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# Testing trial formulations of liquid zinc primers to be combined with powder top coats

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## Abstract

*Generating high barrier top coats for anticorrosive coating systems is increasingly performed using powder coatings. Such top coats are usually combined with a priming zinc or zinc containing layer applied via metallisation, (hot dip) galvanisation or via a powder zinc primer. Since each of these methods implicates certain disadvantages, here, some trial formulations of liquid zinc primers are proposed alternatively, which may be combined with a powder top coat. In order to contribute to an advantageous carbon footprint and a reduced Zn emission, these formulations aimed at improved durability, reduced zinc pigment concentration or a waterbased binder. It is explored to which extent an addition of a degassing agent could prevent pinhole formation in the powder top coat caused by primer solvent residues evaporated during powder top coat curing. Moreover, some test results concerning the protective properties of the zinc primers are reported.*

## Introduction

Present product solutions for offshore powder coatings base on anticorrosive priming layers like Zn galvanised and hot dip galvanised (HDG) steel or (very recently) electrophoretically deposited primers (EDP), which, however, impact the mechanical stability of steel and/or which are largely energy-consuming, not universally applicable or expensive processes. Since zinc containing powder coatings tend to affect the application device and since their use in combination with a powder coating top coat usually requires at least two energy-consuming curing processes, at least in some cases liquid zinc primers may principally be an alternative to be combined with a powder top coat.

Use of liquid (zinc) primers in combination with powder top coats, however, requires sufficiently thermostable primer matrices. Since powder top coats are generally characterised by a large network density, and since large differences in network density between two layers decreases the interphase adhesion, such liquid primers should develop a significant network density. This is more easily achieved, if the (zinc) pigment concentration is kept low. Therefore – and since zinc is regarded to be environmentally critical – trials should be undertaken to reduce the zinc pigment concentration in such primers. Moreover, since solvent residues in the primer may result in pinholes occurring in the powder top coat during curing process, addition of degassing agent in the primer and/or the top coat could prevent the formation of such coating failures.

Some trials to achieve such necessary modifications are proposed in the following.

## Experimental

Fig. 1 gives the composition of the “basic” liquid zinc primer formulations used.

ZS0 may be regarded as a model for typical zinc rich primers (ZRP). In ZxA the overall Zn content is significantly reduced, wherat 18 vol% of Zn is the same conventional zinc dust (CONMET SUPERFINE 620) as used in ZS0 and 7 vol% of Zn is a special zinc powder (BENDA-LUTZ® Zinkpulver plättchenförmig Z 2031). Due to the lower amount of zinc, ZxA is furnished with a zinc phosphate pigment additionally. In ZxB these 18 vol% of zinc dust are furnished with a special surface treatment following the LCST technology [1]. ZxC is a waterbased system and correlates with ZxA regarding the pigment/filler composition.

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	ZS0 nvp		ZxA nvp		ZxB nvp		ZxC nvp	
	vol%	w/w / %	vol%	w/w / %	vol%	w/w / %	vol%	w/w/%
EP resin MG >700	23,8	6,6	31,2	12,3	31,2	12,3	47,0	18,5
polyamino amide adduct	18,2	4,3	23,8	8,1	23,8	8,1	8,0	3,0
zinc dust	50,0	83,9	18,0	43,1			18,0	42,5
zinc powder			7,0	16,9	7	16,9	7,0	16,6
Talkum 10M2	8,0	5,2	15,0	13,9	15,0	13,9	15,0	13,7
Nubirox SP (ZnP)			5,0	5,7	5	5,7	5,0	5,7
zinc dust / Tx					18	43,1		

Figure 1: Composition of some liquid zinc primer formulations

In addition to these four formulations two primer systems are added, which do not contain elemental zinc. Zad1 is a commercial zinc phosphate anticorrosive primer ("2K-EP-Grund ZG-02", ReiColor), whereas Zad2 is a modified version of ZS0, which does not contain zinc, but contains equivalently a mixture of 7 parts CW-2230 (C.H. Erbslöh, anticorrosive pigment) and 1.5 parts Halox 550 WF (C.H. Erbslöh, experimental anticorrosive pigment).

Moreover, in order to explore to which extent an addition of a degassing agent could suppress the formation of pinholes occurring in the powder top coat during curing process, ZS0 is furnished with different amounts of Resiflow LH-240 (Worlée) additionally. Two formulations ZS1 and ZS2 were identified from which a significant reduction of the pinhole formation could be expected and which contained 1.5 w% and 2.5 w% Resiflow LH-240, respectively (cf. Fig. 2).

Detecting continuously the high frequency capacitance  $C_{HF}$  during a fast hydrothermal cycling (sinusoidal temperature sweep between 10°C and 40°C in periods of 30 min; using 0.025 M  $KNO_3$  as an electrolyte), which was performed by a Gamry Reference600 in two-electrode configuration,  $C_{HF}$  vs. time diagrams can be used to determine changes in the dielectric properties of the primer systems induced by this hydrothermal cycling. Based on EIS data  $C_{HF}$  is calculated according to [2]:  $C_{HF} = (2\pi f |Z|_{HF} \sin|\phi|_{HF})^{-1}$ , where HF designates the high frequency data of the impedance spectrum (here:  $f = 100$  kHz),  $|Z|$  is the modulus of the impedance and  $\phi$  the corresponding phase shift.

## Results

Fig. 2 (left) shows a test panel, which was manufactured by applying ZS0 with a 250  $\mu$ m doctor blade in the centre of the substrate. After ventilating a KABE PES-135 powder top coat layer was applied electrostatically and cured for 15 min @ 180°C (sample A). Obviously, the powder top coat exhibits defects and pinholes in the centre, whereas in the border area of the substrate – where no ZS0 primer is present – no such defects are present. Fig. 2 shows also an excerpt of sample B, which corresponds to sample A but was cured after 24 h storage at RT. In addition, before curing for 15 min @ 180°C the test panel was stored 1 h @ 120°C. Apparently, this results in a more homogeneous top coat surface; however, especially in the primer border area one observes some pinholes (see top right side in Fig. 2). Sample C corresponds to sample B, but the ZS0 primer was furnished with 2% of Resiflow LH-240 in this case. Although the top coat surface is not absolutely plane, pinhole formation is significantly lessened in this case.

Continuous HF-EIS recording during hydrothermal cycling of all samples as mentioned in the Experimental part resulted in  $C_{HF}$  vs. t diagrams displayed in Fig. 3.

Since  $C = \epsilon_0 \epsilon_r A/d$  (with:  $\epsilon_0$  = permittivity of free space,  $\epsilon_r$  = dielectric constant of the medium detected,  $A$  = area detected,  $d$  = thickness of the medium detected) and  $\epsilon_r(\text{water}) \approx 80$  – whereas  $\epsilon_r(\text{polymer}) < 8$  – water uptake of the primer should result in an increase of  $C$ . Since heating should induce water uptake (WU), the hydrothermal cycling performed results in capacitive oscillations following the temperature cycling. Typically, such a temperature cycling induces losses of the water uptake reversibility (WUR), which reflects in a timely increase of the capacitive minima (quantified by  $\Delta C3$ ) as well as in an increase of the capacitive amplitudes (quantified by  $\Delta A$ ). This is found for all primers except for ZxC, where  $\Delta C3$  as well as  $\Delta A$  are negative (see Fig. 3).

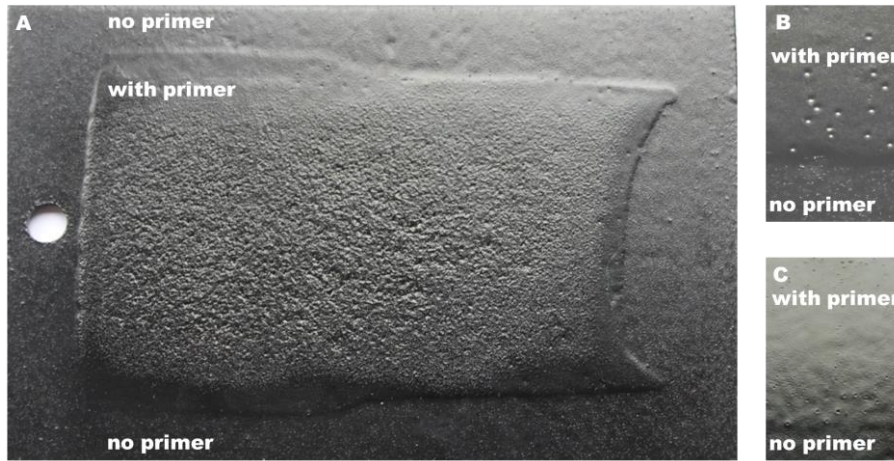


Figure 2: Photographs of some liquid primer / powder top coat trials. Right side shows magnified excerpts displaying the border area of the two-layer coatings system (“with primer”)

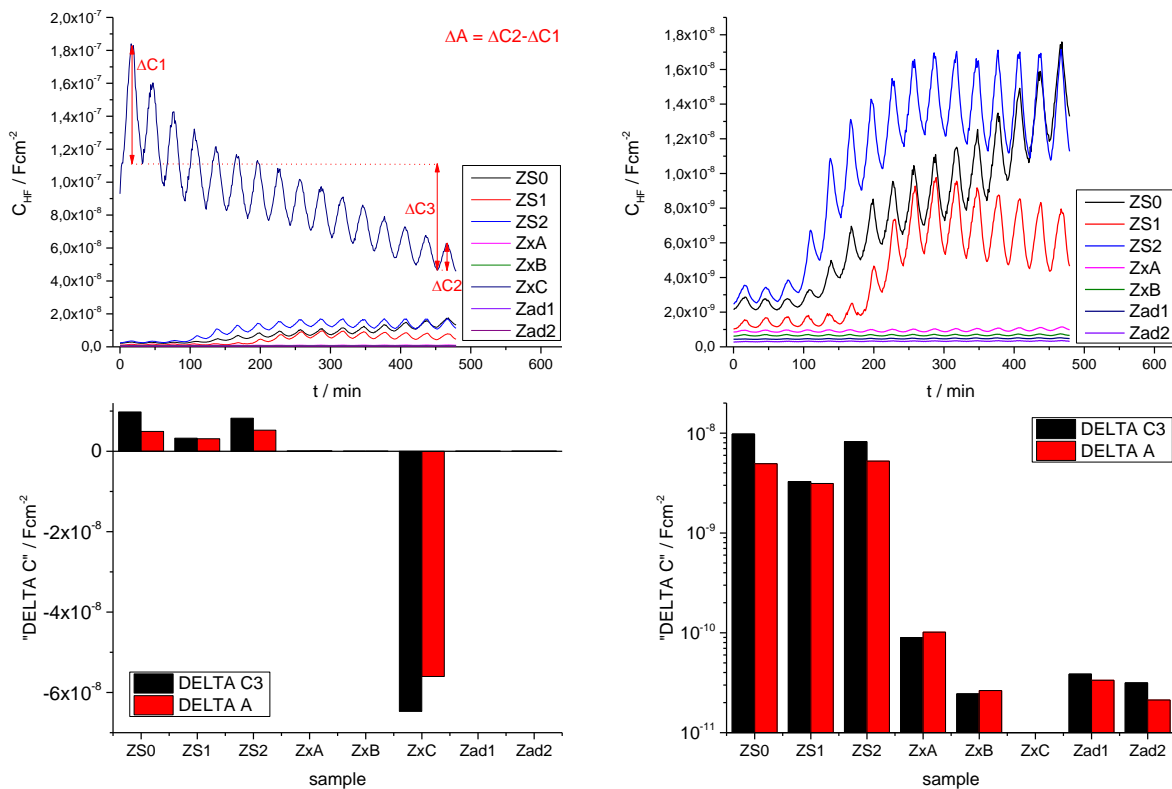


Figure 3: HF-capacitive data obtained during hydrothermal cycling of the primer samples (top) and herefrom calculated parameters related to water uptake (WU) and its reversibility (WUR)

## Discussion

Furnishing liquid zinc primers with around 2% of Resiflow LH-240 could contribute to a reduction of pinhole formation occurring in the powder top coat during curing process. In the same way, a period of heating below the curing temperature of the powder top coat before adjusting the curing temperature improves the homogeneity of the resulting powder top coat surface.

The exceptional capacitive data of ZxC (Fig. 3) may be explained by the facts that (i) it is a waterbased system, whose significant swelling could considerably decrease  $C \sim d^{-1}$  and (ii) the formation of voluminous

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ZnO may reduce the overall C after the first capacitive increase and expels water by occluding the pores. Such an exceptional decrease of the capacitive oscillations is also found for ZS1 and ZS2, here, after 270 min and 320 min of hydrothermal cycling, respectively. Apparently, the degassing agent Resiflow LH-240 may facilitate a strong initial water ingress and provokes similar mechanisms as suggested for the waterbased system ZxC. ZS0, which does not contain any degassing agent, coherently shows a constant increase of the capacitive oscillations. WUR of Zad1 (zinc phosphate primer) and of Zad2 (no Zn/Zn<sup>2+</sup>) are comparable regarding the absolute capacitive increase  $\Delta C_3$ , whereas Zad2 is characterised by the smallest increase of the capacitive amplitudes induced by the hydrothermal cycling. Outstandingly, ZxB, whose zinc dust pigment is furnished with a surface treatment, does also show only little capacitive increase. In contrast, ZxA, which corresponds to ZxB but whose zinc dust pigment is not furnished with a surface treatment, exhibits a significantly larger WUR loss than ZxB. Apparently, furnishing the zinc dust pigment, which most probably is more active than the coarser zinc powder pigment, with an organic treatment seems to keep the WUR on high level. Consistently, WUR of ZS0, which does not contain any zinc powder but zinc dust in high concentration, exhibits the largest loss of WUR in the series ZS0 > ZxA > ZxB.

In order to explore the effect of water under constant temperature impact, a condensed climate test was performed additionally. Its results principally support and complement the capacitive data shown above and will be presented supplementary.

## Conclusions

Although under real-world conditions – where liquid primers are applied via spray-application and therefore evaporate much more of their solvent – the problem of pinhole formation during curing of the covering powder top coat is expected not to be that serious, it seems to be reasonable to deliberate the addition of small amounts of degassing agents to the primer formulations.

The liquid primer formulations reported here exhibit differentiated capacitive data if they are exposed to a fast hydrothermal cycling. This data may be interpreted in terms of the loss of the reversibility of water uptake (WUR), especially when this data is compared with data to be obtained from the classical condensed climate test, where no temperature cycling is performed.

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## References

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