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PERFORMANCE OF BENZOATE -BASED EPOXY COATINGS UNDER SIMULATED MARINE CORROSION CONDITIONS

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Abstract

Traditional anti-corrosive paints contain lead or hexavalent chromium compounds as active pigments, which contaminate the environment and, at the same time, represent a risk to human health. In this sense, it is believed that benzoates as anticorrosive pigments for paints could match environmental concerns with proved anticorrosive efficiency.

The inhibitive properties of soluble benzoate compounds were known from many years ago and were studied employing sodium benzoate and benzoic acid, in different media, still those containing chloride. The employment of soluble compounds (benzoic acid, sodium benzoate, etc.) in anticorrosive paints is limited by the fact that their lixiviation by water penetrating the pores of the coatings would greatly increase coating permeability with the concomitant loss of the protective properties of the paint. However, it is possible to prepare anticorrosive pigments employing metallic benzoates with certain cations (e.g. zinc, aluminium, iron, etc.) whose compounds are widely used in paint technology.

The objective of this investigation was to study the inhibitive properties of zinc basic benzoate-based paints in simulated marine corrosion condition (3% NaCl solution). The anticorrosive properties of lab-prepared pigment were investigated via electrochemical techniques in pigment suspensions. In a second stage, anticorrosive paints containing zinc basic benzoate were formulated and their performance was evaluated by accelerated (salt spray chamber) and electrochemical (EIS) tests.

Experimental results show that zinc basic benzoate is adequate to formulate epoxy anticorrosive paints with improved anticorrosive performance in aggressive conditions, especially with the water-borne binder.

Palavras-chave: corrosion, anticorrosive paints, benzoates, EIS.

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1. INTRODUCTION

The inhibitive properties of benzoate anion were known from many years ago and were studied employing sodium benzoate and benzoic acid, in different media, still those containing chloride [1-15]. The employment of benzoate anion in combination with other anions such as gluconates was also reported [16] and, more recently, the inhibitive properties of calcium benzoate in neutral media were described [17].

The employment of soluble compounds (benzoic acid, sodium benzoate, etc.) in anticorrosive paints is limited by the fact that their lixiviation by water penetrating the pores of the coating would greatly increase its permeability with the concomitant loss of the protective properties of the paint. However, it is possible to prepare anticorrosive pigments employing metallic benzoates with certain cations (zinc, iron, aluminium, etc.) whose compounds are widely used in paint technology. In addition, zinc salts have recognized inhibitive properties due to the cation which may polarize cathodic areas by the precipitation of sparingly soluble salts and by increasing the pH of the medium, thus favouring steel passivation [18, 19].

The objective of this investigation was to study the inhibitive properties of zinc basic benzoate in paints. The pigment was precipitated under definite conditions and its anticorrosive properties were investigated by means of electrochemical techniques (corrosion potential and linear polarization) in pigment suspensions. After that, anticorrosive paints containing zinc basic benzoate were formulated and their performance was evaluated by accelerated (salt spray chamber) and electrochemical (EIS) tests.

2. EXPERIMENTAL SECTION

2.1. Electrochemical characterisation of the anticorrosive pigment

The inhibitive properties of the anticorrosive pigment were evaluated by means of electrochemical techniques, employing SAE 1010 steel electrodes with low surface roughness (mean peak-to-valley height 1.40 μm). The corrosion potential was monitored as a function of time against a saturated calomel electrode (SCE) as reference. The supporting electrolyte was a pigment suspension in 0.025M sodium perchlorate. Sodium perchlorate was chosen as supporting electrolyte in these preliminary studies to avoid the intense corrosion produced by sodium chloride which could make it impossible to observe the different processes which take

place during corrosion. However, final essays on painted steel were carried out with both electrolytes.

Steel corrosion rates, in pigment suspension in 0.5M sodium perchlorate, at different exposure times, were obtained from polarisation resistance measurements. A SCE and a platinum grid were used as reference and counter electrodes, respectively. The swept amplitude was ±0.250 V from the open circuit potential and the scan rate 0.250mV.s^{-1}. Measurements were carried out with a Potentiostat/Galvanostat EG&G PAR Model 273A plus SOFTCORR 352 software.

2.2. Paints composition, manufacture and application

Two different epoxy-paints were formulated and elaborated to carry out this research; one was a solvent-borne type and the other was a water-borne one, see table 1.

SAE 1010 steel panels (15.0 x 7.5 x 0.2cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene and then brushing to reach a dry film thickness of 80±5 µm. Painted panels were kept indoors for 14 days before testing.

2.3. Anticorrosive paint performance evaluation

2.3.1. Accelerated tests

For each type of paint, a set of 3 panels was placed in the salt spray chamber (ASTM B-117). Rusting (ASTM D-610) and blistering (ASTM D-714) degrees were evaluated periodically up to 4000 hours of exposure.

2.3.2. EIS measurements

Impedance spectra of painted panels (frequency range 1.10^{-3} Hz ≤ f ≤ 1.10^{5} Hz) were performed in the potentiostatic mode, at the corrosion potential. Measurements were done as a function of the exposure time to the electrolyte solutions (0.5M $NaClO_4$ and 3% NaCl), using the 1255 Solartron FRA and the 1286 Solartron EI. The amplitude of the applied AC voltage was 0.010 V peak to peak. Two acrylic tubes were attached to each coated panel (working electrode) with an epoxy adhesive in order to perform the electrochemical measurements. The geometric area exposed to the electrolyte, each cell, was 15.9 cm^2. A large area Pt-Rh mesh of negligible impedance and saturated calomel (SCE) were employed as auxiliary and reference electrodes, respectively. The experimental impedance spectra were interpreted on the basis of equivalent electrical circuits using a suitable fitting procedure developed by Boukamp [20].

This electrochemical experiments were carried out at laboratory temperature (20±2 ºC), using a Faraday cage.

3. RESULTS AND DISCUSSION

3.1. Electrochemical assessment of the anticorrosive properties of basic zinc benzoate

The corrosion potential vs. time curve revealed that zinc basic benzoate displaced the electrode potential towards ~ -100 mV vs. SCE, being this value much more positive than that of SAE 1010 steel in the supporting electrolyte (-650 to –750 mV vs. SCE) (Fig. 1).

Steel dissolution in zinc benzoate suspension, after three hours of exposure, was rather polarized and the curve exhibited an ill-defined passivation peak at ~ –350 mV (Fig. 2). The cathodic current in the plateau was too low, 65 $nA.cm^{-2}$, which would point out that cathodic reactions were inhibited if one takes into account that the cathodic current density measured with a platinum electrode in the supporting electrolyte was 220 $\mu A.cm^{-2}$. After 24 hours of exposure the anodic reaction was much more polarized, that is to say that the slope of the I vs. E curve was lower. The cathodic current increased to 20 $A.cm^{-2}$ but it was still lower than the oxygen current on platinum. Corrosion rate, obtained from Tafel plots, was 58.6$nA.cm^{-2}$ after 3 hours of exposure and 3.50$\mu A.cm^{-2}$ after one day has elapsed. These facts, together with the displacement of Ecorr to ~ –100 mV, led to the following conclusion: zinc basic benzoate was able to inhibit steel corrosion.

3.2. The performance of anticorrosive paints through accelerated tests

The best anticorrosive behaviour in the salt spray test was achieved with the water-borne paint (paint 2) whose qualification was 7 after 3600 hours of exposure (Table II). The solvent-borne epoxy (paint 1) had a poorer anticorrosive behaviour because the same qualification was attained after 1400 hours of exposure. In spite of the very important differences observed in this test, it may be pointed out that both types of paints behaved satisfactorily, specially the water-borne paint. The blistering process was also much less severe in the case of the water-borne epoxy because the first blisters were observed around 2500 hours of exposure and they were of small size and low surface density.

3.3. EIS measurements

The relative performance of painted steel samples, submerged in 0.5M NaCl solution, was evaluated by measuring the corrosion potential (Fig. 3) and by analysing the variation of R_i and C_i with the exposure time (Fig. 4).

The corrosion potential of epoxy solvent-borne paint diminished within 3 weeks of immersion, below -300 mV in 3% NaCl. The same paint showed a very different behaviour in 0.5M $NaClO_4$ and the steel corrosion potential remained displaced towards more positive values for a longer period of time exhibiting, at the same time, a slight tendency to repassivation beyond 60 days of immersion. The water-borne epoxy paint underwent an extended immersion period, approximately 300 days of immersion, without showing signs of corrosion in both electrolytes.

Both paints developed a high initial barrier effect ($R_1 > 10^8$ $\Omega.cm^{-2}$) which was rapidly lost before 10 days of immersion; however, values fluctuated between $10^5 - 10^6$ $\Omega.cm^{-2}$, pointing out that a residual barrier effect is still present [21-23]. The exception to the rule was the solvent-borne epoxy paint whose ionic resistance decreased from 40 days of immersion. In change, the water-borne coating showed a sudden increase in the barrier properties after 100 days of immersion, matching values higher than 10^8 $\Omega.cm^{-2}$. This property, together with the high values measured for the parameter R_2, suggested that this pigment very adequate to formulate water-borne coatings with improved performance. C_1 values are in close relationship with R_1 values, that is to say the solvent borne paint exhibited higher values than the water-borne one, in both electrolytes, due to the deterioration of the film after water permeation.

The parameters associated with the faradaic reaction (R_2, C_2) are similar in both electrolytes but the solvent-borne epoxy paint degraded previously in NaCl 3%; however, its anticorrosive behaviour was still satisfactory until 45 days of immersion. R_2 maintained higher than 10^6 $\Omega.cm^{-2}$ during 100 days for the solvent-borne paint in 0.5 M $NaClO_4$ and for more than one year for the water-borne coating in both electrolyte. In the case of this last coating, the charge transfer resistance increased over 10^9 $\Omega.cm^{-2}$ in 0.5 M $NaClO_4$ which is a very high value for an anticorrosive coating. This feature, together with the prolonged life of the water-borne coating in immersion, point out the fact that zinc basic benzoate is a very useful pigment to formulate ecological anticorrosive coatings. In accordance with above discussion, C_2 values indicate that the active area is small in the water-borne paint and reached typical values of uncoated steel in the case of the solvent-borne paint in NaCl 3%.

4. CONCLUSIONS

1. The electrochemical tests performed employing pigment suspensions confirmed the anticorrosive properties of the inhibitor.

2. Accelerated tests showed that zinc basic benzoate also performed satisfactorily in paints. The best results were obtained with the water-borne paint which underwent 4000 hours of exposure in the salt spray chamber.
3. Electrochemical tests showed that the pigment generated very high charge transfer resistance values which were responsible of the protection afforded by the paints. The barrier properties were of much less importance.

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Table I

Paint composition expressed as % by volume

Components	***Solvent-borne paint (1)***	***Water-borne paint (2)***
Zinc basic benzoate	13.3	3.5
Barium sulphate	12.2	2.2
Talc	12.2	2.1
Titanium dioxide	4.9	2.1
Zinc oxide	1.2	0.3
Mica	------	1.8
Resin / Hardener (1 / 1 ratio)	28.4	------
Resin / Hardener (1 / 1.2 ratio)	------	65.8
Additives	------	1.5
Solvents	27.8	20.7
Anti-corrosive pigment / total pigment (v / v)	30	30

Table II

Rusting [a] (ASTM D 610) and Blistering [b] (ASTM D 714) degrees of the painted panels exposed to the Salt Spray Chamber (ASTM B 117)

Paints		***Time / hours***									
		310	770	980	1150	1400	1580	1800	2500	3600	4000
1	R	10	9	9	8	7	6	----	----	----	----
	B	10	8F	6F	6F	4M	4MD	----	----	----	----
2	R	10	9	9	9	9	9	8	8	7	6
	B	10	10	10	10	10	10	10	8F	8F	8F

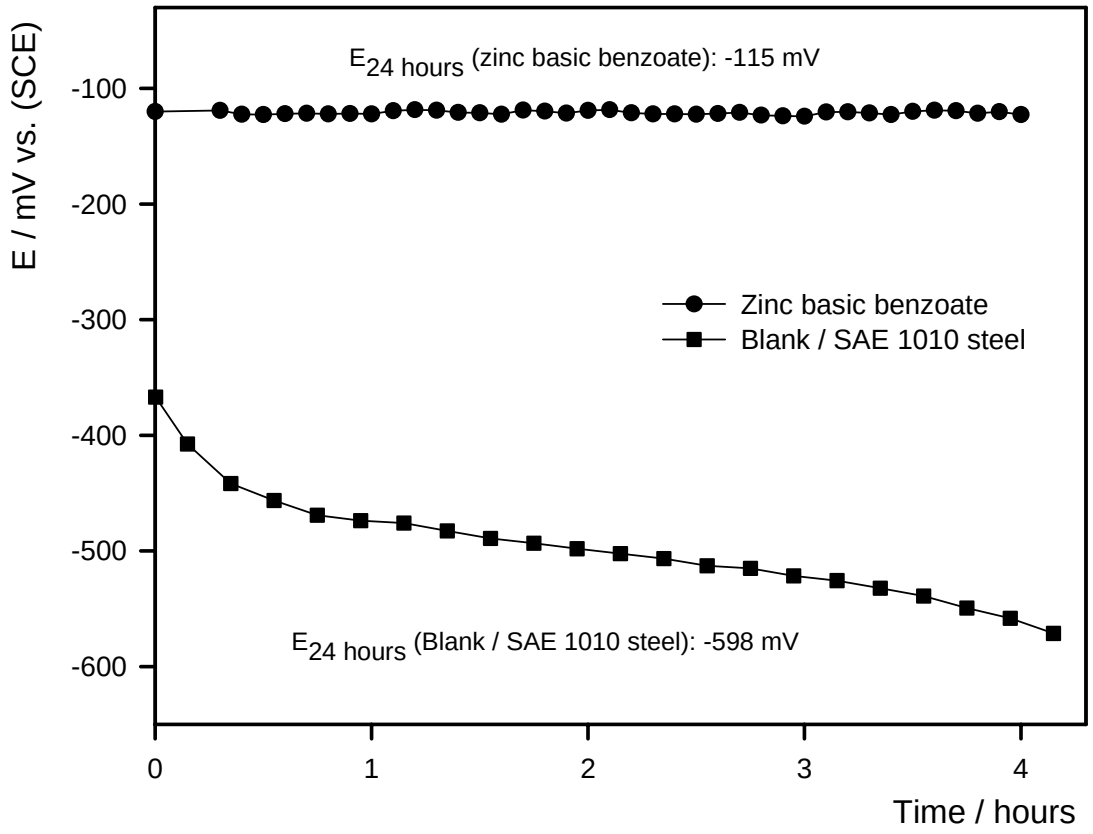
[a]R: rusting degree (ASTM D 610)

Rust Grade	10	9	8	7	6	5	4	3	2	1
rusted area / %	no rusted	0.03	0.1	0.3	1	3	10	16	33	50

[b]B: blistering degree (ASTM D 714)

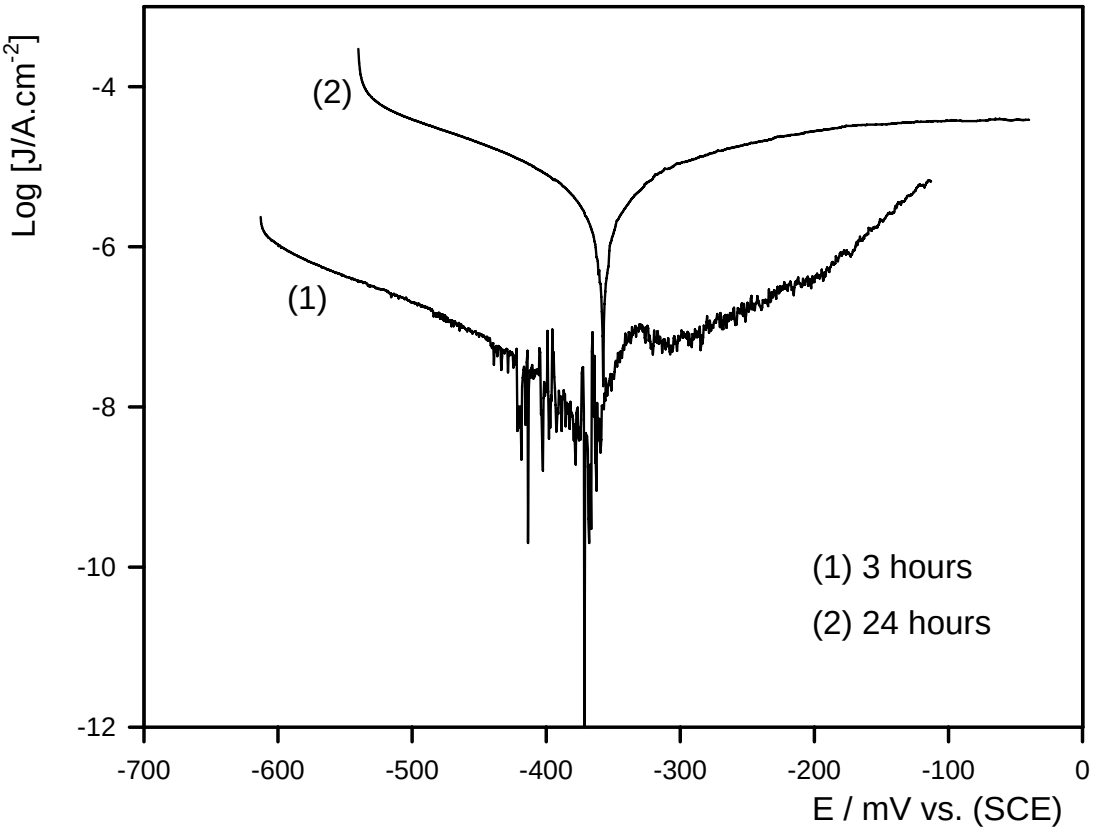
Frequency	Dense, D	Medium dense, MD	Medium, M	Few, F
Size /	10	8	6, 4	2
Comments	No blistering	Smaller size blister easily seen by unaided eye	Progressively larger sizes	

Figure 1



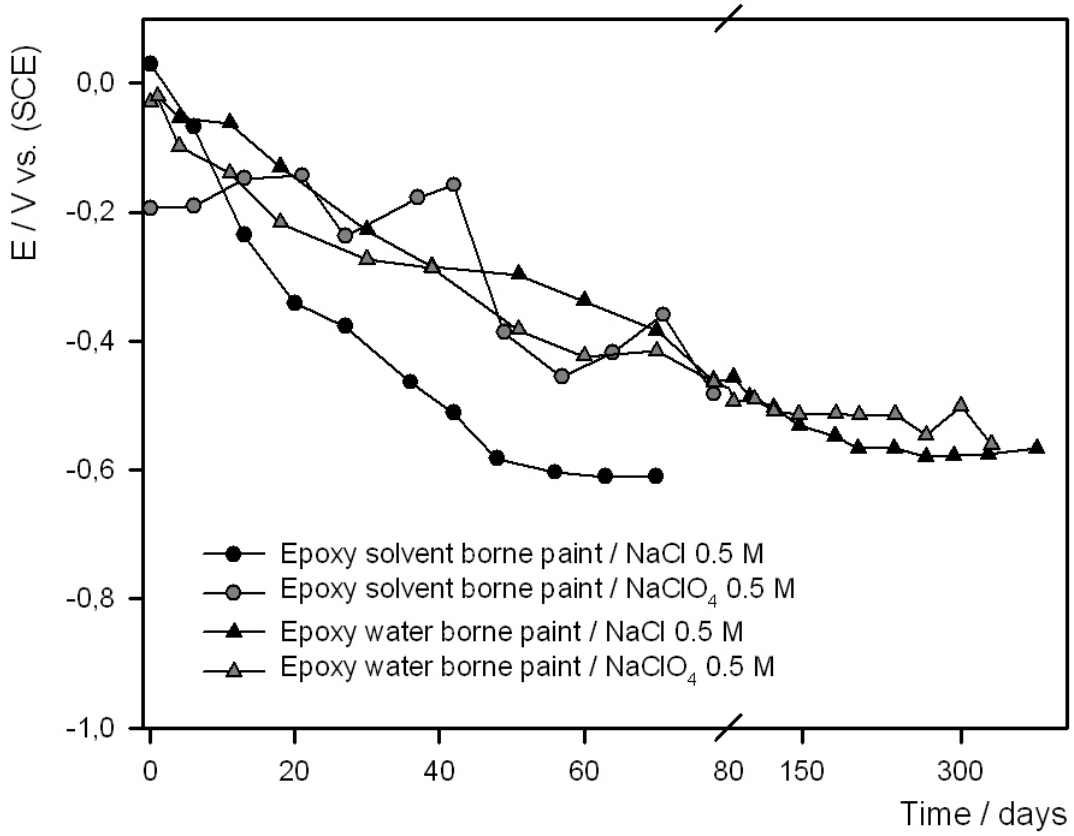
Corrosion potential of SAE 1010 steel in zinc basic benzoate in 0.5M $NaClO_4$ suspension

Figure 2



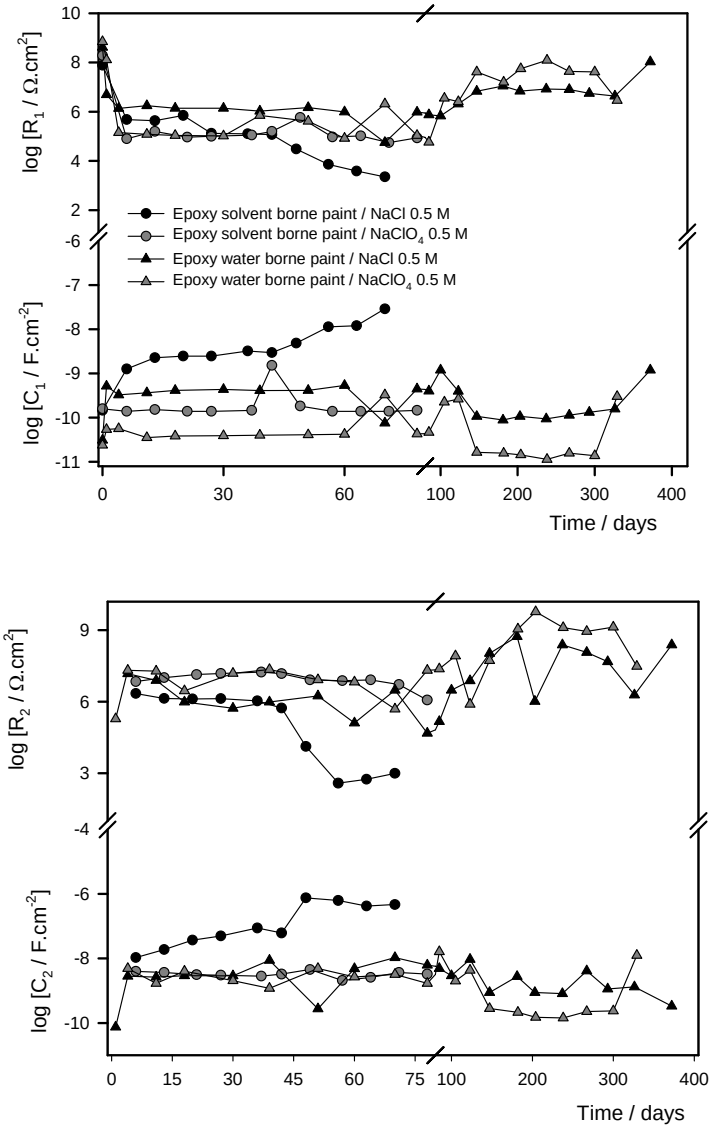
Tafel plots of the SAE 1010 steel electrode in zinc basic benzoate suspension in 0.5M $NaClO_4$, at different exposure times

Figure 3



Corrosion potential of coated steel in 0.5M $NaClO_4$ and 3% NaCl

Figure 4



Fitting parameters, Ri and Ci, for the different coatings, as a function of the immersion time in 0.5M $NaClO_4$ and 3% NaCl