



# Improvement of electrochemical action of zinc-rich paints by addition of nanoparticulate zinc

K. Schaefer\*, A. Miszczyk

Gdansk University of Technology, Chemical Faculty, Department of Electrochemistry, Corrosion and Materials Engineering, ul. Narutowicza 11/12, 80-233 Gdańsk, Poland

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## ABSTRACT

The influence of nanosized particles on electrochemical action of standard zinc-rich paints by means of SEM as well as potential and impedance measurements has been investigated. The motivation for doing this was to obtain additional electrical connection between the spherical microparticles themselves and zinc particles and steel substrate. Overall zinc content was at the level of 92% by weight. Samples with different concentration of nanoparticulate zinc (0%, 5%, 10% and 40%) were tested. Addition of 5–10% nanoparticulates extended the galvanic action of the coating in comparison to the standard zinc-rich coating.

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## 1. Introduction

Zinc-rich primers technology has been used for years, finding application in marine industry, civil infrastructure and military vehicles. Zinc-rich layer is used as a single coat or as a component of the paint system. Coating systems consisting of zinc-rich primer and topcoat offer decorative and barrier as well as anti-corrosive protection to the steel substrate [1–8]. Sacrificial pigments such as zinc pigments require zinc in large quantities in order to enable flow of electric current [9–16]. At the initial stage the zinc dust film being in electrical contact with the steel surface plays the role of a sacrificial anode providing cathodic protection. At a later period zinc corrosion products such as zinc oxide or/and zinc hydroxide are formed, thus barrier protection begins to dominate [9,10]. The greater the amount of zinc corrosion products which form on the zinc particles surface, the higher the probability of losing electrical contact between zinc particles themselves or zinc particles and the steel substrate. Thus it may lead to reduction and in the end complete loss of protection based on the cathodic mechanism. High electrical conductivity of coating is required for providing the first period of protection to the steel substrate [10–12].

The protection mechanism of zinc-rich coatings and their electrochemical performance have been thoroughly studied using mainly potential measurements and electrochemical impedance spectroscopy (EIS) [4,6–8,11,12] as well as electrochemical noise measurements (ENM) [13]. The impedance behavior of zinc-rich paints is different compared to typical barrier coatings. High

performance barrier coatings possess protective properties when their impedance modulus exceeds  $10^6$ – $10^7 \Omega \text{ cm}^2$  in the low frequency range [14]. On the contrary zinc-rich paints exhibit low value ( $10^2$ – $10^3 \Omega \text{ cm}^2$ ) of impedance modulus during the first period of protection. The electrical conductivity of these paints is related to percolation phenomena determining the intensity of sacrificial action of zinc particles [12]. It is stated that in order to obtain continuous electrical contact between zinc particles (i.e. exceed the percolation threshold) a zinc content above 80–86% (depending on type of binder) by weight in dry paint is very important to create percolation paths through the coating [15]. On the other hand, the porosity of the coating strongly affects the accessibility and wetting of zinc particles. In this case the ratio of pigment volume concentration (PVC) to critical pigment volume concentration (CPVC) should be greater than one to enable aqueous electrolyte to penetrate and allow sacrificial action of zinc particles [16].

Nevertheless zinc-rich paints possess several drawbacks. The high content of zinc pigment (well above CPVC) results in poor mechanical properties of the coating and causes problems with the homogeneity of the dry coating. It is also known that a significant fraction of zinc is not used during the coating lifetime due to production of zinc corrosion products. Partial substitution of zinc by the filler would be beneficial as the noxious fumes of ZnO emanate during welding of coated steel parts improving also the adhesion between subsequent layers of the coating system [17]. In order to ensure percolation through the coating, use of conductive fillers is required.

For this purpose an attempt was made to use diiron phosphide [18–20], carbon black [21–23], extender pigments [23], aluminium pigments alone [24], or covered by conducting polypyrrole [25],

\* Corresponding author. Tel.: +48 583471915; fax: +48 583471092.

E-mail address: [schaefer.katarzyna@gmail.com](mailto:schaefer.katarzyna@gmail.com) (K. Schaefer).

and polyaniline powder [26]. In most cases these modifications have not led to the desired effect. This is due to more electropositive character of extenders in relation to zinc pigment causing an adverse effect on the galvanic action of zinc–steel microcells.

Another way to improve protective performance of zinc-rich coatings is to employ particles of different shape and dimension [27,28]. It is well known the sphere has the smallest surface area among all types of geometric blocks with the same volume. Using particles of shape different than spherical may contribute to an increase of electrical contact surface area among themselves and hence reduce the amount of zinc in the coating. This effect was observed for both the lamellar zinc pigment itself and a mixture of both lamellar and spherical zinc particles [23,29,30]. However, lamellar zinc pigment has not been commonly used due to the fact its manufacturing process is more complicated than the one for spherical zinc pigment. Taking into account the above considerations, improvement of the standard zinc-rich paints containing spherical particles would be beneficial for industrial purposes.

It seems that in order to increase electrical contact between the particles themselves and between the zinc particles and the steel substrate, an attempt needs to be made to fill the space between the standard zinc particles with conductive substituents. Considering paint containing spherical zinc particles, it is possible to find that electrical contact between zinc particles is obtained in single points only in the best case, Fig. 1.

If the paint contains e.g. 92% of zinc dust by weight, zinc particles occupy only 52% of paint volume. Non-conducting epoxy binder (with density equal to 1.12 g/cm<sup>3</sup>) occupies 28.6% of paint volume and the rest (19.4%) is an air volume, Fig. 2. Thus in reality contact between particles can be the critical factor in ensuring cathodic protection action of zinc-rich paint containing spherical particles. This statement can be confirmed by SEM micrograph of standard zinc-rich paint containing 92 wt.%, Fig. 3. It can be seen that there is limited electrical contact between zinc particles.

Even minor oxidation of zinc particles surface due to contact with oxygen in the air leads to fast loss of electrical connection between particles. The latter is associated with zinc failing to any longer provide cathodic protection. The presence of only single contact between two neighboring particles is a weak feature of this type of paint. It seems that the need for additional electrical contact can be met by addition of smaller, conductive particles (Fig. 4).

Thus the authors have made an attempt to use nanoparticulate zinc for this purpose. According to the above consideration a small fraction of nanoparticulate zinc (<19.4 vol.%) can be successful (Fig. 5(a)). Greater amount of nanoparticulate zinc than 19.4% (void volume) could separate the zinc micro particles causing loss of electrical contact between them, which is not beneficial from the point of view of the effectiveness of cathodic protection

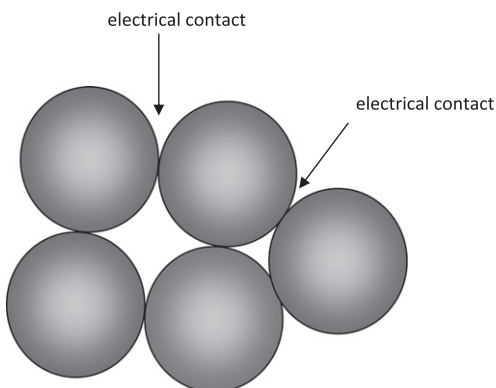


Fig. 1. Electrical contacts between zinc microparticles tightly packed in zinc-rich coating.

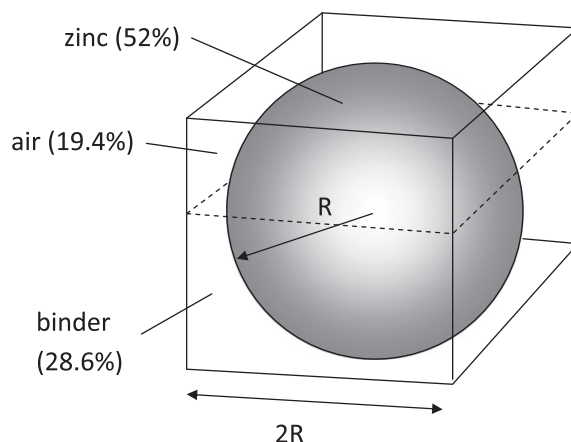


Fig. 2. Volume relation between zinc, binder and air in zinc-rich paint containing 92 wt.% of zinc.

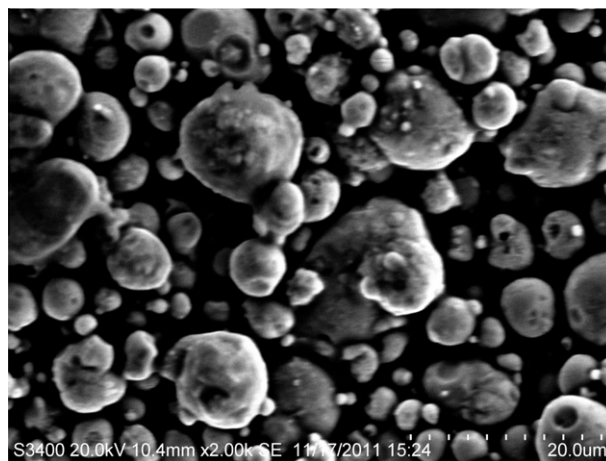


Fig. 3. SEM image of the zinc-rich coating with embedded zinc particles of diameter ( $d = 6\text{--}9\ \mu\text{m}$ ).

(Fig. 5(b)). The tendency to form agglomerates of nanoparticulate zinc would actually be an advantage because it allows electrical conduction paths between microparticles to be obtained. In addition, the introduction of small amounts of the same material but as nanoparticles does not significantly change the formulation of the coating and other properties (e.g. mechanical and electrochemical) of the coating remain the same. Pigments in the form of nanoparticles are increasingly being introduced in the coating composition in order to improve their properties, including the anticorrosive properties [31–33].

In order to confirm these considerations adequate samples were made and their behavior was investigated using electrochemical methods such as Electrochemical Impedance Spectroscopy (EIS) and electrochemical potential measurements. Both the EIS method and open circuit potential measurements have been widely employed to assess electrochemical activity of zinc-rich paints [22,34–38]. Apart from electrochemical measurements more advanced microscopic methods including SEM (Scanning Electron Microscopy) and AFM are being used to enable characterization of the polymer coatings surface. In organic coatings area the AFM method has been employed to investigate the surface properties and distribution of pigment particles [39,40]. Taking into account development of Scanning Probe methods little has been done to characterize and model zinc-rich coatings performance by applying new local measurements methods such as CAFM (Conductive

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