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Environmentally friendly, nano lithium silicate anticorrosive coatings

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ABSTRACT

The aim of this study was to develop environmentally friendly, nano-structured inorganic coatings suitable for the protection of metal substrates. The formulation variables included (i) two binders based on lithium silicate of 7.5/1.0 silica/alkali molar ratio (one of them a commercial colloidal solution, and the other a laboratory-prepared nanosolution), (ii) eight pigment compositions based on two spherical microzinc alone (D 50/50 4 and 8 μm) and mixed with spherical nanozinc in three microzinc/nanozinc (w/w) ratios (90/10, 80/20 and 70/30) and finally (iii) six values of pigment volume concentration, PVC (from 47.5 to 70.0%). The electrode potentials were measured in sodium chloride solution at 25 °C and pH 7.0 during 70 days to establish the evolution of cathodic protection; in addition, panels were exposed in salt spray (fog) chamber to determine the degree of rusting and in 100% relative humidity to evaluate the blistering resistance.

It was concluded that the variables alkaline silicate type, pigment composition and PVC values exhibited an important influence on the anticorrosive efficiency; very good performance was achieved with the nano-structured inorganic binder (7.5/1.0 SiO_2/Li_2O molar ratio) and the fine spherical microzinc (D 50/50 4 μm) modified with nanozinc (similar efficiency for 80/20 and 70/30 microzinc/nanozinc, w/w, ratios), in a wide range of PVC values (from 52.5 to 65.0% and from 47.5 to 60.0%, respectively).

1. Introduction

The zinc-rich coatings and those modified with extenders and/or metal corrosion inhibitors display higher efficiency than other coatings [1–7]. A problem that presents these primers is the extremely reactive characteristic of metallic zinc; consequently, the manufacturers formulate these coatings in two packages, which imply that the zinc must be incorporated to the vehicle in previous form to their application.

Considering the concept of sacrificial anode (cathodic protection), coatings that consist of high purity zinc dust, dispersed in organic and inorganic vehicles have been designed; in these materials, when applied in film form, there is a close contact of the particles among themselves and with the base or metallic substrate to be protected.

With respect to spherical zinc, the transport of current between two adjacent particles is in tangential form and consequently the contact is limited. With the purpose of assuring denser packing and a minimum encapsulation of particles, pigment volume concentration (PVC) must be in the order of the critical pigment volume concentration (CPVC).

The high pigment density (7.10 g cm^{-3} at 20 °C) produces the sedimentation in the package, including the cases of coatings correctly formulated, generating heterogeneities in the film since in the zones of greater relation PVC/CPVC it produces films of poor mechanical properties and of high porosity; in addition, in the neighbouring areas, with low concentration of metallic zinc, the electrical contact is insufficient and consequently the metallic substrate is not suitably protected.

The problems previously mentioned lead to the study other shapes of zinc particles since the physical and chemical properties as well as the behaviour against the corrosion of these primers are remarkably affected by the size and the shape of particles and the pigment volume concentration; thus for example, it is possible to mention the laminar zinc which was intensely studied by the authors in other works [8–11].

Zinc-rich primers (micro spherical zinc with or without nanozinc) and those modified with extenders and/or corrosion inhibiting pigments (laminar zinc with or without nanozinc) can be formulated with binders of organic and inorganic nature. Thus, CPVC values vary strongly with the type of film-forming material selected.

The most common organic binders are epoxy/polyamine-amide, vinyl resins, chlorinated rubbers, unsaturated polymers, etc. On the

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other hand, inorganic binders are based on silicates; they can be classified according to if curing takes place by chemical reaction or thermal treatment (inorganic silicates) or self-curing (inorganic and organic silicates) [12].

Inorganic binders cured with chemical reagents or by heat treatment are generally based on sodium silicate, potassium silicate or lithium silicate in aqueous solutions or colloidal dispersions (about 28/30%, w/w; pH near to 10); in some opportunities, mixed silicates are also used.

For this type of curing, the molar ratio of silicon dioxide/alkali oxide is low (i.e. SiO_2/Na_2O from 2.8/1.0 to 3.2/1.0, w/w). Drying involves the loss of water vapour and takes between 1 and 2 h at room temperature; they cannot be used at temperatures inferior to 0 °C and even in high humidity conditions (at 180 °C they cure in approximately 30 min); these features limit their use. On the other hand, the curing requires the application by spraying on dry film of phosphoric acid or organic phosphate solution with the addition of wetting agents or by heat treatment after drying; the velocity of the process varies directly with the increasing of temperature. The heat treatment to cause the insolubility is limited to small parts.

With respect to the alkyl silicates, they are usually partially hydrolysed ethyl silicates; they dry quickly by evaporation of the solvent mixture (alcohols, aromatic hydrocarbons and glycols). The curing takes place by reaction with the water vapour of the air and like those of the inorganic type by internal reactions of silicification. The curing develops even at very low temperatures (i.e. 7 days at −15 °C; 3 days at 0 °C; 1 day at 20 °C and 30 h between 15 and 18 °C). The hydrolysis reaction involves the elimination of the alcohol generated by chemical reaction with the air moisture; they do not cure at temperatures superior to 100 °C.

The self-curing inorganic binders do not require the use of special treatments after application. They are based on silicates of greater molar ratio silica/alkali than earlier; so for example, the molar values 5.0/1.0 for SiO_2/Na_2O and SiO_2/K_2O and 7.5/1.0 for SiO_2/Li_2O are suitable. These coatings dry by loss of water vapour. They cure by the action of carbon dioxide from the air and complex internal chemical reactions that lead to a reticulated silicification; the rate of curing increases with temperature (i.e. they require one week at 5 °C, one day at 30 °C or 30 min at 180 °C).

The formation of an inorganic polymer by silicification was particularly studied by the authors using soluble silicates and zinc cation to provide water insolubility (diverse soluble salts of the mentioned cation were added to the solution of soluble silicates); in those tests, a rapid formation of a gel at the interface followed by the spread of the reaction within the aqueous phase was observed. Finally, a coagulated mass was separated, observing in addition that the precipitates were predominantly amorphous; in zinc-based coatings; the oxidized pigment provides the ions to generate the insolubility of the film [13].

Unpublished previous experiments carried out for the authors showed that larger ions and those with higher valence are held more strongly in the network; the relative size and charge of the ions influence the solubility of inorganic polymers generated by silicification.

The first stage of curing of these silicates would involve the formation of the silicic acid of high molecular weight; the second reaction would include the formation of metallic silicate polymers from silicic acid and the zinc cation.

The final structure of metallic silicate polymers, after finishing the drying and curing, is similar when they conform either from alkaline silicate or ethyl silicate.

The aim of this manuscript was to develop a system consisting of an inorganic matrix (alkaline silicate) and a nanometer component (silica) evenly distributed in that matrix with the objective of formulating, manufacturing and evaluating the performance of anticorrosive coatings based on spherical microzinc alone or mixed in several ratios with nanozinc to improve the electrical contact and consequently the anticorrosive capacity.

2. Materials and methods

2.1. Components and pigment volume concentration

Film-forming material. Aqueous solutions of lithium silicate of 7.5/1.0 silica/alkali molar ratio were used. Previous experiences with these solutions on glass as substrate allowed infer that as silicon dioxide content in the composition increases the film curing velocity also increases while the water dissolution rate decreases.

For this study, a commercial colloidal lithium silicate (3.5/1.0 silica/alkali molar ratio) was selected (Bersil); this compound is defined as soluble silicate [14].

With the aim of increasing the ratio silica/alkali, a 30% (w/w) colloidal alkaline solution of nanosilica was used (sodium oxide content, 0.32%; pH, 9.2; density, 1.25 g cm^{-3} at 25 °C) [15–19].

The quoted nanosystem was prepared with 7.5/1.0 SiO_2/Li_2O molar ratio; the adding of nanosilica solution in alkaline silicate colloidal solution of 3.5/1.0 silica/alkali molar ratio was slowly carried out without affecting the system stability. A commercial colloidal aqueous solution of 7.5/1.0 SiO_2/Li_2O molar ratio was used as reference.

Pigmentation. In this study two samples of commercial zinc dust were used; the D 50/50 average particle diameters were 4 μm (fine) and 8 μm (regular). Furthermore, in some coatings both pigments of spherical microzinc were partially replaced by nanozinc [20]. In this research, 90/10, 80/20 and 70/30 microzinc/nanozinc (w/w) ratios were used.

Pigment volume concentration. PVC values ranged from 47.5 to 70.0%; the variation of two PVC values between consecutive samples was 2.5% in all cases. Preliminary laboratory tests (salt spray chamber), with values of PVC from 10 to 70% for all formulations, helped to define the range of PVC more convenient to study in each case. With this objective, the considered PVC values were studied starting from 57.5 to 70.0% for all formulations with both spherical microzinc particles as unique pigment and from 55.0 to 67.5%, from 52.5 to 65.0% and from 47.5 to 60.0% for those coatings respectively with 90/10, 80/20 and 70/30 microzinc/nanozinc (w/w) ratios.

2.2. Manufacture of coatings

As mentioned, type of compositions is provided in two packages with the purpose of avoiding the reaction of metallic zinc with any vestige of moisture in some of the components, which would lead to the formation of gaseous hydrogen. In addition, the system could form a gel because of the reaction between silicic acids from of inorganic silicates and zinc cations. Accordingly, prior to the primer application, the metallic zinc was dispersed for 180 s at 1400 rpm in high-speed disperser.

The identification of coatings is shown in Table 1.

Table 1
Sample identification.

Film-forming material	A. Commercial colloidal solution, 7.5/1.0 silica/alkali molar ratio B. Laboratory-prepared nanosolution, 7.5/1.0 silica/alkali molar ratio
Spherical microzinc	I. Spherical microzinc (fine), D 50/50 4 μm II. Spherical microzinc (regular), D 50/50 8 μm
Pigment composition	1. Spherical microzinc, 100% 2. 90/10 spherical microzinc/nanozinc (w/w) ratio 3. 80/20 spherical microzinc/nanozinc (w/w) ratio 4. 70/30 spherical microzinc/nanozinc (w/w) ratio

2.3. Panels preparation

SAE 1010 steel panels were previously degreased with solvent in vapour phase; then they were sandblasted to ASa 2½ grade [21] obtaining 25 μm maximum roughness Rm. The application was made by air-spray in a single layer reaching a dry film thickness between 75 and 80 μm. In all cases, and to ensure the film curing before beginning the tests, the specimens were kept in controlled laboratory conditions (25 ± 2 °C and 65 ± 5% relative humidity) for seven days.

The study was statistically treated according to the following factorial design: 2 (binder type) × 2 (average diameter of spherical microzinc particles) × 4 (composition of the metallic pigment) × 6 (PVC value), which make a total of 96 combinations manufactured in duplicate. In turn, the panels were prepared in duplicate.

2.4. Laboratory tests

After curing, panels of 150 mm × 80 mm × 2 mm were immersed in 0.1 M sodium chloride solution during 70 days at 25 °C and pH 7.0. *Visual and microscopic observations* were realized throughout the test. In addition, the *electrode potential* was determined as a function of exposure time; two clear acrylic cylindrical tubes were fixed on each plate (results were averaged). The tube size was 10 cm long and 5 cm diameter, with the lower edge flattened; the geometric area of the cell was 20 cm^2. A saturated calomel electrode (SCE) was selected as reference electrode. The potential was measured with a digital electrometer of high input impedance.

Similar panels were tested in salt spray (fog) chamber for 1500 h [22] and in 100% relative humidity for 1000 h [23]. After finishing the tests, the panels were evaluated to establish the *degree of rusting* [24] in salt spray (fog) chamber and the *degree of blistering* [25] in 100% relative humidity.

3. Results and discussion

3.1. Material characterization

Lithium silicate. The commercial colloidal lithium silicate selected (3.5/1.0 silica/alkali molar ratio in solution at 25%, w/w) dissolves in water to form a viscous solution with a high degree of stability. It has 25.2° Be density, 12.5 cP viscosity at 0.01 s^{-1} and 11.0 pH.

Nanosilica. Density ρ of the nanosilica used in this experience is 2.31 g cm^{-3} at 25 °C. The morphology and the associated particle size was evaluated by SEM (Scanning Electron Microscopy, Philips SEM 505, with analytical capacity through the microprobe system EDAX DX PRIME 10 for analysis qualitative/quantitative) while the specific area by the BET method (Brunauer, Emmett and Teller, Micrometrics apparatus ASAP 2020); in both cases, before carrying out the measurements, the samples were heated at 300 °C for 2 h to produce the thermal desorption of organic substances that could be adsorbed during manufacture and that would block the active centres of silica surface reducing the amount of N_2 adsorbed during the estimation of BET isotherm. In the case of the observations made by SEM, the test samples were coated with Au–Pd after subjecting to heat treatment, Fig. 1.

The aggregates of individual particles showed an effective diameter of 1237 nm (SEM); the specific area was 104 m^2 g^{-1} (BET). The ratio $6/\bar{d}\rho$ indicates accurately the specific area of the particles, suggesting that individual particles had an average diameter $\bar{d}$ of approximately 25 nm.

Film-forming materials. Glass properties (density, refractive index and interfacial tension) were studied. With regard to density, a slight decrease was noticed with addition of silica: 2.297 g cm^{-3} value for the 3.5/1.0 SiO_2/Li_2O molar ratio and respectively 2.238 and 2.251 g cm^{-3} values for binders A (7.5/1.0 ratio, commercial colloidal solution) and B (7.5/1.0 ratio, laboratory-prepared nanosolution). On the other hand, the refractive index (portable digital refractometer, Reichert AR200) for such systems was reduced from 1.482 (3.5/1.0 ratio) to 1.462 and 1.473 respectively for those before-mentioned commercial and nano-structured binders; it is worth mentioning that these values are in the range having the organic polymeric materials and extenders commonly used in the formulation of coatings.

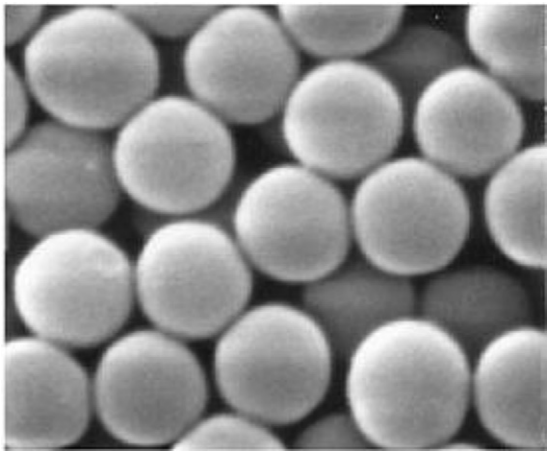

Fig. 1. SEM micrograph of nanosilica particles.

Regarding the superficial tension (Du Noüy tensiometer, Beijing Jinshengxin Testing Machine Co., Ltd., model JZHY-180) of A and B silicified binders at 25 °C, they respectively showed values of 191 and 205 dina cm^{-1}. The last allowed concluding that the nano-structured binder has a lower superficial affinity by metallic zinc particles and consequently lower wettability, penetration and spreading during the pigment incorporation prior to application.

Pigmentation. The main features of the commercial zinc dust of 4 μm (fine) and 8 μm (regular) are respectively 98.1 and 98.3% of total zinc and 94.1 and 94.2% of metal zinc, which means 5.0 and 5.1% of zinc oxide; in addition, metal zinc particles displays respectively 2282 and 1162 cm^2 g^{-1} values of specific area (BET).

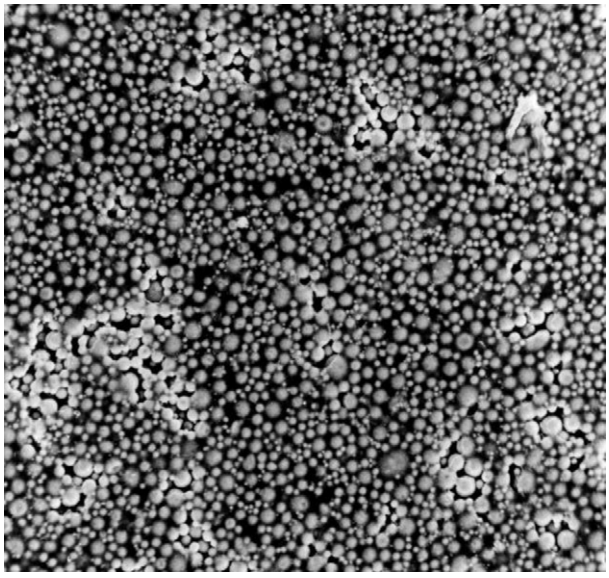

Fig. 2. SEM micrograph of nanozinc particles.

The nanozinc selected is a grey powder, Fig. 2; it has a spherical shape with an average diameter of 35 nm (SEM), which gives it a high specific area (BET, 42 $m^2 g^{-1}$); its purity is very high (about 99.8%, w/w).

3.2. Immersion in 0.1 M sodium chloride solution

Before beginning the test, coating films were characterized by applying X-ray (Shimadzu MXF-2400, Jenck S.A.). These studies showed an interatomic distance between Si and O approximately of 1.62 Å and in addition that the oxygen is linked to two silicon atoms or to one of silicon and another one of the metal. The polymer structure has a random arrangement with zinc cations placed into holes in the network.

Visual and microscopic observations allowed to conclude, particularly in those panels with scribe, that primers based on binder B showed greater amount of white products from corrosion of metallic zinc than in those panels protected with primers made from binder A. To explain this performance, it is necessary to consider the higher interfacial tension that displays the binder B (inferior wetting, that is lower adhesion, penetration and spreading during metal zinc incorporation previous to application), which generates more porous films and therefore higher cathodic protective activity.

On the other hand, primers that included zinc fine particles (4 μm) also showed a galvanic activity more important than those made with zinc regular particles (8 μm). A similar conclusion was reached with the primers based on microzinc/nanozinc as pigment with respect to those based on spherical microzinc only. In turn, when the amount of nanozinc was increasing in the pigmentation (lower microzinc/nanozinc ratio) was also observed a rise of the galvanic activity of metallic zinc; this action was similar at different depths of the paint film (about the same amount of white salt from the oxidation of zinc particles), which demonstrates good electrical contact between the micro and nano particles and the base metal, Fig. 3.

The above-mentioned results also suggest that formulations with the highest nanozinc in the pigmentation could form an anode too active, which implies an unnecessarily high corrosion.

3.3. Corrosion potential

Immediately after starting the immersion of all coated panels in the electrolyte, the potential was inferior to −1.10 V, a value located in the range of protection of the electrode. It is worth mentioning that cathodic protection was considered finished when the corrosion potential of coated panel increased to more positive values (anodic ones) than −0.60 V (referring to SCE) since a severe corrosion was observed (about 3% of the rusted area).

The electrode potential measurements as a function of immersion time indicates that both types of binders had a significant influence on the electrode potential: in general, more negative values were obtained with nano-structured film-forming materials, which means that the primers based on binder B showed better cathodic protection than those manufactured with binder A.

On the other hand, slight differences in electrode potential could also be attributed to the average diameter of zinc particles; it was observed greater galvanic activity in samples prepared with 4 μm than 8 μm (values more negative of electrode potentials for the former than for the latter).

The experimental values indicate a significant shift towards more positive values of potential in those primers with decreasing amounts of nanozinc in their composition (70/30, 80/20 and 90/10 microzinc/nanozinc, w/w, ratio, in that order); considering the performance, the worst primers were only formulated with microzinc as pigment.

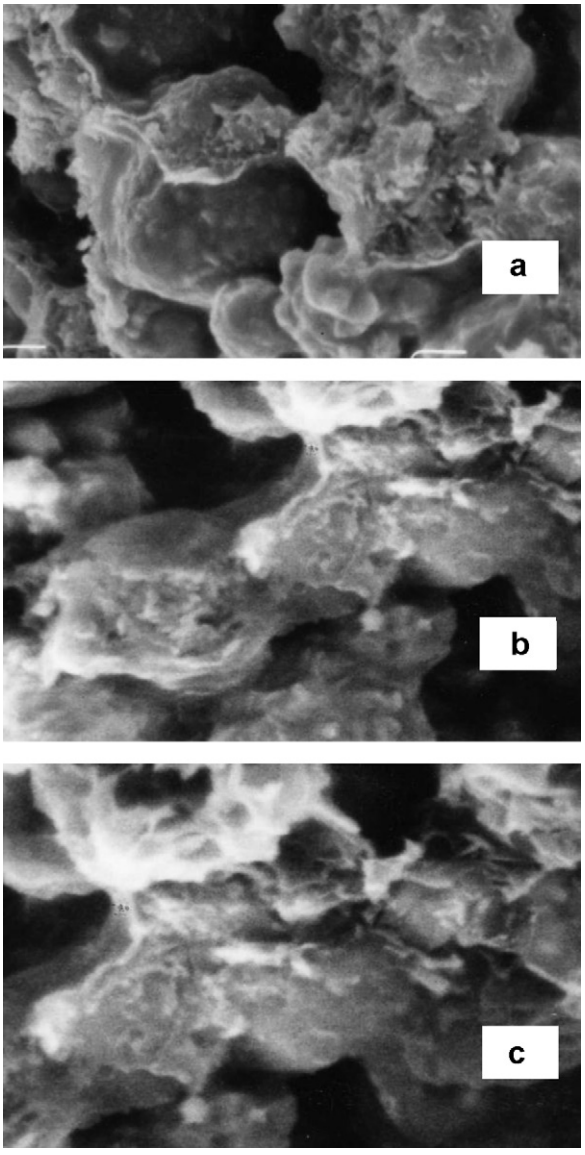

Fig. 3. Coating formulated with 70/30 spherical microzinc/nanozinc (w/w) ratio and binder B. Cross-section view SEM micrographs at several distance from the steel/zinc coating interface: (a) about 5–6 μm; (b) about 25–27 μm and (c) about 65–67 μm.

Fig. 4 displays the electrode potential vs. immersion time in sodium chloride solution of coatings formulated with the same value of PVC (57.5%) and based on binder B (7.5/1.0 nanosilica/lithium oxide molar ratio as film-forming material) and fine microzinc (D 50/50 4 μm). It allows concluding that for a constant value of PVC the performance of coatings increase as the percentage level of nanozinc in pigmentation also increases.

Fig. 5 includes also primers based on binder B and fine microzinc; this figure displays just the most efficient primers selected taking into account the lowest value of PVC corresponding to each pigment composition: B.I.1 (65.0%), B.I.2 (62.5%), B.I.3 (57.5%) and B.1.4 (55.0%) since in these primers the zinc is the component of major cost in the formulation. In summary, Fig. 5 shows that in spite of diminishing the PVC, coatings with increasing percentage levels of nanozinc in pigmentation also show an increasing efficiency.

Fig. 6 shows the behaviour of coatings formulated with low PVC (47.5%), also through of variation of the electrode potential during immersion time in sodium chloride solution. The analysis of the curves indicates an enhanced performance of the binder B in relation to binder A, which arises by comparing the curves B.I.4 vs. A.I.4

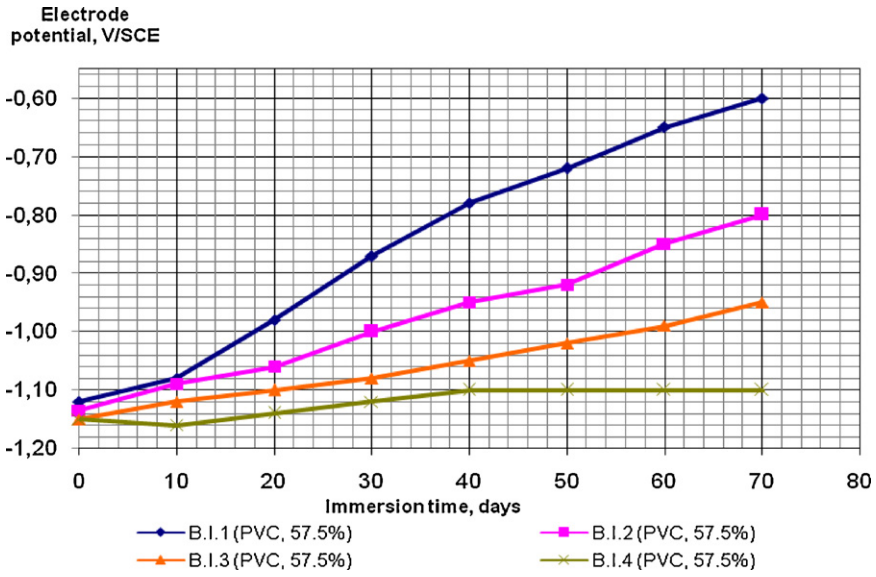

Fig. 4. Electrode potential vs. immersion time in 0.1 M sodium chloride solution: influence of pigment composition.

and B.II.4 vs. A.II.4. In addition, it shows an improved efficiency of microzinc of 4 μm in relation to that of 8 μm, which emerges by analysing the curves A.I.4 vs. A.II.4 and B.I.4 vs. B.II.4.

In summary, there is a total correlation between conclusions of visual and microscopic observations and results of the electrode potentials obtained during immersion in 0.1 M sodium chloride solution; therefore, the basis of the quantitative results of electrode potentials are the same that those spelled out in the visual and microscopic observations.

3.4. Degree of rusting

The results of panels tested during 1500 h in salt spray (fog) chamber (35 ± 1 °C; pH 6.5–7.2; continuous spray of 5 ± 1%, w/w, NaCl solution) are shown in Tables 2 and 3, which include only the average values of the tests performed. The failure at scribe (Procedure A) was evaluated according to the advance from the cutting area; the value 10 defines a failure of 0 mm while zero corresponds to 16 mm or more. Over the unscribed area (Procedure B), the failure was measured taking into account the percentage of area corroded by the environment; the scale ranges from 10 (no failure) to 0 (over 75% of the rusted area).

The results indicate that performance improved as nanozinc content increased (minor microzinc/nanozinc ratio). Those obtained by Procedures A and B displays that the primers based mainly on both spherical microzinc and formulated with reduced values of PVC showed a sharp decline in corrosion performance while those that included nanozinc, despite having been manufactured with a significantly lower level of pigmentation, maintained their efficiency. The reduction of PVC (minor total zinc level) involves the decreasing of coating costs.

These results would be based on the reduced electrical contact between particles of both types of microzinc and the metal substrate, beyond the corrosion products could not only increase the electrical resistance of the film but also could decrease the amount of available zinc. The incorporation of nanozinc seems to

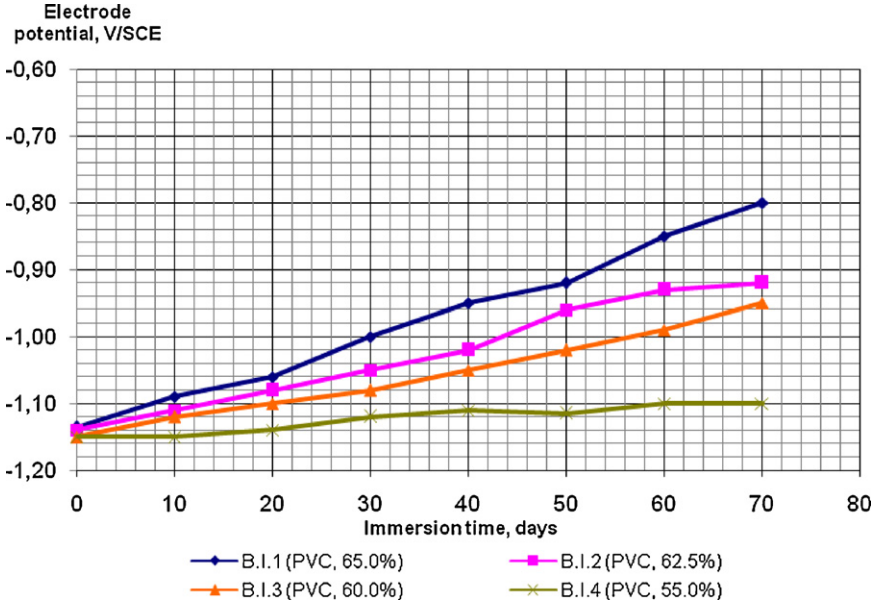

Fig. 5. Electrode potential vs. immersion time in 0.1 M sodium chloride solution: simultaneous influence of PVC and pigment composition.

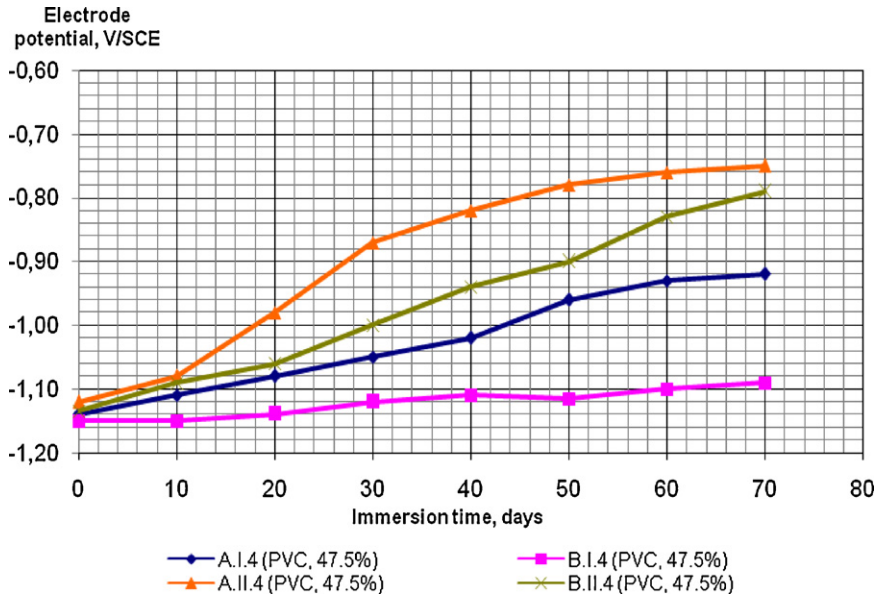

Fig. 6. Electrode potential vs. immersion time in 0.1 M sodium chloride solution: influence of type of binder and size of microzinc.

Table 2
Degree of rusting in salt spray (fog) chamber: failure at scribe.

Primer	Pigment volume concentration, %									
	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0	67.5	70.0
A.I.1	*	*	*	*	4	4	6	6–7	6	6
A.I.2	*	*	*	5	5–6	6–7	7–8	7	6–7	*
A.I.3	*	*	7	7–8	8	7–8	7	6–7	*	*
A.I.4	7	8	8	8	7–8	8	*	*	*	*
A.II.1	*	*	*	*	4	4	5	6–7	6–7	7
A.II.2	*	*	*	5	5	6	7	7	6–7	*
A.II.3	*	*	5–6	5–6	6–7	7	7–8	7	*	*
A.II.4	6	6	7	7–8	7–8	7–8	*	*	*	*
B.I.1	*	*	*	*	5	5–6	6–7	7	7	7
B.I.2	*	*	*	5–6	6–7	7	8	7	7	*
B.I.3	*	*	7–8	8	8–9	8	8–9	7–8	*	*
B.I.4	8–9	8–9	8–9	9	9	9	*	*	*	*
B.II.1	*	*	*	*	3–4	5–6	7	6–7	6–7	6
B.II.2	*	*	*	5–6	6–7	8	6–7	6–7	6–7	*
B.II.3	*	*	6	7	8–9	8	8	8	*	*
B.II.4	7	7–8	8	9	8–9	8	*	*	*	*

* PVC not considered.

Table 3
Degree of rusting in salt spray (fog) chamber: failure over the unscribed area.

Primer	Pigment volume concentration, %									
	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0	67.5	70.0
A.I.1	*	*	*	*	4–5	5–6	6	7	7–8	7
A.I.2	*	*	*	6	6–7	7	7–8	7–8	8	*
A.I.3	*	*	7–8	7–8	8–9	8–9	8–9	8–9	*	*
A.I.4	8	8–9	9	9	8–9	8–9	*	*	*	*
A.II.1	*	*	*	*	4–5	5–6	6	6–7	7	7–8
A.II.2	*	*	*	5–6	6–7	6–7	7–8	7–8	7–8	*
A.II.3	*	*	7	7–8	8	8	7–8	7–8	*	*
A.II.4	7	7–8	8	8	8–9	8–9	*	*	*	*
B.I.1	*	*	*	*	5–6	6	6	7–8	7–8	7–8
B.I.2	*	*	*	6–7	7–8	7–8	8	8	8	*
B.I.3	*	*	8	8	8–9	8–9	8–9	8–9	*	*
B.I.4	9	9	9	9–10	9–10	9–10	*	*	*	*
B.II.1	*	*	*	*	5–6	6	6–7	7	7–8	8
B.II.2	*	*	*	6	6–7	7	7–8	8	8	*
B.II.3	*	*	7	7–8	8–9	8–9	8–9	8–9	*	*
B.II.4	7–8	8	8–9	9	9	9	*	*	*	*

* PVC not considered.

Table 4
Degree of blistering in 100% relative humidity.

Primer	Pigment volume concentration, %									
	47.5	50.0	52.5	55.0	57.5	60.0	62.5	65.0	67.5	70.0
A.I.1	*	*	*	*	9-F	9-F	10	10	10	10
A.I.2	*	*	*	8-F	9-F	10	10	10	10	*
A.I.3	*	*	8-MD	9-F	10	10	10	10	*	*
A.I.4	6-MD	8-MD	9-F	10	10	10	*	*	*	*
A.II.1	*	*	*	*	9-F	9-F	10	10	10	10
A.II.2	*	*	*	9-F	9-F	10	10	10	10	*
A.II.3	*	*	8-F	9-M	10	10	10	10	*	*
A.II.4	8-MD	9-M	9-F	10	10	10	*	*	*	*
B.I.1	*	*	*	*	8-F	9-F	9-F	10	10	10
B.I.2	*	*	*	8-M	8-F	10	10	10	10	*
B.I.3	*	*	8-MD	9-M	9-F	10	10	10	*	*
B.I.4	4-MD	8-F	9-F	10	10	10	*	*	*	*
B.II.1	*	*	*	*	8-F	9-F	10	10	10	10
B.II.2	*	*	*	8-F	9-F	9-F	10	10	10	*
B.II.3	*	*	8-F	8-F	9-F	10	10	10	*	*
B.II.4	8-M	8-M	9-F	10	10	10	*	*	*	*

* PVC not considered.

Table 5
Average values of the simultaneous statistical treatment of all variables.

Nature of effect	Effect type	Degree of rusting			Degree of blistering	Simultaneous analysis
		Scribed area	Unscribed area	Average		
Binder type	A	6.5	7.3	6.9	9.0	8.0
	B	7.2	7.8	7.5	8.8	8.2
Microzinc	I	7.0	7.8	7.4	8.8	8.2
	II	6.6	7.4	7.0	9.0	8.0
Pigment composition*	1	5.7	6.4	6.0	9.3	7.6
	2	6.4	7.2	6.8	9.2	8.0
	3	7.4	8.0	7.7	8.8	8.2
	4	7.8	8.6	8.2	8.2	8.2

* PVC not considered.

have favoured the conductivity, according to the abundant amount of zinc corrosion products visual and microscopically observed, to the results of the electrode potentials and to those obtained in the salt spray (fog) chamber.

3.5. Degree of blistering

The results of the panels exposed during 1000 h in 100% relative humidity are included in Table 4; the size of the blisters is described in an arbitrary numerical scale of 0–10, where 10 represents absence while the frequency is qualitatively defined as follows: D (Dense), MD (Medium Dense), M (Medium) and F (Few).

The compositions that included only microzinc showed virtually no blistering. On the other hand, the results of blistering resistance worsened, particularly for the low PVC values, with the increasing incorporation of nanozinc in pigmentation.

3.6. Simultaneous analysis of degree of rusting and degree of blistering

To study the variables considered (main effects), a statistical interpretation was carried out. First, the variance was calculated and later the Fisher F test was done. The results indicated that binder type, pigmentation composition and PVC values displayed an important influence on the performance of the sacrificial coatings.

Depending on the conclusions reached, it was considered desirable for the statistical analysis to take into account all values of PVC studied to allow a certain margin of safety in the performance due to possible heterogeneities in primer composition attributable to poor incorporation of metallic zinc and/or sedimentation in container before applying.

With the purpose of establishing the efficiency of each protective coating from an anticorrosive point of view, the average value of degree of rusting was calculated for scribed and unscribed areas, and then the value obtained was averaged with the average value of degree of blistering. With respect to this last aspect, initially the mean value corresponding to the size and the frequency was calculated; to quantify the frequency the following numerical values were assigned: no blister, 10.0; F (Few), 7.5; M (Medium), 5.0; MD (Medium Dense), 2.5 and D (Dense), 0.0.

Concerning the precision of experimental tests, in standard deviation terms, it was as maximum 0.2 for degree of rusting, 0.6 for degree of blistering, and 0.4 for simultaneous degree of rusting and degree of blistering.

Table 5 confirms the superior performance of nano-structured binder B in relation to commercial colloidal binder A, the major efficiency of fine microzinc (4 μm) compared to regular one (8 μm) and the increasing performance of primers as the level of nanozinc increased.

On this last variable of formulation, it is worth mentioning that 80/20 and 70/10 microzinc/nanozinc (w/w) ratios showed the same protective capacity. It occurs due to the enhanced anticorrosive ability (7.7 and 8.2, respectively) and the decreased resistance to blister formation (8.8 and 8.2, respectively) as the amount of nanozinc in primer pigmentation increased; nevertheless, according to this simultaneous statistical interpretation of all effects, the 80/20 (w/w) ratio should be selected for economic reasons since coatings of similar performance may be formulated with lower PVC values.

4. Conclusions

4.1 To explain the better efficiency of laboratory-prepared nanosolution, 7.5/1.0 SiO_2/Li_2O molar ratio as comparing with commercial colloidal solution, 7.5/1.0 SiO_2/Li_2O molar ratio it is necessary to consider that the first ones are based on binders with higher superficial tension. The last one implies inferior wetting, which means lower adhesion, penetration and spreading during metal zinc incorporation previous to application; consequently, they wet with more difficult the zinc particles while the second ones do it in a better way (more reduced interfacial tension).

The above-mentioned characteristic explains the great porosity of zinc-rich nano lithium silicate films and so their higher cathodic protective activity as comparing with zinc-rich conventional lithium silicate films.

4.2 Results indicate that with respect to the pigment composition in primers, higher performance was achieved with spherical microzinc (fine), D 50/50 4 μm than spherical microzinc (regular), D 50/50 8 μm; in relation to the influence of nanozinc, this was successfully used to partially substitute the microzinc in zinc-rich coatings. When the amount of nanozinc was increasing in the film (from 90/10 to 70/30 spherical microzinc/nanozinc, w/w) was observed a rise of the galvanic activity of metallic zinc. The above quoted may be based on fact that the decrease of particle size increases significantly the surface area per unit mass; since all surfaces have a free energy, the relationship between the last one and the mass in small particles is so high that generates a strong attraction between them. Therefore, the small particles in a poor dispersion, as done in zinc primers, form dense aggregates with a large number of ultimate particles associated; the last one leads to porous between aggregates and therefore to high galvanic activity. In addition, both the elevated electrical contact between the small particles in aggregates and the aggregates themselves may lead to films with protective current of high intensity (materials always have a property interexchange current density, which obviously leads to a major current intensity as the surface area increases); the surface distribution of current would be also improved. The before-mentioned would support the visual and microscopic observations that showed a localized attack in the formulations based on spherical zinc of large diameter.

On the other hand, the cited high galvanic activity in primers of reduced film permeability would allow to conclude that the osmotic phenomenon would have been enough to promote blistering (blisters filled with liquid) for being formulated away from the critical PVC (the osmotic pressure exceeded the film adhesion). Therefore, the compositions formulated with PVC values relatively close to CPVC showed virtually no blistering.

4.3 Referring to PVC values (zinc content in dry film), previous results of laboratory tests demonstrated that a higher amount of microzinc leads to a longer useful life of primers. Nevertheless, it is important to mention that considering the physical characteristic of the primer film required for each particular case must make the choice of zinc content. When pigment volume concentration exceeds largely the CPVC, film properties such as adhesion, flexibility, abrasion resistance, etc. are drastically reduced while when the percentual level is slight under the critical value the efficiency is also considerably diminished.

In the case of primers, which have got incorporated nanozinc as partial replacement of spherical microzinc, results allow concluding that it is possible to reduce appreciably the PVC without affecting significantly the efficiency in service. Although there are porous between aggregates, both the elevated electrical contact between the small particles in aggregates and the aggregates themselves would base the global results leading to the reduction of the PVC values.

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References

[1] L.D. Vincent, Materials Performance 39 (5) (2000) 38–41.
[2] J. Vilche, E. Bucharsky, C.A. Giudice, Corrosion Science 44 (2002) 1287–1292.
[3] B. Muller, J. Langenbucher, Corrosion Science 45 (2003) 395–400.
[4] S. Mukherjee, Paintindia 49 (7) (1999) 41–46.
[5] H. Marchebois, S. Touzain, S. Joiret, J. Bernard, C. Savall, Electrochimica Acta 49 (17/18) (2004) 2945–2951.
[6] A.C. Bastos, M.L. Zheludkevich, M.G.S. Ferreira, Progress in Organic Coatings 63 (2008) 282–290.
[7] H. Marchebois, S. Joiret, C. Savall, J. Bernard, S. Touzain, Surface & Coatings Technology 157 (2002) 151–158.
[8] C.A. Giudice, J.C. Benítez, A. Pereyra, Journal of Coatings Technology 1 (4) (2004) 291–304.
[9] C.A. Giudice, J.C. Benítez, A. Pereyra, Pitture e Vernici European Coatings 81 (3) (2005) 33–44.
[10] A.M. Pereyra, C.A. Giudice, L.K. Herrera, F. Echeverría, J.G. Castaño, Surface Coatings International 89 (B3) (2006) 245–289.
[11] A.M. Pereyra, C.A. Giudice, European Coatings Journal 9 (2007) 40–45.
[12] C.A. Giudice, A.M. Pereyra, Pitture e Vernici European Coatings 83 (7) (2007) 48–57.
[13] A.M. Pereyra, C.A. Giudice, Fire Safety Journal 44 (2009) 497–503.
[14] M. Dietzel, Geochimica et Cosmochimica Acta 64 (19) (2000) 3275–3280.
[15] M. Tsai, C. Yang, P. Huang, Materials Science and Engineering 123 (2005) 238–243.
[16] M. Tsai, C. Yang, W. Wu, Materials Research Bulletin 40 (2005) 1609–1615.
[17] T. Jesionowski, A. Krysztafkiewicz, Journal of Dispersion Science and Technology 20 (1999) 1609–1612.
[18] A. Krysztafkiewicz, T. Jesionowski, S. Binkowski, Colloids and Surfaces A 173 (2000) 73–79.
[19] N. Aluru, et al., in: W. Gooddard, D. Brenner, S. Lyshevski, G.J. Iafrate (Eds.), Nanostructure Studies of the $Si–SiO_2$ Interface, Handbook of Nanoscience, Engineering and Technology, CRC Press, Washington, DC, USA, 2003 (Chapter 11.2).
[20] D. Baer, P. Burrows, A. El-Azab, Progress in Organic Coatings 47 (2003) 342–348.
[21] Swedish Standard SIS 05 59 00, Pictorial Surface Preparation Standards for Painting Steel Surfaces, 1967.
[22] ASTM B 117-09, Standard Practice for Operating Salt Spray (Fog) Apparatus, 2009.
[23] ASTM D 2247-11, Standard Practice for Testing Water Resistance of Coatings in 100% Relative Humidity, 2011.
[24] ASTM D 1654-08, Standard Test Method for Evaluation of or Coated Specimens Subjected to Corrosive Environments, 2008.
[25] ASTM D 714-02, Standard Test Method for Evaluating Degree of Blistering of Paints, 2009.