Possibilities of Affecting the Corrosion-Inhibition Efficiency of the Coatings by Means of the Zinc Powder Particle Sizes and Shapes

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Summary: The paper deals with morphology and physicochemical aspects of zinc powder concerning the properties of coatings. The sizes or, sooner, the size zinc powder particle distribution manifest themselves especially in the mode of arrangement and affecting the electrochemical mechanism of action in the coating. The lamellar and isometric particle shapes affect by the pigmentation mode and height especially the barrier action and physicomechanical properties of the coating.

Introduction

The zinc metal particles have presented an anticorrosive pigment frequently used for the coating compositions destined to heavy corrosion protection of metals already for many years.[1]

The zinc metal was used in coating compositions in the year 1840, when zinc metal was applied for its high covering capacity without knowledge of its high anticorrosion efficiency. The zinc pigmented coatings were considered until recently for the coatings acting above all by the electrochemical mechanism, as the layer creating the so-called sacrificed electrode. The cathodic protection[2] of steel is secured by the time when the pores are sealed, and the electrochemical mechanisms passes to the barrier mechanism. The coatings contain in addition to zinc also binders, which are to package the zinc particles and thus to increase thus the resistance to such a degree that the electric conductivity drops down below a critical value, under which the coating cannot act in the sense of electrochemical protection. The electric conductivity of pigmented film is in connection with the concentration of zinc particles in coating composition binder. The highest electric conductivity is reached at a concentration of zinc particles in a range of 92-95%.[3] In applications to the corrosion protection[4,5], two types of zinc particle

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shapes are used most often, namely the spherical (ball-shaped)[6] and lamellar (plate-like) shapes.[7]

Experimental

Preparation of the coatings pigmented with zinc

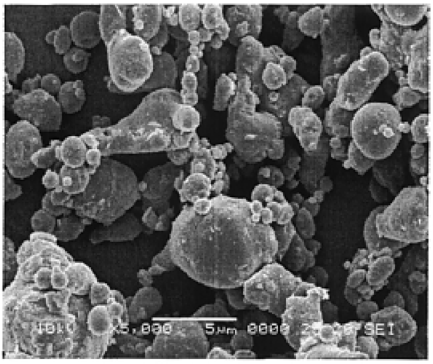
The study of zinc pigment effects occuring in the coatings requires to select a suitable binder unsaponifiable by the alkaline products of the electrochemical reactions running in the system. Such binders comprise two-component epoxy resins hardened by polyamines, a single-component polyurethane hardened by atmospheric moisture, and epoxy ester resins desiccating due to an oxidative process induced by atmospheric oxygen effects[9,10]. The coating formulations were prepared in such a way that the systems with volume content of spherical zinc, a pigment volume concentration (PVC) value = 0, 10, 20, 30, 40, 50, 60, critical pigment volume concentration (CPVC) value, and PVC value = 70% were obtained. The PVC = 0 denotes the nonpigmented binder - a transparent lacquer; the zinc content at CPVC relates to individual types of zinc pigment. On using the lamellar zinc a concentration, defined as PVC = 5, 10, 15, 20, 30, 40, and as $CPVC_{50.6}$ = 60% was used.

Results

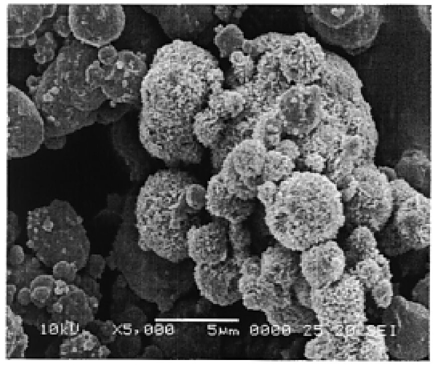
Pigments delivered by various zinc producers were used for the study of shape and primarily of the particle sizes of zinc pigments (Table 1. and Figure 1.). For further studies of the effect of zinc powder in anticorrosive coatings the zinc pigments, can be divided to two groups:

1. zinc with isometric - spherical particles
2. zinc with nonisometric - lamellar particles

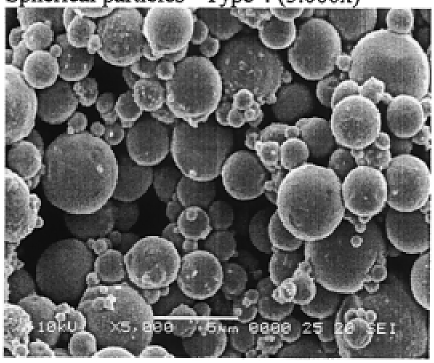
Table 2 brings the selected results of mechanical tests performed in coatings with spherical zinc particles (Type 5) and lamellar zinc particles (Bend test, ISO 1519, and Cross cut test, ISO 2409).



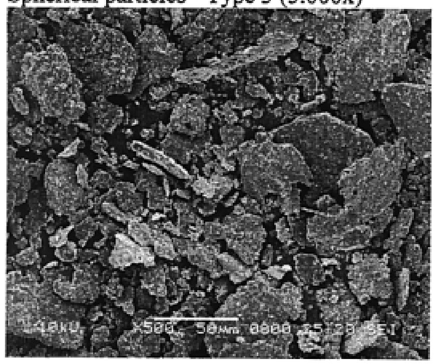
Spherical particles - Type 4 (5.000x)



Spherical particles - Type 3 (5.000x)



Spherical particles - Type 5 (5.000x)



Spherical particles - Type 6 (500x)

Figure 1. Morphology of particles of zinc powder tested.

The differences between the two types of zinc particles are more clearly evident in Figure 2 wherein the mass gains of the absorbent (silica gel) due to water vapor, passing through the coating film. The obtained dependences show that the lamellar zinc-pigmented coatings create a more efficient barrier for water vapor than the isometric spherical particles-pigmented coatings. The barrier created by the coating film to water vapor can be realized on the basis of a model shown in Figure 3 for the lamellar and spherical zinc particles. The photos are a result of the scanning electrone microscopy (SEM) coating analysis (Jeol, JSM 5 600 LV) of both types pigmented to a PVC=50%. The diffusion resistance value (μ) for the coatings pigmented to a PVC=50% is for he lamellar zinc (Type 6) = $7{,}21.10^8$, and diffusion resistance value (μ) for the spherical zinc (Type 5) = $1.9.10^8$.

Table 1. Characterization of types of zinc powder tested.

Type of zinc powder	Mean particle size[a)] µm	Specific surface[b)] m^2/g	Characterization of zinc particles by SEM	CPVC %
Type 1 Spherical	5.0	0.240	Zinc particles under 1 µm are freely present, particles are not significantly covered by oxidation products	66.6
Type 2 Spherical	4.2	0.29	Zinc particles forming agglomerates, particles are partially covered by oxidation zinc products	65.9
Type 3 Spherical	2.9	1.427	The surfaces of many particles are covered by oxidation products, large representation of rather small particles forming agglomerates	58.1
Type 4 Spherical	3.9	0.519	Many zinc particles of irregular shape, overhelming content of particles smaller than 2µm	65.7
Type 5 Spherical	5.6	0.443	The pigment particles are of precisely spherical shape, the surface of particles is not oxidized	66.3
Type 6 Lamellar	25.6	2.079	A large representation of particles smaller than 1µm, and with the largest particles round 50 µm	50.6

[a)] by laser beam diffraction *(Coulter LS 100)*
[b)] specific surface calculated by BET isotherm *(ASAP 2000)*

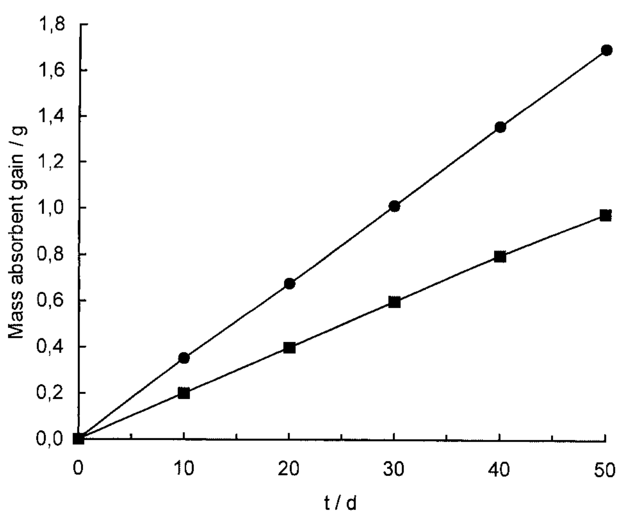
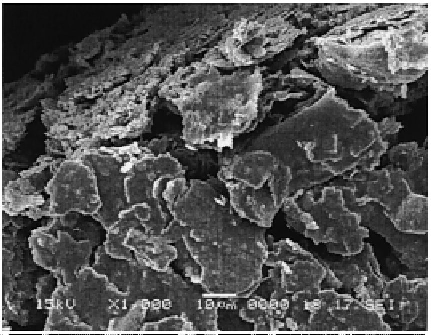


Figure 2. Dependence of the mass absorbent gain on time for the coatings pigmented to a PVC = 50%; ■ lamellar zinc – Type 6, ◆ spherical zinc – Type 5.

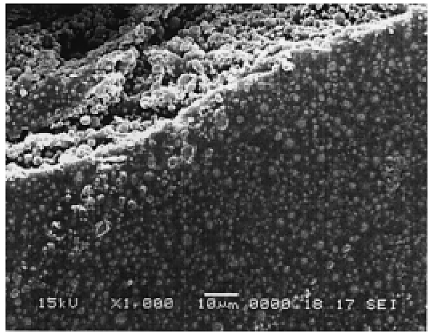
Table 2. Mechanical properties of coatings pigmented with lamellar and spherical zinc particles in dependence on the zinc volume concentration.

PVC %	Bend test mm	Cross cut test Degree
	Lamellar zinc particles (Type 6)	
0	< 4	0
5	< 4	0
10	4	0
15	4	0
20	4	0
30	5	0
40	5	0
CPVC	10	1
60	15	2
	Spherical zinc particles (Type 5)	
0	< 4	0
30	< 4	0
40	< 4	0
50	< 4	1
60	6	2
CPVC	15	4
70	25	4

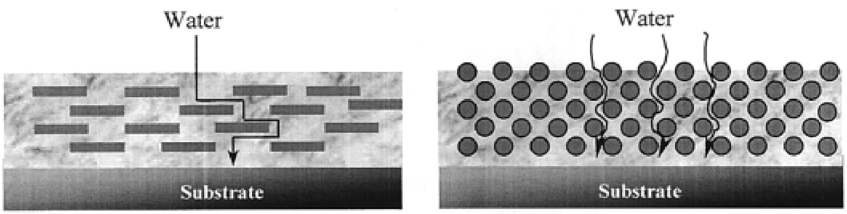
The Figure 4 brings graphical representations of the corrosion-testing results obtained in the salt spray test (ISO 7253) for formulated coatings (zinc powder Type 3). The dependence courses show clearly that the protective function of the coatings pigmented with zinc indicates improvements with the increases in concentration of zinc up to a respective PVC value (round 50 - 60 vol. %). After this concentration limit ($CPVC_{Zn}$ = 58 %) has been exceded the deterioration, i. e. a reduction of the anticorrosion protection of substrate metal takes place. The optimum values of anticorrosion efficiency are achieved at a concentration of zinc particles in the paint film of 50-55 vol. %. Provided the CPVC value for an epoxy-based zinc coating is known ($CPVC_{zinc\ type\ 3}$ = 58 %) a conclusion can be taken that the optimum protection is provided by a coating pigmented just below this value.

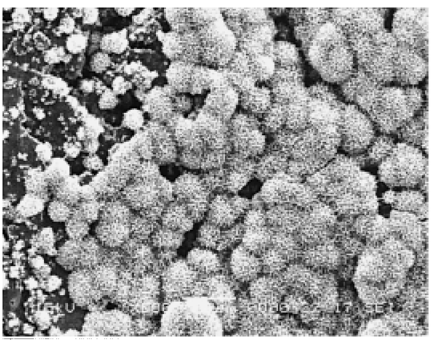


Lamellar zinc particles-pigmented coating (1.000x)

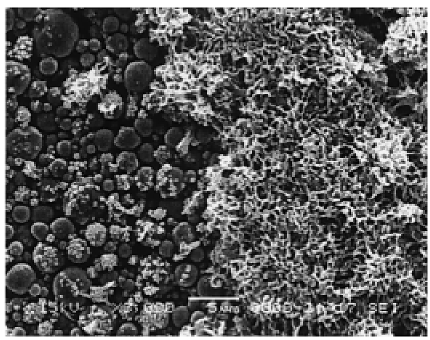


Isometric zinc particles-pigmented coating (1.000x)





Corrosion products of lamellar zinc (1.000x)



Corrosion products of isometric zinc (3.000x)

Figure 3. Ilustrative scheme of water vapor penetration through the coatings.

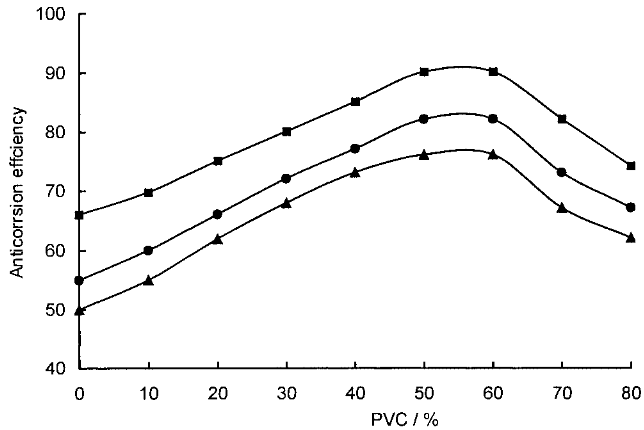


Figure 4. Anticorrosive efficiency of the coatings in dependence on the amount of zinc pigment (zinc type 3, an 1000-hour exposure in salt-spray chamber); ■ = epoxy resin, ● = polyurethane, ▲ = epoxyester.

In case of two-component (2-C) epoxy resin-based films containing zinc in a concentration range of 0-75 vol. % the SEM gave photos of the film surfaces and sections (Figure 5). This figure shows clearly that at the pigmentation by 15 vol. % of zinc powder the zinc particles (Type 3) are almost invisible, both in the film section and surface. At this concentration the protective action is in its essence only of barrier binder nature, and no other mechanisms of protection can take place. At a PVC value of 60 % the zinc concentration lies already above the CPVC value. The surface shows that the individual zinc particles are coated with the binder in shells, and at the same time among thus formed agglomerates the pores occur, which are of large sizes. The agglomerates are covered by the binder, here the electrochemical effect can partly manifest itself. At a zinc concentration of 75 vol. % a shortage of binder necessary for covering the zinc particles is observed, the particles become bare, and the coating is rather porous. In this case we cannot speak of any binder barrier protection against the diffusing substances, but the neutralization and electrochemical mechanisms manifest themselves really well.

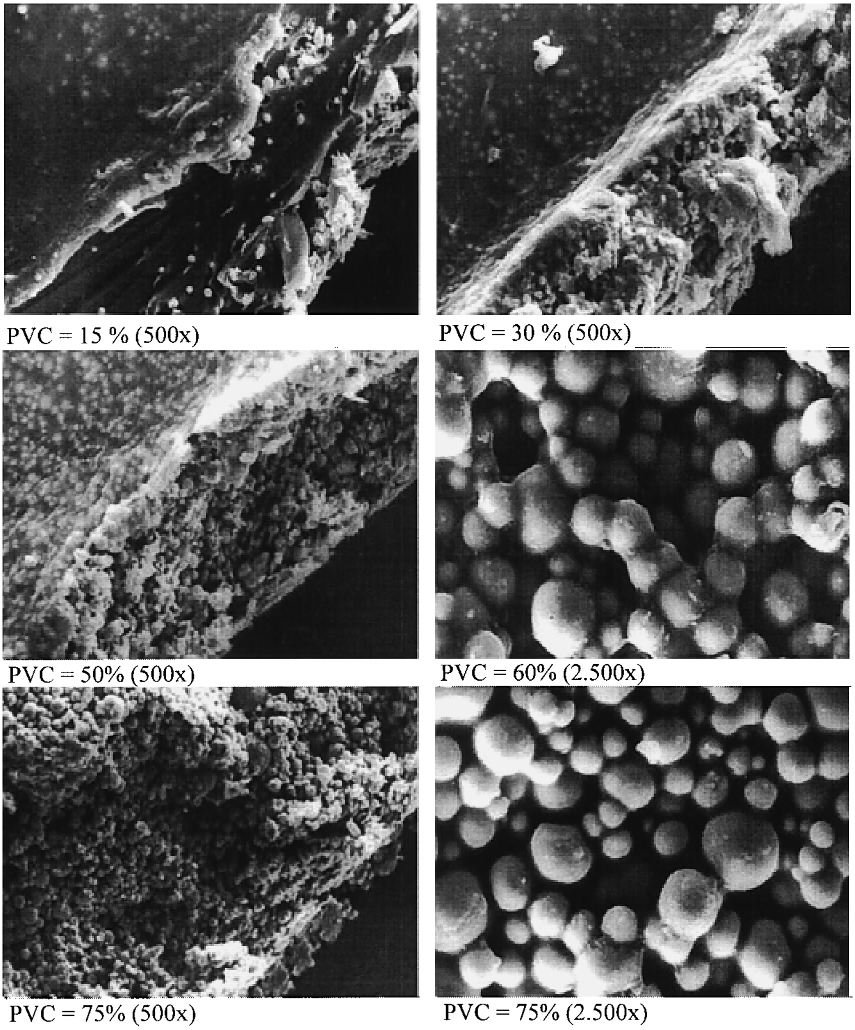


Figure 5. The section and surface of the epoxy-resin based coatings at a PVC 15-75% zinc.

The results given in Figure 6 offer an idea of the anticorrosion efficiencies of coatings pigmented with zinc in an amount corresponding to the CPVC value (salt-spray test ISO 7253).

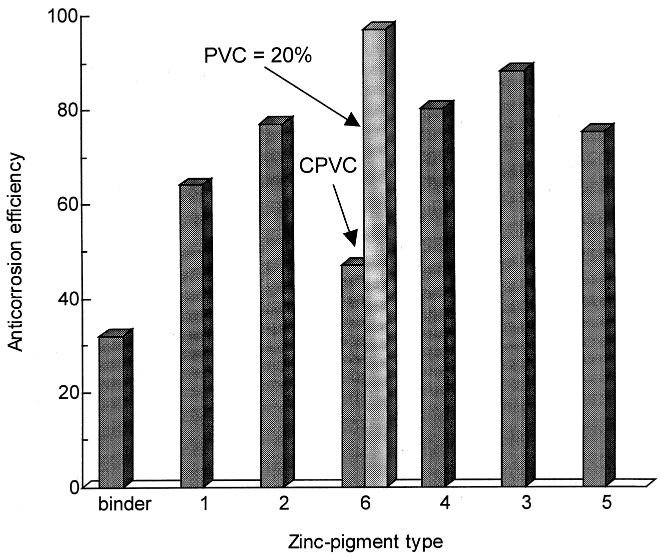


Figure 6. Effect of the zinc particle types on the overall anticorrosion coating efficiency following a 800 h exposure to a salt chamber medium.

The Figure 6 shows clearly that the spherical zinc particles (types 1, 2, 3, 4, and 5) in epoxyester coatings exhibit anticorrosion efficiencies in a range of 64-88%. Thus the difference between followed zinc types represents a 24% anticorrosion efficiency. The smaller zinc powder particles (Type 3), mean the higher anticorrosion efficiency in the coating. It can be concluded, that at an 800-hour exposure to salt chamber conditions the results of anticorrosion efficiency on using the lamellar zinc are almost by 40% worse than those obtained on using the spherical particles. The situation looks out quite differently at a lower concentration of lamellar zinc. At a PVC=20% the efficiency of lamellar zinc-pigmented coating reaches already 97%. If we compare the coating efficiency at a zero content of lamellar particles of an efficiency at a PVC=20% and at a PVC=CPVC=50% it is evident that already at low concentrations a rapid growth of anticorrosion efficiency takes part.

Conclusion

The action mechanism of zinc metal in coating films allows to conclude on the capacity to neutralize the acid corrosive medium penetrating through the film, in addition to the electrochemical protection, i.e. the capacity to create "sacrificed" electrode by shifting the potential to the region in which the corrosion of steel does not run. The alkaline products at the surface of zinc particles effectively restrict the diffusion of acidic components from the coating-film surface towards the substrate metal. This explanation is valid quite generally, as the protection effectiveness of such coatings depends on the concentration and location of pigment particles in the binder system concerned. The film will protect effectively the substrate as far as the optimum concentration of zinc pigment is used. It was found that the size of zinc particles considerably affected the anticorrosion properties of coatings. Better results were found on applying small zinc particles to coatings. Large spherical particles offer a lower anticorrosion efficiency. This phenomenon can be explained by easier filling free spaces among zinc spheres of smaller sizes. At larger particles the filling of pores by means of oxide is incomplete and the leakages can lead to more easy liquid and gas penetrations through paint film. At zinc powder of lamellar type the sealing of rather voluminous pores at CPVC is connected with problems, and the coatings exhibit a lower anticorrosion efficiency. The most appropriate concentration of lamellar zinc particles is round a PVC=20 vol %, whereat by up to one third higher anticorrosion properties in comparison with a series of isometric zinc particles can be reached.

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