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A multipurpose compound for protective coatings

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ABSTRACT

International regulations concerning the protection of both the environment and industrial workers have prompted paint manufacturers and end users to look for suitable replacements for traditional pigments.

One of the aims of this investigation was to study the inhibitive properties of ferric benzoate-based paints in simulated marine corrosion condition (3% NaCl solution). Anticorrosive paints containing ferric benzoate were formulated and their performance was evaluated by accelerated (salt fog chamber) and electrochemical (corrosion potential and ionic resistance) tests.

In addition, the action of ferric benzoate as a probable antifouling agent was studied through laboratory tests and marine exposure. Ferric benzoate hydrolyzes in seawater producing a pH decrease. In this sense, the effects of the pH and the anion benzoate dissolved in seawater and leached from an antifouling paint were evaluated on *Balanus amphitrite* nauplii. Although benzoate anion showed an intense narcotic effect on nauplii, the results of this research clearly demonstrated that the antifouling activity is due to the combined action of this anion and the pH decrease, i.e. there exists a synergic effect. Field trials confirmed laboratory assays; paints containing ferric benzoate were effective for inhibiting organism settlement and as corrosion of metal.

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1. Introduction

The anticorrosive properties of a given pigment depend on the nature of the anion and/or the cation. In this sense, the inhibitive properties of benzoate anion were known since 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 studied [17]. Sodium benzoate and benzoic acid were used as corrosion inhibitors not only for ferrous substrates but also for other metals [18–25]. The mechanism of the anticorrosive action of benzoates involves the anion adsorption onto the active sites of the metallic surface which provides an effective coverage and, consequently, corrosion rate decreases [16,26,27].

Soluble salts of benzoic acid were also employed in concrete [28,29] and in the field of paint technology. In this last case, they were used as soluble inhibitive additives in anticorrosive coatings [30–38].

The use of soluble compounds (benzoic acid, sodium benzoate, etc.) in anticorrosive paints is limited by the fact that their lixiviation, due to water that penetrates 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 lower-soluble metallic benzoates with certain cations (iron, zinc, aluminium, etc.) whose compounds are widely used in paint technology.

By the other hand, biofouling is the undesirable growth of plants and animals on man-made surfaces immersed in seawater. Biofouling costs the shipping industry approximately \$3 billion a year, and a significant portion of this cost is the increased fuel consumption needed to overcome hydrodynamic drag. Increased fuel consumption also contributes to pollution, global warming, and acid rain. The main compounds used worldwide to control fouling are the organotin antifoulants, such as tributyltin oxide (TBTO) included in antifouling paints, they are very effective on fouling prevention but have serious consequences to human health and

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environment [39,40]. They cause acute toxicity, bioaccumulation, decreased reproductive viability and imposex in oysters [41–44]. These harmful effects led to an EPA special review of organotin antifoulants, this act mandated restrictions on the use of tin. The ban of harmful substances in antifouling paints requires the development of new antifouling strategies and it is clear that alternatives should be as effective as conventional paints but of lower toxicity and environmental friendly.

In relation to the effect of benzoic acid on organisms, it inhibits the enzymes that control acetic acid metabolism and oxidative phosphorylation in bacteria and yeast, and acts on the cellular wall [45]. Additionally, Chet et al., Mitchell et al. and Chet and Mitchell [37,46,47] reported the use of benzoic acid to inhibit microbial film formation. Benzoic acid and sodium benzoate are classified in the United States as Generally Recognized as Safe (GRAS) and their use in food is permitted up to the maximum level of 0.1%, in Europe the maximum level allowed depends on the foods in which they are used [48].

From the point of view of corrosion prevention the aim of this paper is to study the inhibitive properties of lab-prepared ferric benzoate included in paint formulations. It is well known that this compound is easy to synthesize in the lab and raw materials used for its preparation are non-polluting and biodegradable.

Anticorrosive paints containing ferric benzoate were formulated and their performance was evaluated by accelerated (salt spray chamber) and electrochemical (corrosion potential and ionic resistance measurements) tests.

Additionally, antifouling properties of this compound were studied. It is well known that ferric benzoate hydrolyzes in seawater and produces a pH decrease. In this sense, the current study describes the effects of pH, ferric benzoate dissolved in seawater and leach from an antifouling paint on *Balanus amphitrite* nauplii. Also, field experiments with antifouling paints containing ferric benzoate were carried out.

2. Materials and methods

2.1. Corrosion

2.1.1. Paints composition, manufacture and application

Two epoxy-paints were formulated, one of the solvent-borne type (paint 1) and the other water-borne one (paint 2). The resin used to formulate epoxy solvent-borne paint was a bisphenol epoxy-polyamide resin (1:1, v/v) and the mixture xylene/methyl isobutyl ketone/butyl cellosolve (13/45/42%, w/w) was used as a solvent. It was decided to check the anticorrosive properties of the pigment employing solvent-borne paint because their behaviour has been well documented for many years. The PVC/CPVC (pigment volume concentration/critical pigment volume concentration) relationship was 0.8 as suggested elsewhere. The anticorrosive pigment load was 30% (v/v) of the total pigment content; the same value suggested when orthophosphates are employed as anticorrosive pigments [49,50]. Titanium dioxide, barium sulphate and talc were incorporated to complete the pigment formula. In order to achieve an acceptable dispersion degree, all the pigments were dispersed in the vehicle for 24 h by using a ball mill [51]. Paints formulations are shown in Table 1.

An epoxy resin based on a mix of bisphenol A and bisphenol F was chosen to formulate water-borne paints. The curing agent (hardener), which also acts as emulsifier, was a modified polyamidoamine with 50% of solids. The resin/hardener ratio was 100/120 (w/w). Neutral demineralized water was employed as solvent.

The anticorrosive pigment content was 30% of the total pigment content. Titanium dioxide, barium sulphate, talc and mica were

Table 1

Anticorrosive paints composition expressed as % by volume

Components	Paint 1	Paint 2
Ferric benzoate	13.6	3.5
Barium sulphate	12.5	2.2
Talc	12.5	2.1
Titanium dioxide	5.0	2.1
Zinc oxide	1.2	0.3
Mica	–	1.8
Epoxy resin/hardener resin (1/1 ratio)	26.6	–
Epoxy resin/hardener (1/1.2 ratio)	–	65.8
Additives	–	1.5
Solvents	28.6	20.7

incorporated to complete the pigment formula. Mica was added to the formulation due to its barrier properties and the ability to reduce the “flash rusting” degree [52]. The PVC value (20%) was chosen in order to enhance the coatings barrier effect. Water-borne paint composition is also shown in Table 1.

Water-borne paint was prepared in a high-speed disperser. Due to the relatively high viscosity of the hardener it was necessary to add, firstly, the water and then, the pigments in accordance with their increasing oil absorption index; mica was added at last to avoid the break-up of lamellar particles.

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

2.1.2. Study of paint anticorrosive performance through accelerated and electrochemical tests

A set of three panels, painted with each paint type, was placed in the salt spray chamber (ASTM B-117). Rusting (ASTM D-610) and blistering (ASTM D-714) degrees were evaluated during 4200 h of exposure. Wet adhesion was also determined according to a standard test (ASTM D 3359-method B).

Coatings on the steel panels were removed with suitable solvents after the exposure to the salt spray chamber. The protective layer morphology was studied by scanning electron microscopy (SEM) employing a PHILLIPS SEM 505 coupled with an EDAX OX PRIME 10 (energy-dispersed form) to determine the surface elemental composition. Corrosion products were identified by UV-visible diffuse reflectance spectroscopy with a GBC CINTR 40/UV-VISIBLE SPECTROMETER. Spectra were scanned, at 50 nm/min, in the 200–800 nm range.

The electrochemical cells employed to evaluate the anticorrosive performance of painted steel were constructed by delimiting 3 cm² circular zones on the painted surface. An acrylic tube (7.0 cm high) was placed on the specimen and filled with the electrolyte (0.5 M sodium perchlorate solution). The corrosion potential of coated steel was measured employing a calomel electrode (SCE) as reference and a high-impedance voltmeter. The resistance between the coated steel substrate and a platinum electrode was also measured employing an ATI Orion, model 170, conductivity meter, at 1000 Hz.

2.2. Fouling

2.2.1. Laboratory tests

Nauplii of the cosmopolitan barnacle *B. amphitrite* (Cirripedia, Balanidae) were taken using a plankton net (25 μm) at Club de Motonáutica (38°02'S–57°32'W, Mar del Plata, Argentina). These larvae were isolated under stereomicroscope and maintained in artificial seawater (ASTM D 1141/75) with aeration, pH 8.2, in a culture chamber at 20 ± 1 °C, 14 h of light and 10 h of dark.

Table 2
Antifouling paint composition expressed as % by volume

Ferric benzoate	28.5
ww rosin	29.0
Phenolic varnish	5.8
Solvent	36.7

The effects of pH and ferric benzoate aqueous extracts on larval survival were tested. Non-toxic solutions were prepared before each experiment using acetic acid, phosphoric acid and magnesium oxide in artificial seawater and pH was adjusted. Aqueous extracts of ferric benzoate were obtained from a saturated solution. Thirty nauplii actively swimming towards a light source were collected by a pipette, injected in small crystallizing vessels and exposed to 50 ml of different solutions ranged between pH 3 and 9. Observations were made under stereomicroscope during 30 min. The inability of nauplii to stay in the water column and the loss of phototactic reaction were scored as the toxic response.

Laboratory tests to evaluate the efficiency of a soluble matrix antifouling paint containing ferric benzoate as a pigment were carried out. Series of 8 cm × 16 cm acrylic tiles were painted and, after three coats of paint, final dry film thickness was 150 μm. Paint composition is presented in Table 2.

Series of plates were put in 1 l crystallizing vessels for 1–7 days and every day a leachate sample from the paint was obtained. Larvae were exposed to the solutions in order to evaluate the combined effect of both pH and benzoate anion. On the other hand, the effects of rosin and paint without ferric benzoate were also studied. All experiments were performed by triplicate and compared with controls without adding testing compounds.

To study the “refreshing effect”, larvae were removed from the test solutions, placed in vessels with artificial seawater and the recovery or non-recovery was estimated.

2.2.2. Field tests

Painted plates were vertically hung from the marinas at the Club de Motonáutica at 50 cm below water line. Unpainted acrylic panels and panels painted with a coating without ferric benzoate as pigment were used as controls. Tests were performed in three replicates.

3. Results and discussion

3.1. Corrosion

3.1.1. Salt spray chamber

Results obtained in the salt spray chamber revealed that ferric benzoate is a suitable anticorrosive pigment for paints. The solvent-borne epoxy paint (paint 1) showed a very good anticorrosive behaviour up to 2130 h of exposure (0.3% of the surface rusted, qualification 7). The best anticorrosive behaviour was obtained with the water-borne coating (paint 2), with a very good qualification (9) after 3000 h and a good one (7), 1000 h later (Table 3). This performance is highly satisfactory if it is compared with similar paints formulated with zinc phosphate. This best behaviour of the water-borne coating may be attributed to the binder adsorption on the steel surface and the inhibitive properties of ferric benzoate [53].

Except for the water-borne coating, which blistered after 1770 h, blistering was detected in the solvent-borne coating from early exposure times and did not change significantly during the whole test period. The blister surface density was low in all the cases (Table 3).

The wet adhesion of the solvent-based epoxy paint maintained high values (4–5 B) during the first 1800 h of exposure (Table 4); this fact could partially explain the very good anticorrosive behaviour of the paint. After this period, adhesion fell down significantly, but the steel substrate remained protected up to 3000 h. The water-based paint retained a high percentage of its original adhesion (4 B) up to 3500 h of exposure. As it was previously said substrate protection was satisfactory during 4000 h in the salt spray test. In every case once the adhesion to the substrate was lost, the protection was mainly due to the inhibitive action of ferric benzoate.

3.1.2. SEM and UV

After the exposure to the salt spray chamber the organic coating was removed with suitable solvents. Xylene was employed for softening the paint film which was finally removed with tetrahydrofuran (THF) and/or 1-methyl-2-pyrrolidone. The morphology of the protective layer formed beneath the paint films was observed by SEM. In all cases, the main constituents of the layer were non-expansive iron oxides or iron oxyhydroxides (Fig. 1a). These compounds were formed instead of ferric benzoate because of their lower solubility product constants. The main constituent of the layer was a crystalline iron oxide layer green under epoxy paints (Fig. 1b). It is thought that the lower coating permeability and the pigment inhibitive action, in both types of epoxy paints restrained the corrosion process and favoured the development of these crystalline oxides.

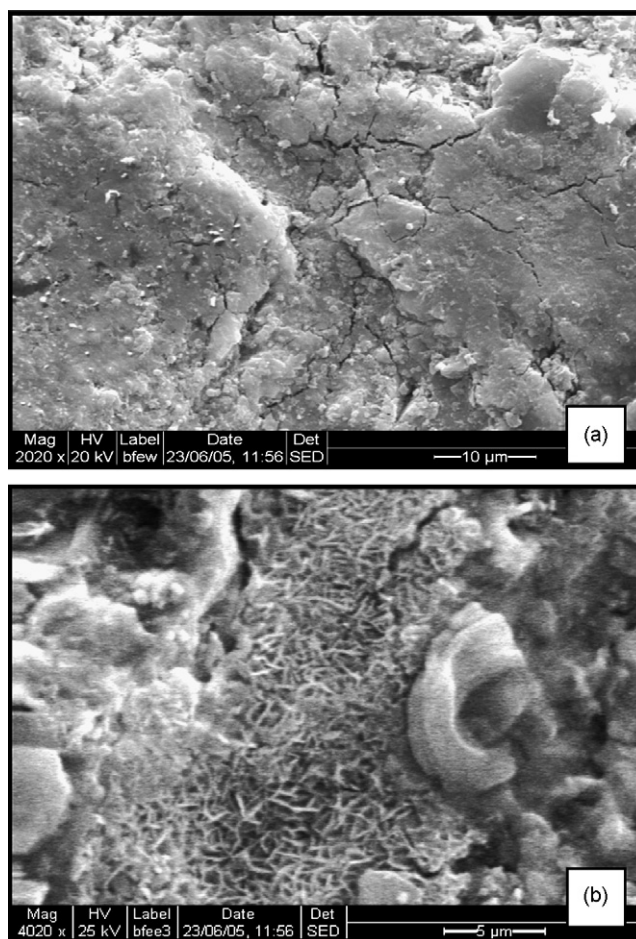


Fig. 1. SEM micrograph of the steel surface after removing the different coatings on panels exposed to the salt spray chamber (ASTM B 117): (a) water-borne epoxy coating (2000×) and (b) solvent-borne epoxy coating (4000×).

Table 3
Rusting (ASTM D 610) and blistering (ASTM D 714) degrees of the painted panels exposed to the salt spray chamber (ASTM B 117)

Time (h)	Paints				
	1		2		
	R	B	R	B	B
310	10	10	10	10	10
620	10	10	9	10	10
770	10	8F	9	10	10
980	10	8F	9	10	10
1150	9	8F	9	10	10
1400	9	6F	9	10	10
1580	9	6F	9	10	10
1770	8	6F	9	10	10
2130	7	6F	9	8F	8F
3100	–	–	9	8F	8F
3600	–	–	8	8F	8F
4000	–	–	7	8F	8F
4200	–	–	6	8F	8F

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: 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	

The diffuse reflectance UV–visible spectra are shown in Fig. 2. These UV–visible spectra were deconvoluted by adjusting the spectral curve with multiple Gaussian peaks with the software MICROCAL ORIGIN 6.0. The fitting accuracy was assessed by means of the parameter χ^2 , which was comprised between $1-4 \times 10^{-5}$. Once deconvolution was accomplished, bands assignment was done employing the wavelength chart provided by Larramona and Gutiérrez [54]. The protective layer formed at the steel/solvent-borne epoxy paint interface was complex in nature. The absorption bands at 380–432 nm (variable width) and 646 nm revealed the presence of goethite (α -FeOOH), while the absorption bands at 294 and 700 nm correspond to lepidocrocite (γ -FeOOH). The existence of hematite (α -Fe₂O₃) was evidenced by the set of absorption bands located at 220, 292, 346 and 455 nm [54–57]. Ferric basic benzoate was also formed during the corrosion process as it could be appreciated by the absorption band at 329 nm. The band at 273 nm, attributable to ferric benzoate was also perceived (Fig. 2).

The protective layer formed just beneath the water-borne coating basically contained the alpha compounds: α -FeOOH and α -Fe₂O₃, although these bands corresponding to γ -Fe₂O₃ could be detected. As in the previous cases, ferric benzoate was also formed and it is thought to be the primary corrosion product because many absorption bands of this compound appeared in the deconvoluted spectrum. Oxides and oxyhydroxides were formed as a consequence of a long exposure of painted specimens to corroding medium.

3.1.3. Electrochemical measurements

The values matched by the corrosion potential (E), Fig. 3, and the ionic resistance (R_i), Fig. 4, of coated steel were employed as a criterion of coating integrity [53,58,59]. Full protection of the steel substrate was achieved when the corrosion potential was higher than -0.100 V vs. standard calomel electrode (SCE) and the ionic resistance higher than $10^8 \Omega \text{ cm}^2$.

Table 4
Wet adhesion test (ASTM D 3359) of painted panels as a function of the exposure time to the salt spray chamber (ASTM B 117)

Time (h)	Paints					
	1	2	3	4	5	6
0	5B	5B	5B	5B	5B	5B
96	5B	5B	5B	5B	5B	5B
576	4B	4B	4B	4B	4B	4B
744	4B	4B	4B	4B	4B	4B
912	4B	4B	4B	4B	4B	4B
1176	4B	4B	4B	4B	4B	4B
1800	4B	4B	4B	4B	4B	4B
2400	3B	3B	3B	3B	3B	3B
3500	2B	2B	2B	2B	2B	2B
3800	–	–	–	–	–	–

Tape-test method B (ASTM D 3359/97)

Classification	5B	4B	3B	2B	1B	0B
Removed area (%)	0	<5	5–15	15–35	35–65	>65

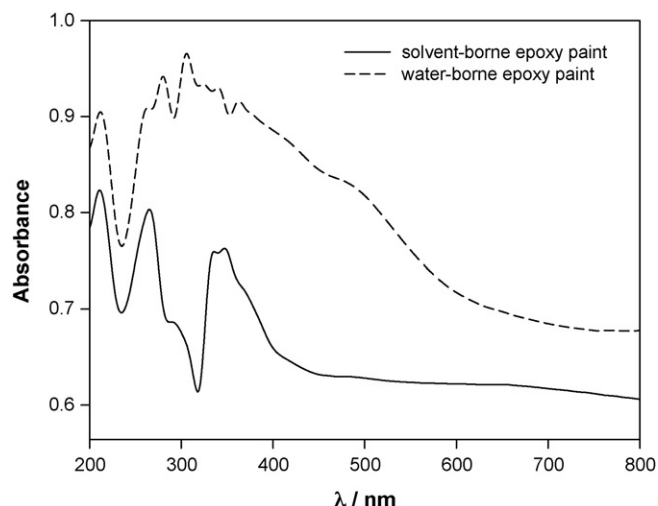


Fig. 2. UV-visible diffuse reflectance spectra of the steel surface of coated panels exposed to the salt spray, after paint removal by suitable solvents.

The examination of E_{corr} vs. time plots shows that both paints protect steel against corrosion for almost 2 years in the more aggressive condition, i.e. solution 3% NaCl.

The corrosion potential of steel coated with the solvent-borne paint (paint 1) fell down, after 90 weeks of testing, close to -0.600 V (Fig. 3), a typical value of painted steel undergoing corrosion. Previously, the potential was displaced to more positive values due to the inhibitive properties of ferric benzoate and the oscillatory behaviour of the corrosion potential was attributed to a repassivation process.

The E_{corr} of paint (paint 2), oscillated around -0.100 V during the whole test, indicating a good protection of the steel substrate (Fig. 3).

As it was said previously, both paints attained a good anticorrosive performance, but, from the environmental point of view, it is important to highlight the outstanding results obtained with the water-borne paint. The employment of this paint not only avoids the contamination with toxic and carcinogenic chromates but also volatile organic compounds (VOCs) emission is could be notably reduced.

After 90 weeks of immersion, all paints showed ionic resistance values higher than $10^6 \Omega \text{cm}^2$, pointing out the existence

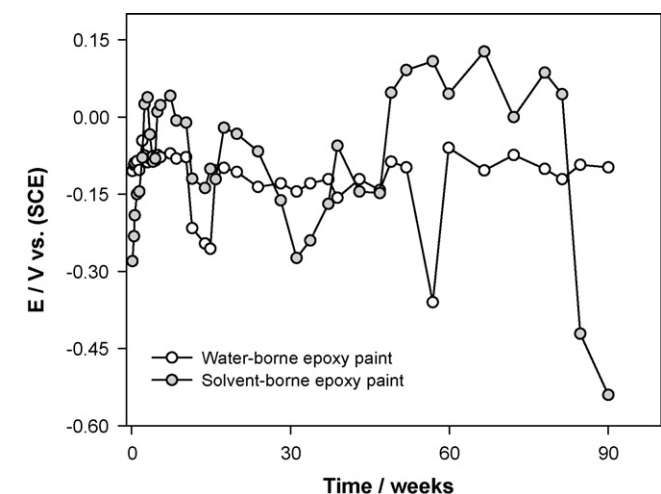


Fig. 3. Corrosion potential of coated steel in 3% NaCl.

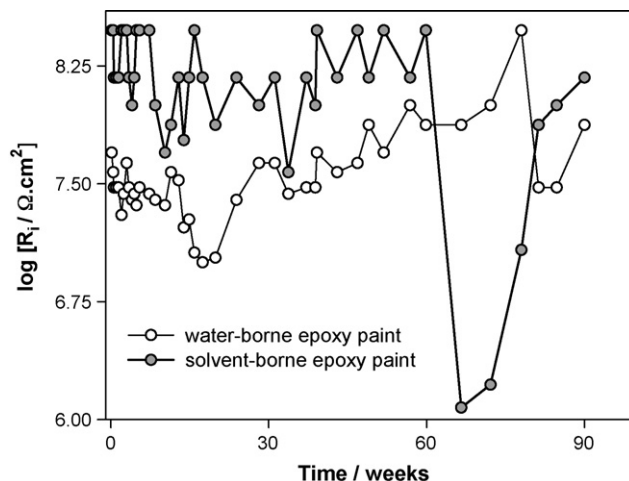


Fig. 4. Ionic resistance of coated steel in 3% NaCl.

of an acceptable barrier effect [58–60]. The solvent-borne paint developed important barrier properties ($R_i > 10^8 \Omega \text{cm}^2$) which were maintained during, at least, 60 weeks. After this period pores seemed to be opened and then blocked by corrosion products. It must be pointed out that solvent-borne paint developed, as a general rule, higher ionic resistance values than water-borne coating. However, both paints showed a good barrier effect (Fig. 4).

3.2. Fouling

3.2.1. Laboratory tests

In assays conducted in the laboratory, percentages of larval inactivity against pH of solutions were plotted (Fig. 5). Larval activity was dependent on the pH of the solutions. In those solutions below pH 6.5 and above pH 8.5 nauplii immediately immobilized its appendages and stopped its swimming movements so that the number could readily be counted at suitable time intervals. In contrast, in non-toxic solutions between pH 6.5 and 8.5 larvae swim actively and larval behaviour was normal. Vetere et al. [61] conducted a series of experiments aimed to study the action of sodium benzoate on *B. amphitrite*, they reported that all sodium benzoate solutions from 0.01 to 0.1 M maintained a constant pH (8.2) and

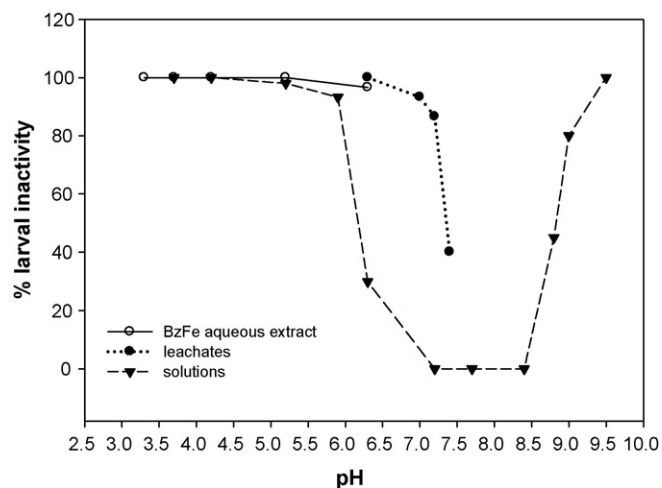


Fig. 5. Percentage of larval inactivity vs. pH. (○) Aqueous extract of BzFe; (●) leachates from paint; (▼) different pH solutions.

consequently the observed larval inactivity was due to benzoate anion. This effect was temporary because larvae recovered rapidly when they were transferred to fresh seawater.

The aqueous extract of ferric benzoate affected larval activity as a consequence of low pH values generated by the hydrolysis of this compound in seawater. In this experiment, larvae exposed to ferric benzoate solutions below pH 4 could not recover.

The pH values of solutions obtained from paints ranged between 6 and 7.5. Larval swimming movements were rapidly inhibited by exposure to leachates from ferric benzoate antifouling paints.

A comparison made between inhibitory effect of different pH solutions vs. leachates from paints on *B. amphitrite* larvae clearly demonstrated that leachates were more effective, i.e. the combination of narcotic effect of benzoate anion plus a pH decrease was stronger than the action of pH decrease only. A “critical point” at pH 6.3 could be observed, in non-toxic solutions larval inactivity was 30% while in ferric benzoate extracts and leachates from paints larval inactivity were 96.6% and 100%, respectively (Fig. 5).

Series of experiments carried out to estimate the effects of w/w rosin and other components of paint formulation (i.e. paint without ferric benzoate) showed that these compounds did not affect larval survival and activity. Antifouling paint formulations include solvents that can produce a biocidal effect due to a migration of organic solvent to the surface of the film. This effect is sometimes referred as “burst effect” and may cause some of the fouling inhibition; in this study we proved that solvent had no effect on larvae activity [62].

3.2.2. Field tests

Settlement assays carried out in the sea were in accordance with laboratory tests. After 2 months' exposure, paints containing ferric benzoate were effective in inhibiting barnacle settlement and also most of fouling organisms at Mar del Plata harbour. Two macroalgae species, *Enteromorpha intestinalis* and *Ectocarpus* sp., occurred in low densities on illuminated side of painted tiles. However, these algae had a weak bond to substrate and consequently were easily detached and sloughed off. In spite of this, paint films were not altered by algal detachment and maintained in good conditions. The paints significantly limited the strength of the joint between fouling and panel, making the bond so weak that it can be broken by the weight of the fouling or by the motion of the water. These results were similar to those expected for another type of paints like “fouling-release coatings” [43,63]. On the other hand, on control panels (acrylic panels and panels painted with a coating without ferric benzoate) fouling dominated by *B. amphitrite*, *Polydora ligni*, *Enteromorpha* and *Ectocarpus* was observed.

Nowadays, worldwide trends in antifouling technology are focused to mechanisms or compounds identification by which fouling organisms are repelled or inhibited. In nature some organisms may be heavily fouled on their surfaces while others are rarely epiphytized, indicating the potential antifouling mechanisms [64–66]. Some mechanisms may involve dissolution of adhesives by enzymatic action, interference in metabolic processes of the organisms, inhibition of the attachment, growth or metamorphosis, modification of surface of the organisms as repellents or biocides [67–70]. However, identification and laboratory isolation of natural-origin active compounds may be difficult and sometimes expensive. In contrast, the use of compounds that can be synthesized from common and cheap raw materials in the lab allows a rapid evaluation of its properties. In this sense, ferric benzoate is a compound easy to synthesize in the lab [71], non-polluting, biodegradable, and showed a good antifouling performance.

4. Final considerations

Accelerated tests showed that ferric benzoate performed satisfactorily with different binders and its anticorrosive behaviour is equal or even better than zinc phosphate.

UV-visible diffuse reflectance spectroscopy proved to be a very useful tool to investigate the metallic surface once the coating has been removed.

Electrochemical tests showed that the pigment action is the main but not the only responsible of the protection afforded by the painting systems. The barrier properties also contributed to the anticorrosive protection.

It is possible to formulate efficient water-borne anticorrosive paints and is itself a desired result from a point of view of the environmental care.

On the other hand, the ferric benzoate antifouling properties have been demonstrated in this research work. The hydrolysis of ferric benzoate produces not only a decrease of pH but also an increase in soluble benzoate (and/or benzoic acid) concentration. In the paint/seawater interface the pH value is about 4. It could be concluded that the sum of the two factors (pH + benzoate anion) is greater than their individual effects.

Finally, further research is needed to study ferric benzoate behaviour on long-term assays in order to include it in a complete painting scheme, i.e. anticorrosive and antifouling coatings. In this sense, incompatibility problems between bottom and top coatings could be solved.

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