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A SVET investigation on the modification of zinc dust reactivity

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Abstract

Weldable primers are thin zinc-rich organic coatings that are weldable due to the electrical conductivity provided by the zinc dust. They are used in the automotive industry to provide corrosion protection in regions of difficult access. The zinc particles are highly susceptible to corrosion attack and, due to the small thickness, the protection conferred by these systems is limited.

In this work, corrosion inhibitors, two inorganic (cerium and lanthanum nitrates) and two of organic nature (benzotriazole and 2-mercaptobenzothiazole), were tested in order to reduce the reactivity of zinc dust. The samples used were of three kinds: a commercial weldable primer, pure zinc metal sheet and zinc dust. The corrosion testing was done in 0.05 M NaCl using the scanning vibrating electrode technique (SVET) that showed to meet well the purposes of the work. According to the results, all tested inhibitors can be used to reduce the corrosion of zinc and to increase the service life of weldable primers. The organic inhibitors were the best in retarding the degradation of the weldable primer during immersion in 0.05 M NaCl. Conversely, the corrosion inhibition of zinc dust was successful only with the inorganic inhibitors, principally cerium nitrate.

Keywords: Corrosion inhibitors; SVET; Weldable primers; Zinc dust; Zinc

1. Introduction

Paints incorporating zinc dust have been used for decades to protect steel structures in marine and industrial environments [1,2]. The anticorrosive ability comes essentially from the cathodic protection provided by the zinc dust. Another type of paint rich in zinc was introduced in the middle of the 1990s with the purpose of making organic coatings weldable [3]. These new systems, named weldable primers consisted on zinc rich epoxy-based coil coatings applied on chromate pre-treated electrogalvanised steel (EG). The function of the zinc dust was to make the primer weldable by providing the electrical conductivity between the welding electrode and the metal substrate. The welding capability of organic coatings is of great importance for the automotive industry [4,5]. The amount of zinc dust added is usually not sufficient to provide cathodic protection. The anticorrosion protection comes from the barrier effect given by the primer. The protection can be improved by increasing the thickness of the primer, but zinc alloying with the copper of the welding electrodes reduces the life of these electrodes, which determines low coating thicknesses, typically 2.5–4.5 μm. Inhibiting additives may also be incorporated to enhance the corrosion resistance.

By the end of the 1990s, a second generation of weldable primers was developed with the objective of doubling the corrosion resistance and improve the weldability of these systems. In the new primers, the zinc dust was mixed with iron phosphide, Fe_2P, which possess high melting point and is inert regarding the copper of the welding electrodes. As a result, higher coating thickness could be achieved leading to higher corrosion resistance. The welding properties were also better. Table 1 compares the first and second generation primers and shows that the main purposes of the "second generation" were met: both corrosion resistance and weldability were improved. However, formability, tool wear and tool pollution became worst. Hence, the need to improve the current systems still remains. One way to do it is to modify the "first generation" primers in order to improve the corrosion resistance and the weldability, but preserving the good qualities. The work reported here explores this idea by modifying chemically the zinc dust. The surface modification

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Table 1
General characteristics of weldable primers of first and second generation

	First generation	Second generation
Thickness (μm)[a]	2.5–4.5	4–8
Adhesion[a]	Good	Fair–good
Anti-corrosion[b]	Three times better than the substrate (EG)	Six times better than the substrate (EG)
Formability[a]	No scratches	Scratches
Tool wear[a]	No wear	Large
Weldability[b]	~800 Spot welds	~1100 Spot welds

[a] From Ref. [4].

[b] Based on Ref. [5].

with corrosion inhibitors may partially or completely passivate the zinc dust particles reducing their reactivity and the corrosion of weldable primers. It may also provide a reservoir of inhibitors to be activated later when water crosses the paint film towards the metal substrate.

Four inhibitors, two inorganic (cerium and lanthanum nitrates) and two organic (benzotriazole and 2-mercaptobenzothiazole) were tested. These inhibitors have been studied in our group for inhibition of some metals, namely aluminium alloys [6–8]. The corrosion inhibition of zinc and zinc alloys by cerium and lanthanum salts has been reported [9–12] and a few papers described studies on zinc inhibition by benzotriazole (named BTA hereafter) [13,14]. Like BTA, 2-mercaptobenzothiazole (in the following MBT) is a copper corrosion inhibitor that forms hydrophobic complexes with many other metals and therefore can be experimented as corrosion inhibitor for such metals [15,16].

In this work, a commercial weldable primer was used as model coating and its degradation was investigated in different inhibitive solutions. Pure zinc electrodes were studied since this element is the main constituent of the zinc dust and of the galvanized substrate to where the primer is applied. The inhibitors were also tested with zinc dust in different pre-treatment conditions, which is the main goal of this work: the selection of inhibitive pre-treatments for zinc dust in order to reduce both the reactivity of zinc and the corrosion of weldable primers.

The corrosion testing was done with the scanning vibrating electrode technique (SVET) that showed to suit well the purposes of the work. It measures potential differences in solution created by ionic fluxes originated by the corrosion process [17]. A prior calibration permits to convert the measured potential differences into current densities [18]. The technique possesses the great advantage of resolving the anodic and cathodic distributions on the surface of a metal, which is of remarkable value in corrosion research.

2. Experimental

2.1. Materials and reagents

Three different materials were subjected to corrosion testing:

(i) A galvanized steel coil-coated with a weldable primer for the automotive industry was used as model coating system. It consisted on a 1 mm thick DC04 steel sheet [19] with an electroplated zinc layer of 5.5 μm of nominal thickness and top-coated with a commercial weldable primer, 3.5 μm thick. Scanning electron microscopy pictures of the cross section and top view of the system are presented in Fig. 1(a) and (b), respectively.

(ii) Zinc foil (99.95% pure, Goodfellow, UK) was used to prepare the metal electrodes.

(iii) Commercial zinc dust was sieved to collect particles bigger than 50 μm – Fig. 1(c) – to meet the spatial resolution of SVET.

The corrosive test solution was prepared with NaCl (p.a., Pronalab, Portugal) and the inhibitors tested were cerium (III) nitrate hexahydrate (99%, Aldrich), lanthanum (III) nitrate hexahydrate (>99%, Fluka), 1H-benzotriazole (99%, Aldrich) and 2-mercaptobenzothiazole (97%, Aldrich). The solvents used were either distilled water or absolute ethanol.

2.2. SVET measurements

The SVET equipment was manufactured by Applicable Electronics Inc. (USA) and controlled by the ASET program (Sciencewares, USA). The microprobes were prepared from microelectrodes provided by Microprobe Inc. (USA) and had a spherical platinum black deposit of 10–20 μm on the tip. The measurements were made with the electrode tip vibrating at 200 μm above the surface (100 μm above the zinc particles for the zinc dust), with a frequency of 122 Hz, and the amplitude of vibration was the same as the tip diameter. The acquisition time in each point was 0.3 s + 0.2 s of waiting time between points to minimize the perturbation induced by the translation of the microelectrode. Maps with 30 × 30 (~750 s) or 50 × 50 points (~1700 s) were obtained. SVET values are, in general, positive for anodic currents and negative for cathodic currents.

Different electrochemical cells were used for each type of sample studied:

(i) Pieces of weldable primer with 1 cm × 1 cm were glued to an epoxy cylinder (sample holder) with a height of 1 cm and a radius of 1.5 cm. A mixture of beeswax and colophony covered the sample and delimited a working area of ~3 mm × 4 mm—Fig. 1(d).

(ii) Zinc electrodes were cut from the original foil and embedded in an epoxy cylinder. The surface was polished by SiC paper of grades 220, 400, 600, 800 and 1200, washed in

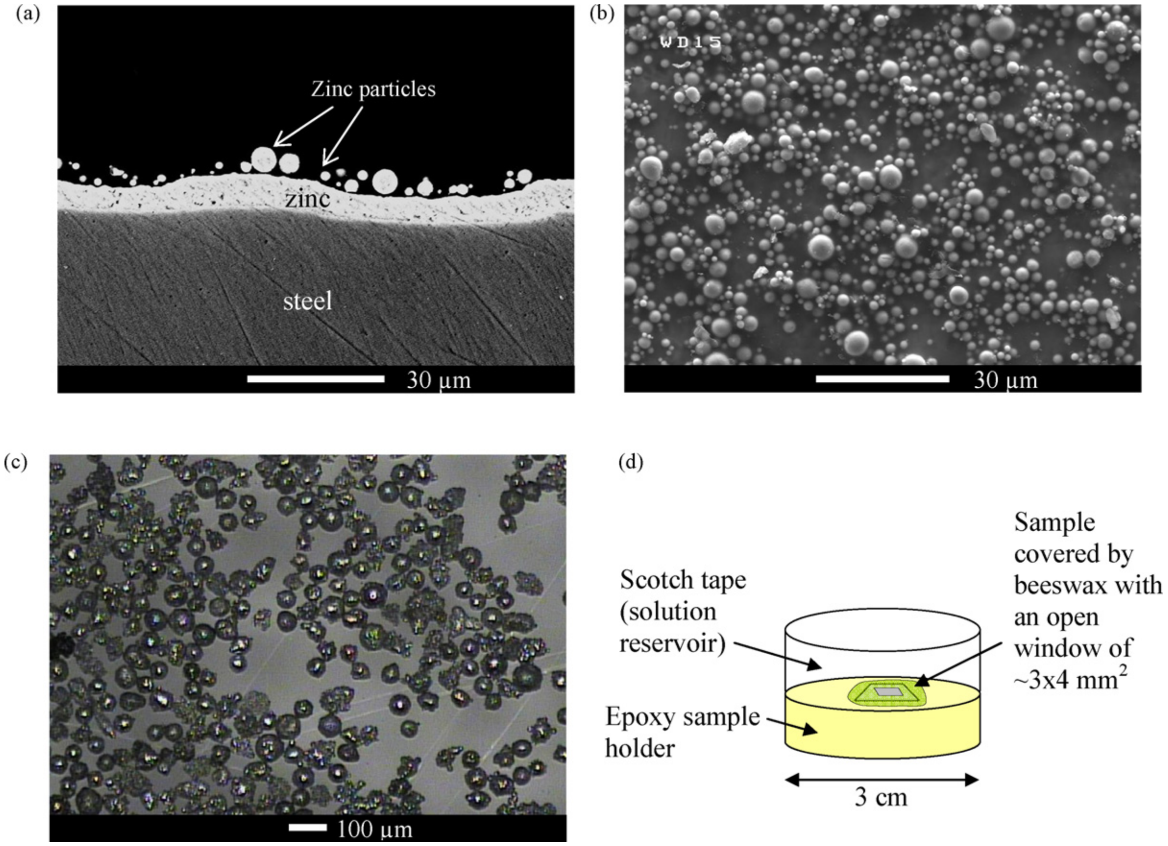

Fig. 1. Scanning electron micrographs of (a) cross section and (b) top view of the weldable primer; (c) zinc dust particles sieved for SVET measurements; (d) scheme of the cell used for testing the weldable primer.

distilled water and dried with absorbent paper, followed by warm air flow. Immersion occurred immediately after.

(iii) Sieved zinc dust particles were placed on the surface of a Petri dish (25 mL, Normax, Portugal) leaving many isolated particles and several agglomerates with particles electrically connected.

In cells (i) and (ii) scotch tape was applied around the epoxy cylinder to form the solution reservoir.

2.3. Testing sequence

(i) Weldable primer samples were exposed to 0.05 M NaCl and to 0.05 M NaCl + 0.5 g L^{-1} of each inhibitor to check for their inhibitive action when present in solution.

(ii) Pure zinc electrodes were submitted to a pre-treatment stage of 2 h with 0.5 g L^{-1} of each inhibitor in distilled water and then, in a second stage, they were immersed in 0.05 M NaCl. This permitted to check for the formation of an inhibitive film, during the initial stage, and its ability to retard the metal corrosion, in the second stage.

(iii) Zinc dust was pre-treated by immersion in Petri dishes using the four inhibitors at four different concentrations (10^{-4} M, 10^{-3} M, 10^{-2} M, 10^{-1} M), two solvents (distilled water and absolute ethanol) and three times of treatment (1 min, 1 h, 24 h). After the selected time, the pre-treatment solution was replaced by 0.05 M NaCl. Fresh portions of the NaCl solution were renewed 10 times successively to insure no inhibitor remained in solution. Corrosion of zinc dust was monitored during several days. Due to the low solubility of MBT in water, the aqueous solutions of this compound contained 5% of ethanol and were filtered to remove undissolved reagent.

3. Results

3.1. Study with weldable primers

The weldable primer corroded rather quickly when immersed in 0.05 M NaCl. Corrosion activity was detected by SVET after just a few minutes of immersion and in 2 h it was already possible to observe dark spots on the surface. These dark spots corresponded to paint delamination. Anodic activity appeared in some localized points of the dark spots with the surrounding area being cathodic. The activity detected by SVET came mainly from the corrosion of the electrogalvanised layer under the blisters. Given the particles' small size, the corrosion of the zinc dust was not detected by SVET at 200 μm from the surface. Fig. 2(a) shows a picture of the sample after 3 days of immersion, with blisters and corrosion products precipitated on the surface. The map acquired at the same time showed intense

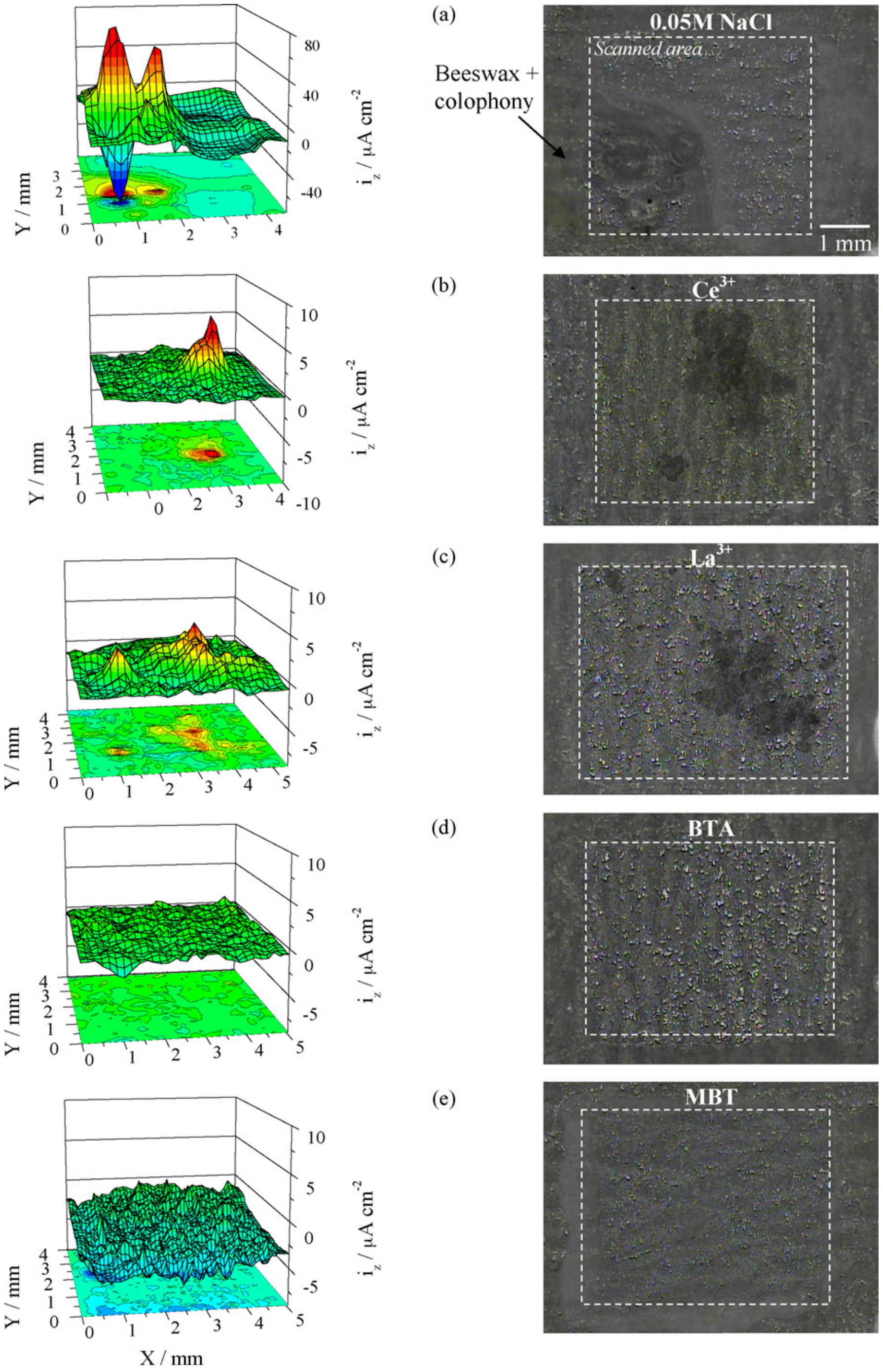

Fig. 2. SVET maps and corresponding pictures of the weldable primer after 1 week of immersion in the different solutions. Map and picture (a) were acquired after 3 days of immersion.

anodic and cathodic peaks located in the delaminated part of the sample.

The addition of inhibitors to the corrosive solution reduced markedly the degradation of the weldable primer. Fig. 2(b)–(e) show maps obtained after one week of immersion in the inhibitive solutions. The inorganic inhibitors decreased the degradation but delamination still took place, with small activity localized in some points. The organic inhibitors provided better protection as shown by maps with no activity and video images with no signs of degradation on the surface.

3.2. *Study with pure zinc electrodes*

Fig. 3 shows SVET current maps and pictures of pure zinc acquired after 1 day of immersion in 0.05 M NaCl. Fig. 3(a) is for zinc without pre-treatment and Fig. 3(b)–(e) correspond to pre-treated zinc. The results point to a better zinc corrosion inhibition by Ce^{3+} and La^{3+} compared to BTA and MBT, which presented poor inhibitive properties. This conclusion is valid for the treatment conditions used and should not be generalised, as the inhibition treatment is usu-

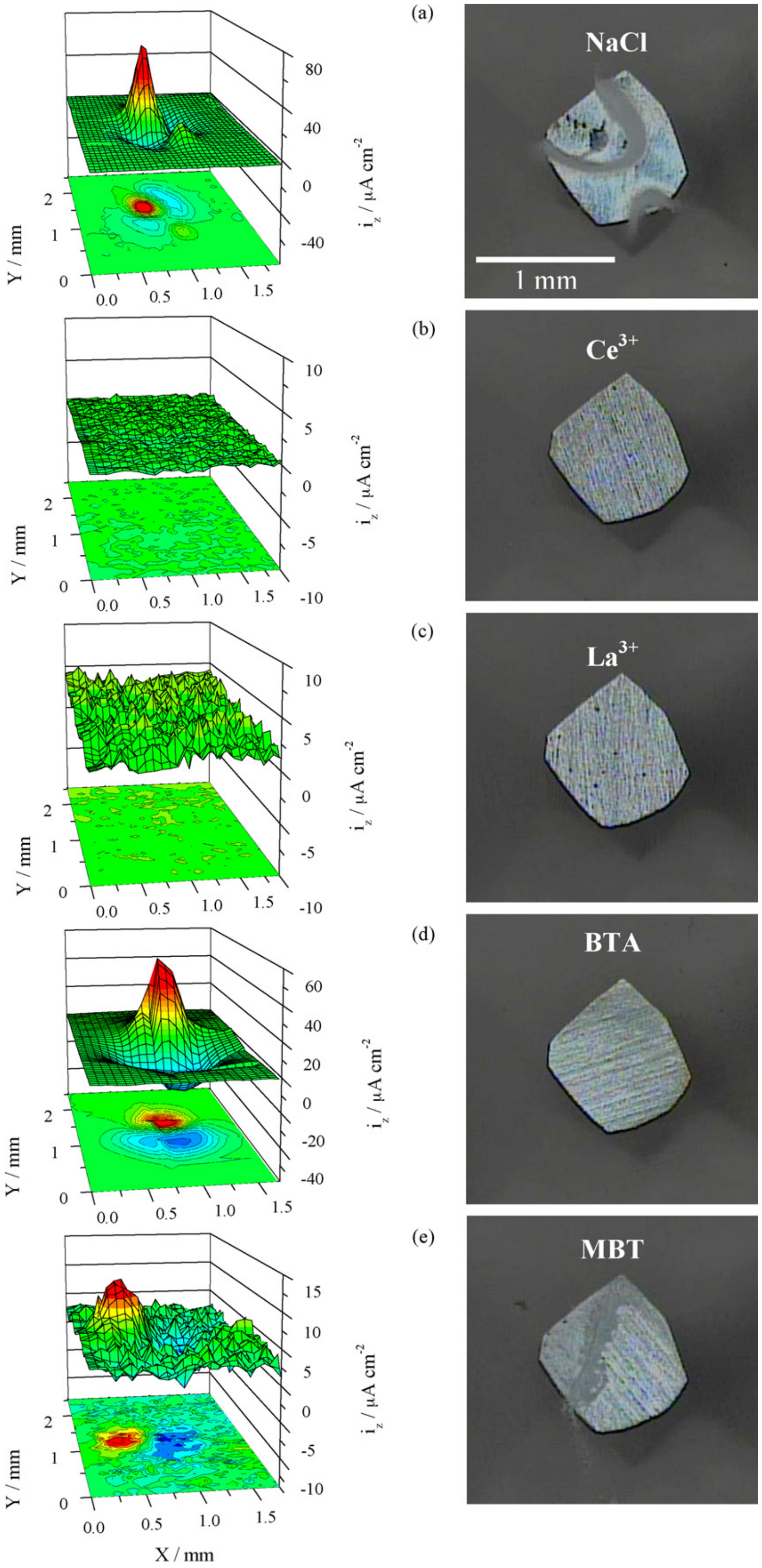

Fig. 3. SVET maps and corresponding pictures of pre-treated pure zinc after 24 h of immersion in 0.05 M NaCl; (a): the control sample, without pre-treatment.

ally dependent on the concentration and time of treatment [11,16,20,21].

The possible influence of the nitrate anion was investigated by exposing pure zinc electrodes and the weldable primer to 0.05 M NaCl + 4.5 mM of NO_3^- (the approximate concentration of NO_3^- in 0.5 g L^{-1} of cerium and lanthanum nitrates). Pure zinc corroded actively, in the same manner as in 0.05 M NaCl. The corrosion of the weldable primer was marginally lower compared to 0.05 M NaCl but noticeably higher compared to solutions with Ce^{3+} and La^{3+}. These results point to no significant inhibition coming from the nitrate ions in the conditions tested.

3.3. Study with zinc dust particles

The corrosion of zinc dust in 0.05 M NaCl after pre-treatment was followed by visual inspection and SVET for several days. For each pre-treatment condition many individual particles and agglomerates existed in the Petri dish. Fig. 4 gives examples of the three main situations encountered: (a) no inhibition (zinc dust without pre-treatment after 19 h in 0.05 M NaCl), (b) partial inhibition (zinc dust pre-treated for 24 h with cerium nitrate 10^{-2} M in distilled water followed by 24 h of immersion in 0.05 M NaCl) and (c) complete inhibition (zinc dust pre-treated for 24 h with cerium nitrate 10^{-1} M in distilled water followed by 48 h of immersion in 0.05 M NaCl). The differences are clear, from maps with anodic and cathodic activity and many corrosion products around the particles in (a) to absence of corrosion in both map and picture in (c). Isolated particles withstood corrosion better than agglomerates. In several solutions tested, agglomerates were all corroding but many isolated particles remained unattacked for days. Single particles under corrosion showed activity divided in two regions, one anodic and the other cathodic. It was not observed more than one anodic and one cathodic region in those particles. The two regions were separated by a wall of precipitated corrosion products, probably zinc hydroxide, which divided the particle in two parts of approximately the same area. This is depicted in Fig. 5(a) for an isolated particle after 2 h 30 min of immersion in 0.05 M NaCl. With time the precipitated corrosion products completely covered the particle. Fig. 5(b) shows a particle pre-treated for 24 h in cerium nitrate 10^{-2} M in distilled water followed by immersion in 0.05 M NaCl. No corrosion was detected after 8 days of corrosion testing.

The main objective of this work was the selection of pretreatment conditions for the inhibition of zinc dust corrosion. Given the number of conditions under test, and the number of isolated particles and agglomerates for each case, it would be virtually impossible to use SVET for all cases. Instead, a qualitative approach based on visual inspection permitted to rank the

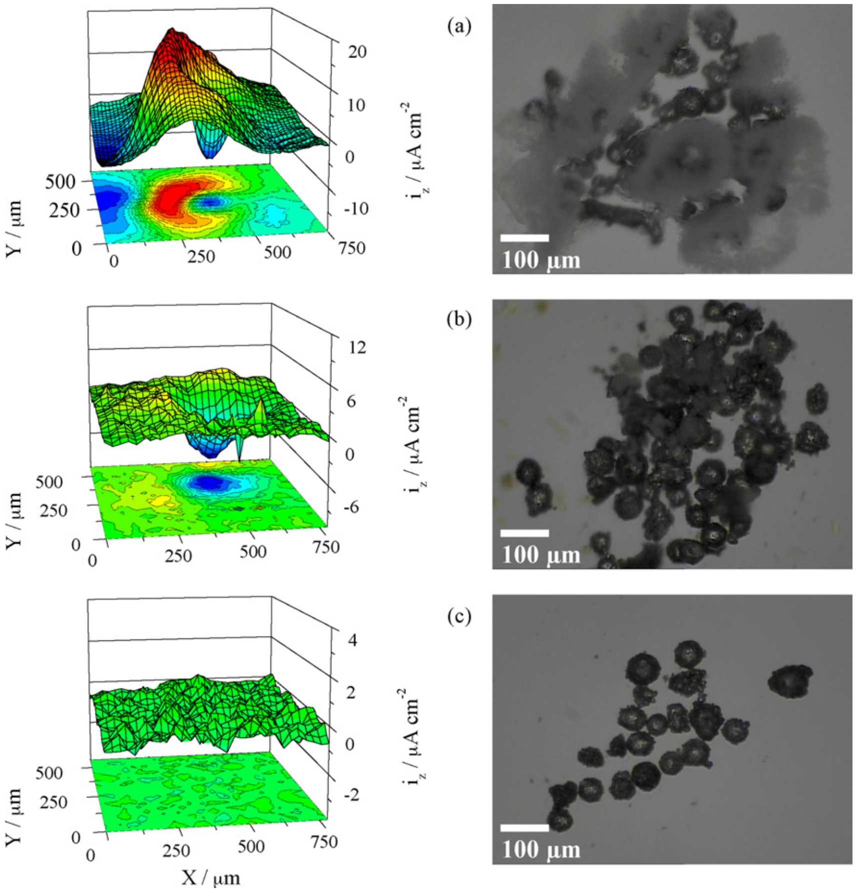

Fig. 4. (a) Zinc dust after 19 h of immersion in NaCl 0.05 M; (b) zinc dust pre-treated for 24 h in Ce^{3+} 10^{-2} M in distilled water followed by 24 h of immersion in 0.05 M NaCl; (c) zinc dust pre-treated for 24 h in Ce^{3+} 10^{-1} M in distilled water followed by 48 h of immersion in 0.05 M NaCl.

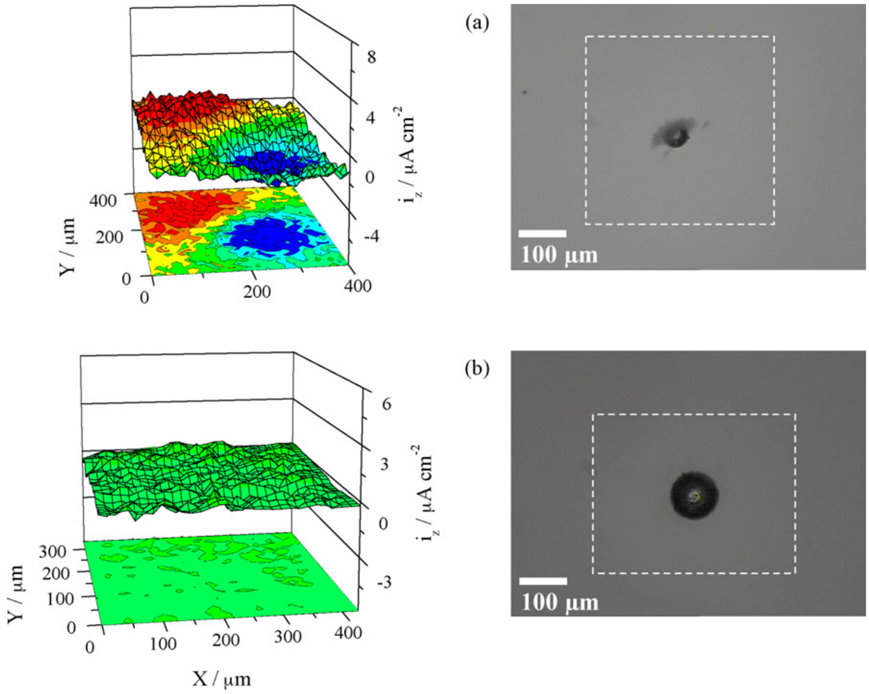

Fig. 5. (a) Single zinc particle after 2 h 30 min in 0.05 M NaCl; (b) single zinc particle immersed 24 h in Ce^{3+} 10^{-2} M followed by 8 days in 0.05 M NaCl.

Table 2
Condition of zinc dust pre-treated with Ce^{3+} after 24 h of immersion in 0.05 M NaCl

Solvent	Time	10^{-4} (M)	10^{-3}(M)	10^{-2} (M)	10^{-1} (M)
H_2O					
	1 min	0	0	0	0
	1 h	4	4	4	4–5
	24 h	3	4	5	4
Ethanol					
	1 min	0	1	2–3	4
	1 h	2	2	2–3	3
	24 h	2–3	2–3	3	3–4

Table 4
Condition of zinc dust pre-treated with BTA after 24 h of immersion in 0.05 M NaCl

Solvent	Time	10^{-4} (M)	10^{-3} (M)	10^{-2} (M)	10^{-1} (M)
H_2O					
	1 min	1	2	2	0
	1 h	0	1	1	1
	24 h	0	1	0	0
Ethanol					
	1 min	0	0	1	2
	1 h	0	0	0	0
	24 h	0	1	0	0

conditions under test. SVET was then used to confirm the results where good corrosion resistance was observed. This seemed to be an acceptable approach as the key idea was to select the best conditions for inhibition.

Tables 2–5 summarize the results obtained for all conditions after 24 h of immersion in 0.05 M NaCl using the following empirical scale:

0 : Corrosion similar to the uninhibited medium;
1 : A few isolated particles with no corrosion;
2 : Corrosion products in agglomerates less abundant that in 1; isolated particles without corrosion more abundant than in 1;

Table 3
Condition of zinc dust pre-treated with La^{3+} after 24 h of immersion in 0.05 M NaCl

Solvent	Time	10^{-4} (M)	10^{-3} (M)	10^{-2} (M)	10^{-1} (M)
H_2O					
	1 min	1	1–2	2	3
	1 h	1	2	3	4
	24 h	2	2–3	3	3
Ethanol					
	1 min	1	1	3–4	4
	1 h	2	2	3	3
	24 h	3	2–3	3	3–4

Table 5
Condition of zinc dust pre-treated with MBT after 24 h of immersion in 0.05 M NaCl

Solvent	Time	10^{-4} (M)	10^{-3} (M)	10^{-2} (M)	10^{-1} (M)
H_2O					
	1 min	0	0	0	0
	1 h	0	0	0	0
	24 h	0	0	0	0
Ethanol					
	1 min	0	0	0	0
	1 h	1	1	1	1
	24 h	1–2	1–2	1–2	1–2

3 : About 50% particles with no signs of corrosion and 50% particles attacked;
4 : All single particles and the majority of agglomerates with no attack;
5 : No signs of corrosion.

Despite the simple method of evaluation, it was possible to rank adequately the pre-treatments. The best results were obtained with cerium nitrate solutions 10^{-2} M and 10^{-1} M in distilled water, for times from 1 h to 24 h. No satisfactory action was achieved with the organic inhibitors in any of the combinations (inhibitor-concentration-solvent-time) tested.

4. Discussion

In weldable primers, the oxidation of the zinc particles may pose problems of cosmetic corrosion. The passivation of the zinc dust can help solving the problem. Additionally, in some circumstances, the zinc dust in traditional zinc rich primers may be too active and can be consumed rather quickly. In these cases it may be possible to partially passivate the surface of zinc dust particles in order to reduce their reactivity but maintaining the electrical connectivity and the galvanic protection ability. The possibility to passivate the zinc particles' surface, partially or completely, was checked by treating the zinc dust in inhibitive solutions for a given time.

The experimental results presented in Section 3.1. indicate that the four inhibitors can be used to reduce the corrosion of weldable primers and extend their service life, specially the organic ones, and BTA in particular. It has been demonstrated that zinc can be prevented from corrosion in 0.05 M NaCl when these inhibitors are present [22]. However, results in Sections 3.2 and 3.3 show that when the inhibitors are present solely during an initial pre-treatment time, only the inorganic ones confer corrosion protection. This is probably related to the different inhibition mechanisms of the inorganic and organic inhibitors under study. Based on existing literature, Ce^{3+} and La^{3+} precipitate as oxides or hydroxides in cathodic places forming a highly insoluble layer that reduces the cathodic activity [9–12,23,24]. The rate of the hydroxide layer formation usually is relatively high. The inhibition of zinc by BTA and MBT is believed to follow the same mechanism as for copper, iron, and aluminium alloys: adsorption on the metal surface followed by the development of a film of complexes of the organic molecules and the metal ions in the surface [6,13,15,16,20,25,26]. This process can be relatively slow and take many hours, as observed, for example, for the 2024 aluminium alloy [6]. Moreover, the organic monolayer may be desorbed from the metal surface when the solution with inhibitor is substituted by the inhibitor-free solution. In the case of inorganic inhibitors the formed oxide/hydroxide layer is extremely insoluble and therefore very stable.

Good protection of zinc dust was achieved by treating the particles in cerium nitrate solutions 10^{-2} M and 10^{-1} M in distilled water and for times from 1 h to 24 h. This means that the use of modified zinc dust in weldable primers can be a solution to improve its anticorrosive performance. The work will continue with the incorporation of modified zinc dust in new formulations and test them for corrosion resistance.

This strategy does not work in the case of organic inhibitors. An alternative is the direct incorporation in the formulation as additives. Although simple, this way brings the risk of incompatibilities with the binder or other components, together with the change of characteristics of the paint such as rheology and adhesion, among others. Moreover, being soluble, these inhibitors would increase the paint water uptake and its susceptibility to blistering. To prevent these risks, the inhibitors can be encapsulated in micro- or nano-containers and be released only when corrosion takes place. A "smart" release of the inhibitors from the containers may be triggered by environment changes provoked by the onset of corrosion: pH, metal cation concentration and ionic strength [27].

5. Conclusions

The possibility of modifying chemically the surface of zinc dust particles in order to reduce their reactivity in weldable primers was investigated using two inorganic inhibitors (cerium nitrate and lanthanum nitrate) and two organic inhibitors (benzotriazole and 2-mercaptobenzothiazole). SVET was the main technique used to assess the corrosion performance and showed to suit well the purposes of the work.

All four inhibitors tested can decrease the degradation of weldable primers, but the highest performance was obtained with the organic ones. The best way to incorporate the inhibitors into the paint formulation still needs further investigation. One approach, tested in this work, is the treatment of the zinc dust with inhibitors prior to incorporation. Promising results were found with cerium nitrate solutions in distilled water. The work will continue with the incorporation of modified zinc dust in new formulations.

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References

[1] C.G. Munger, Corrosion Prevention by Protective Coatings, third ed., NACE, 1986.
[2] H. Leidheiser (Ed.), Corrosion Control by Organic Coatings, NACE, 1981.
[3] A. Schnell, F. Androsch, K. Stellnberger, Revue de Métallurgie 7–8 (2004) 537.
[4] A. Besseyrias, C. Magny, Galvatech 2004 Conference Proceedings 2004, p. 271.
[5] A. Schnell, F.-M. Androsch, Galvatech 2004 Conference Proceedings, 2004, p. 279.
[6] M.L. Zheludkevich, K.A. Yasakau, S.K. Poznyak, M.G.S. Ferreira, Corros. Sci. 47 (2005) 3368.
[7] M.L. Zheludkevich, R. Serra, M.F. Montemor, K.A. Yasakau, I.M. Miranda Salvado, M.G.S. Ferreira, Electrochim. Acta 51 (2005) 208.

[8] A.M. Cabral, W. Trabelsi, R. Serra, M.F. Montemor, M.L. Zheludkevich, M.G.S. Ferreira, Corros. Sci. 48 (2006) 3740.

[9] B.R.W. Hinton, L. Wilson, Corros. Sci. 29 (1989) 967.

[10] K. Aramaki, Corros. Sci. 43 (2001) 1573.

[11] K. Aramaki, Corros. Sci. 43 (2001) 2201.

[12] M.F. Montemor, A.M. Simões, M.G.S. Ferreira, Prog. Org. Coat. 44 (2002) 111.

[13] K. Aramaki, Corros. Sci. 43 (2001) 1985.

[14] K. Wang, H.W. Pickering, K.G. Weil, J. Electrochem. Soc. 150 (2003) B176.

[15] J.C. Marconato, L.O. Bulhões, M.L. Temperini, Electrochim. Acta 43 (1998) 771.

[16] Y. Feng, S. Chen, H. Zhang, P. Li, L. Wu, W. Guo, Appl. Surf. Sci. 253 (2006) 2812.

[17] H.S. Isaacs, Y. Ishikawa, "Applications of the vibrating probe to localized current measurements", in: R. Baboian (Ed.), Electrochemical Techniques for Corrosion Engineering, NACE, Houston, 1986.

[18] C. Scheffey, Electric fields and the vibrating probe, for the uninitiated, in: R. Nuccitelli (Ed.), Ionic Currents in Development, A.R. Liss Inc., NY, 1986.

[19] EN 10130:1991, Cold Rolled Low Carbon Steel Flat Products for Cold Forming, Technical Delivery Conditions.

[20] F. Ammeloot, C. Fiaud, E.M.M. Sutter, Electrochim. Acta 42 (1997) 3565.

[21] R. Babic, M. Metikos-Hukovic, Thin Solid Films 359 (2000) 88.

[22] A.C. Bastos, S.V. Lamaka, M.L. Zheludkevich, M.G.S. Ferreira, IV International Materials Symposium, Conference Proceedings, Porto, 2007.

[23] A.J. Aldykewicz Jr., H.S. Isaacs, A.J. Davenport, J. Electrochem. Soc. 142 (1995) 3342.

[24] A.J. Aldykiewicz Jr., A.J. Davenport, H.S. Isaacs, J. Electrochem. Soc. 143 (1996) 147.

[25] L. Tommesani, G. Brunoro, A. Frignani, C. Monticelli, M. Dal Colle, Corros. Sci. 39 (1997) 1221.

[26] J.L. Yao, B. Ren, Z.F. Huang, P.G. Cao, R.A. Gu, Z.-Q. Tian, Electrochim. Acta 48 (2003) 1263.

[27] D.M. Shchukin, M. Zheludkevich, H. Mohwald, J. Mater. Chem. 16 (2006) 4561.