

Advanced Examination of Zinc Rich Primers with Thermodielectric Spectroscopy

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Abstract: Zinc-rich primers (ZRPs) are widely used coatings for corrosion control on steel surfaces. Usually ZRPs use high zinc concentration in the paint and a little amount of organic resin used as a binder. Commonly, two fundamental protection mechanisms operating in ZRPs can be recognised, namely the galvanic protection and the barrier effect. The high zinc content can secure cathodic protection to the base metal, and the zinc corrosion products can make the barrier effect. In this research study, the cathodic corrosion protection capabilities of zinc rich alkyd primers prepared with different spherical zinc dust volume concentrations (0-20-40-60-80% by weight) are tested. The mechanical, electrochemical and dielectric properties are measured in order to find a correlation between these and the protection capabilities of the coating.

Keywords: zinc-rich primers; thermodielectric spectroscopy; cathodic protection; alkyd resin

1 Introduction

Zinc-rich coatings and primers have the unique ability to provide galvanic protection to the steel surfaces to which they are applied. These coatings have a large amount of metallic zinc dust combined with the binder. ZRP's binder is usually an organic resin such as epoxy, alkyd or urethane. After the proper application of a zinc-rich coating to a steel substrate, the binder holds the zinc particles in contact with each other and the steel surface. This contact between two dissimilar metals, when in the presence of an electrolyte, will form a galvanic cell. The zinc particles become the anode in the galvanic cell, and the steel substrate serves as the cathode. Galvanic action causes the zinc to be corroded while the steel is protected from corrosion attack. Zinc-rich coatings are unique in that they provide protection to the steel surface even with voids, scratches, pinholes and other small defects in the coating system.

The basis of the cathodic protection by a zinc-rich paint to a steel substrate is the electrical conductivity between the zinc particles in the coating and between the zinc particles and the steel substrate. [1-2]

The protection mechanisms of ZRP coatings are the following [3]:

- During the formation of the galvanic cell between the base metal and coating's zinc particles, the base metal will have cathodic protection.
- The corrosion products of zinc particles will be deposit on to the base metal, where they will appear as a corrosion inhibitor.
- The corrosion products of zinc will transform into basic zinc-carbonate ($4 \text{ ZnO} \cdot \text{CO}_2 \cdot 4\text{H}_2\text{O}$), which will act as a pore sealant.
- The Zn particles are able to bind the acidic components which will result in a higher pH environment.

During galvanic protection the valuable base metal is connected to a more negative corrosion potential (less noble) metal. This system results in a “short circuit” galvanic battery and the current between the metals will secure the necessary cathodic polarization of the protected metal if the rate of contacted surface areas is necessarily good. In the ideal situation, the outer resistance (R_0) of the system is zero and the inner resistance (R_1) is also very close to zero. (*Fig. 1*)

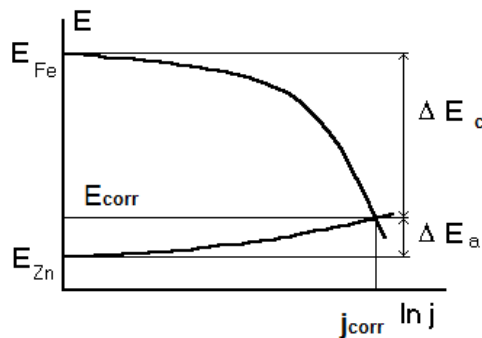


Figure 1

The potential-current diagram when $R_0 = 0$ and $R_1 \approx 0$

If the system resistance is bigger, ($R = R_0 + R_1$) for example, if a poor conductivity material is placed ($R_0 \neq 0$) between the two metals (Zn and Fe), or if the conductivity of the electrolyte around the metals is large ($R_1 \gg 0$), then the protection current is limited by R resistivity. When R is growing, there is a point where the current is not enough to cause cathodic polarization. (*Fig. 2*)

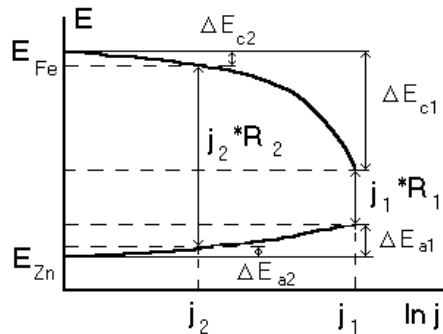


Figure 2

The potential-current diagram when $R_0 \neq 0$ and $R_1 \gg 0$

As already stated, in zinc-rich coatings and primers, the Zn particles must contact with each other and with the base metal. The coating should be a relative good conductor. In ZRPs the cathodic protection appears only in the beginning, when the surfaces of the zinc particles don't deposit by ZnO, and the pores are not saturated by Zn corrosion products. The oxidation of Zn particles to ZnO and their transformation to basic Zn-carbonate can be considered a barrier effect.

Another important factor that influences the ZRPs protection characteristic is the size and shape of the zinc particles added to the primer. The added zinc particle's shape can be spherical, lamellar or mixed. As other research studies have shown, the lamellar zinc (or mixed) provides better protection to the base metal. The smaller particle sizes provide better anti corrosive properties. [4-6]

When elevating the zinc pigment volume concentration (PVC) a point can be reached called critical pigment volume concentration (CPVC) where there is a just sufficient polymer matrix to wet and fill the voids between the individual particles. At PVCs below the CPVC, the composite consisting of pigment particles is randomly embedded in a continuously connected matrix of polymer. Above the CPVC, there are void structures in the film due to insufficient polymer, but the pigment particles can still be thought of as continuously connected. The polymer is still continuously connected globally, but voids will cause the polymer to lose local connectivity, and thus the sharp drop-off in the mechanical properties of the coating just above the CPVC. Above the CPVC, a new fluid phase – air – will be present in the film and its properties are drastically affected, especially its density, transport, mechanical, and optical properties. [7]

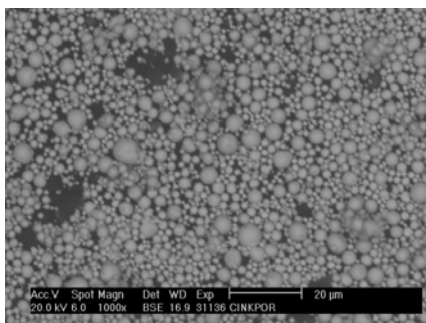
The CPVC depends on the resin and pigment type and other additive materials. In ZRPs when lamellar shape zinc particles are used, this is a much lower value (~40-50%) than when spherical shape zinc is used (~70-80%). [8]

2 Experimental Work

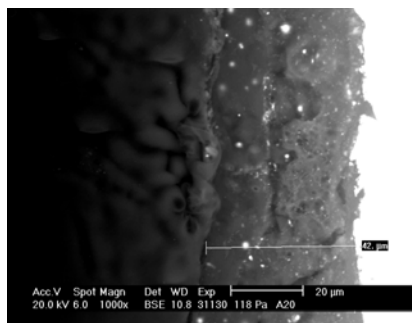
Model coatings were made – with different concentrations of 1-5 μm diameter spherical shape zinc dust of an alkyd resin – and applied onto clean steel plates with film casting frame to examine the protection capabilities of ZRPs. The zinc contents were 0-20-40-60-80-90% by weight. After at least two weeks of conditioning, samples of the same thickness were selected ($75\pm 5 \mu\text{m}$) and measured by the following techniques:

- Thickness measurement with MINITEST 500 equipment,
- Flexibility with Erichsen cup test,
- Hardness with König pendulum (compared to glass standard),
- Dielectric properties with thermoelectric spectrometer [9] between 20-200 $^{\circ}\text{C}$ temperature range and between 0,1 – 100 kHz frequency range,
- Electrochemical measurements with Solartron SI1287 electrochemical interface,
- Scanning Electron Microscopy (SEM) with Philips XL30 ESEM.

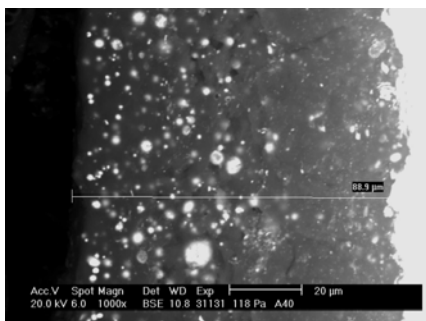
The cross-sections of the prepared samples are shown on *Figure 3* with the examination of SEM. (The base metal is on the right side.)



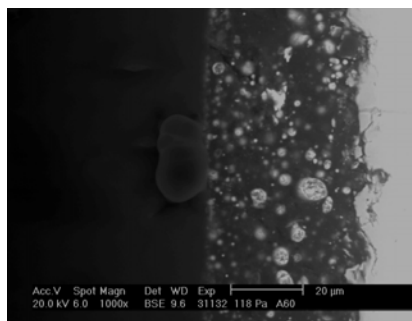
The used Zinc-dust particles



Alkyd resin with 20% Zn dust content



Alkyd resin with 40% Zn dust content



Alkyd resin with 60% Zn dust content

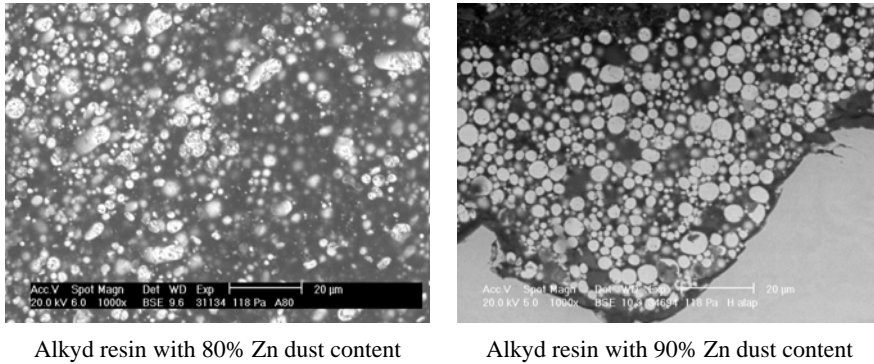


Figure 3

The SEM pictures of the prepared samples' cross section

The ZRP structure changes when more zinc dust is added to the base resin. Therefore, the dielectric properties also change, since they are directly related to each other. With the use of thermodielectric spectroscopy the dielectric properties such as relative permittivity can be measured in the function of temperature and frequency. In organic polymers, different kinds of polarizations can happen when we put them into an electric field. The most important one in our case is the dipole orientation polarization, which can be characterized by its activation energy at the relaxation temperature. Its dependence on temperature and frequency following the Arrhenius equation:

$$\frac{1}{\tau_r} = \omega_r = A \cdot \exp\left(-\frac{E_A}{RT}\right) \quad (1)$$

where: τ_r is the relaxation time [s],

ω_r is the angular frequency of relaxation [s^{-1}],

E_A is the activation energy of the orientation process [$J \cdot mol^{-1}$],

R is the universal gas constant [$J \cdot K^{-1} \cdot mol^{-1}$],

T is the temperature [K],

A is the pre-exponential constant.

In *Figure 4* the measured thermodielectric spectra can be seen for different Zn dust content measured at 100 kHz. Unfortunately, the highest Zn content coating (90%) cannot be measured because of short circuit in the dielectric cell. Therefore, this is not examine further.

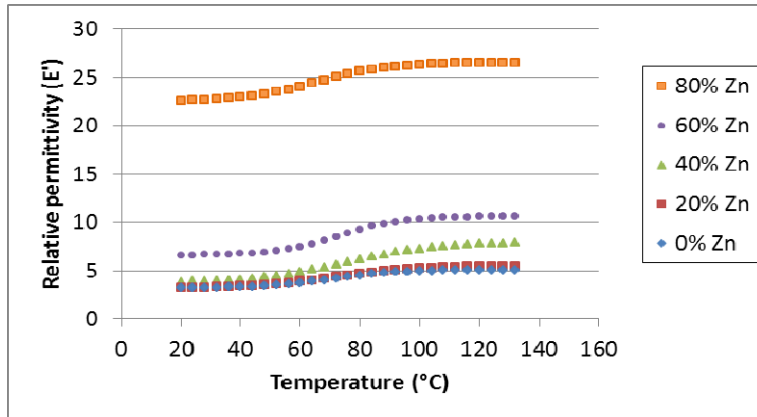


Figure 4

The measured thermodielectric spectra for 100 kHz frequency

When the zinc dust content of the coating was elevated, the relative permittivity also increased slowly below CPVC and rapidly above CPVC. In the following *Table 1* the measurements are summarized and the averaged results can be seen.

Table 1

The results of the measurements

Zinc content (m/m%)	t_R (°C)	E_A (kJ·mol ⁻¹)	Flexibility (mm)	Hardness (%)	Relative permittivity (ϵ')*
0	65	94,4	9,8	20	4,2
20	69	233,2	3	60	4,3
40	78	241,1	2,8	65	6
60	72	310,7	1	69	9
80	64	405,3	0,2	74	25
90	-	-	0,1	81	-

*For the $f=100$ kHz thermodielectric spectrum's relaxation temperature.

The dielectric properties – the activation energy of the dipole orientation (E_A) and the relative permittivity – reveal the polymer matrix to be more rigid when the zinc content is elevated. The dipole orientation's relaxation temperature (t_R) does not change so much. The mechanical properties change consistently; so flexibility decreases when the hardness rises with the elevated zinc content. Furthermore, with this examination an unknown sample zinc-content can be estimated.

During standard corrosion examination a 5 mm cross defect was made on the coated steel plates, which were covered with a 3% NaCl solution and left for ten days (*Fig. 5*) in order to check the presence of protection with the measurement of circuit potential.

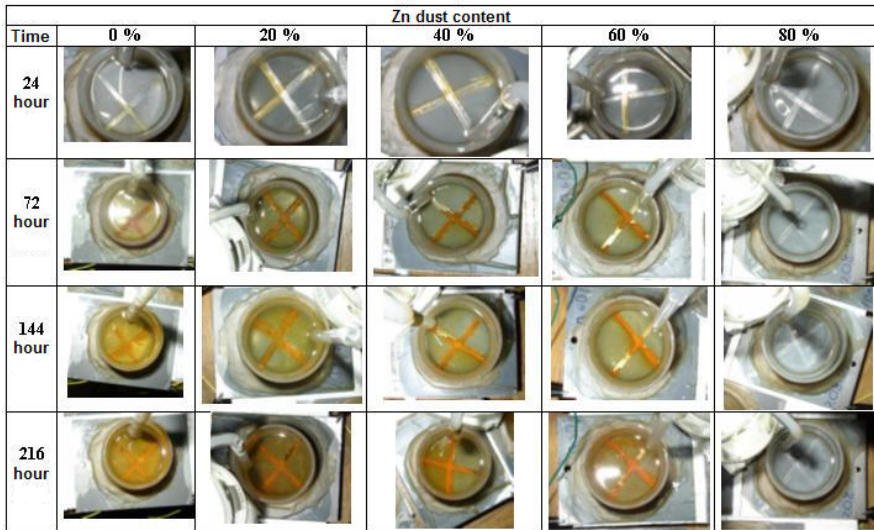


Figure 5

The cross damage test of the different zinc content ZRPs

Only the high zinc content (80%) coating provided sufficient cathodic corrosion protection, since during the ten days of the standard corrosion examination only this sample was free from iron corrosion products. During this type of electrochemical measurement only the 80% zinc content coating shifted the potential to a lower value compared to the others. (Fig. 6)

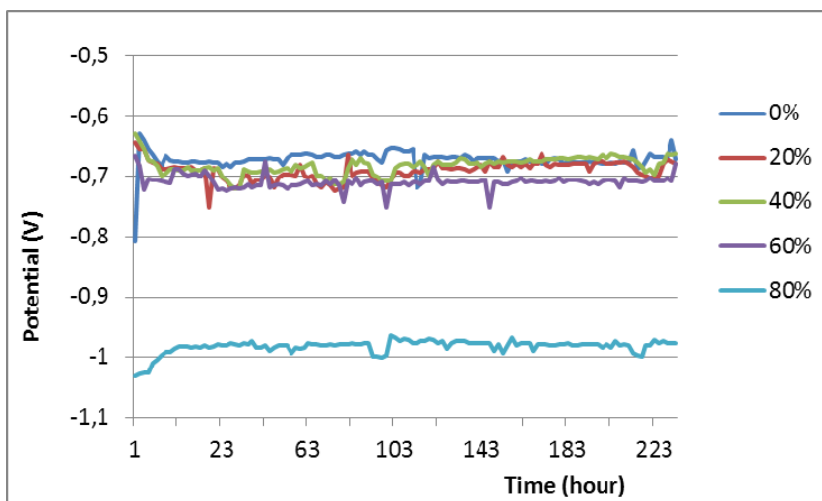


Figure 6

The potential (vs. SCE) measurements of the different zinc content ZRPs

In the case of the prepared samples, the low zinc concentration ZRP coatings cannot support cathodic protection to the base metal. This as well can be seen on the cross section pictures since when the zinc content is low, no zinc particles were connected to the base metal. We can only see this protection effect above 80% zinc dust weight concentration, as has been proved in other papers as well. [9-11]

Conclusions

Thermodielectric spectroscopy was found to be a useful tool for assessing the cathodic protective behavior of ZRP organic coatings. The higher the zinc content we have in a ZRP the higher will be the activation energy of the dipole orientation. Therefore, the thermodielectric measurements can be used for zinc content estimation. Above CPVC, the dielectric permittivity increases rapidly, and thus it is also easy to check this value with TDS. A good cathodic protection can only be achieved with high Zn dust content coatings, which also result in high relative permittivity. During our experiment, we found (in our case) that the Zn dust amount should be higher than 80% in the dry weight in order to support cathodic protection. This results in 5~6 times higher relative permittivity of the protective coating (~25) than alkyd binder's alone.

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