zinc pigments resulted in a situation in which a decrease of the duration until entering the barrier phase but also an exposure induced potential

increase was observed. This may indicate that the treatment can indeed prolong the protective effect. VS50beh2 shows a very stretched potential profile along the border to the barrier phase.

- For the primers partially added with Minatec (Mi) it may be concluded:

- A high Zn concentration with high Minatec concentration results in a short duration until entry in the barrier phase (VS40-VMi10); the result is a high final potential. Apparently, the thus generated high conductivity leads to a quick leveling of the zinc.
- A decrease in the Zn concentration (VS25-VMi10), as well as in the Minatec concentration (VS40-VMi3) substantially prolongs the duration until entry in the barrier phase; in both cases lower final potentials are obtained.

- When varying the type of the conductivity additive, a 3% Minatec concentration in VS40 (primer 12) causes the highest extension until entry in the barrier phase.
- When adding carbon black (primer 13) a substantial reduction of the duration until entry in the barrier phase is observed; a deep fine potential is obtained.
- In primer 15, Bariumferrit effects a reduction of the duration until entry in the barrier phase; the final potential is only slightly affected in comparison to 3a.

In order to clarify to what extent a correlation exists between the parameters derived from the potential profiles and the protective effect of the primers, the zinc primers of the Helgoland outdoor exposure were exposed to the salt spray and condense water test. This showed that there is a principal correlation between the detected corrosion protection effect and the duration until entry in the barrier phase accessible from the potential profile measurements, as long as no conductivity additives are contained. The latter may therefore be used targeted to beneficially influence the protective effect of a primer with a defined zinc pigmentation. The electrochemical results of the systems with a Minatec share show that the relations of concentration must individually be adjusted in order to achieve an optimal resistance of corrosion protection. It is however valid, that a too high as well as a too low percentage of components contributing to the total conductivity lead to a decrease in the resistance of corrosion protection.