

Antifouling Paints with Zinc “Tannate”

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During the past decade, the necessity of new ecofriendly antifouling pigments was established. Among these new pigments, special attention should be paid to tannin and its derivatives. Tannins are synthesized by plants as part of their defense mechanism against the attack of pathogens. The objective of this work was to study the antifouling efficiency of paints containing zinc “tannate” in artificial seawater. The zinc “tannate” was precipitated at pH 4 and pH 8. Insoluble and soluble matrix antifouling paints, with different plasticizers, were formulated and tannins leached from the paints immersed in artificial seawater were determined by the Folin–Denis assay for polyphenols. The antifouling action of paints was assessed in a natural seawater environment. The results showed that the leaching rate of tannin from insoluble matrix paint decreases, reaching a constant value after 25 days of immersion. In the case of the soluble matrix paints, a lesser amount of tannin was leached, depending on the tannin and the plasticizer employed. The results in a natural sea environment are dependent on the matrix and the plasticizer employed.

Introduction

The formation and growth of marine fouling on ship hulls leads to important economic losses, because of the increase in fuel consumption (to maintain cruising speed) and the damage of the metal substrate by corrosion. Historically, different types of coatings have been used to avoid biofouling settlement. The materials used as coatings have varied from metallic copper sheets to organic coatings with biocides.^{1,2}

Antifouling coatings owe their behavior to the release of toxic substances to the marine environment. This leaching process produces a high concentration of antifouling compounds in the seawater film in close contact with the painted surface, thereby repelling or killing fouling organisms when they try to attach to the surface. The performance of an antifouling paint is dependent on the biocide and the way the biocide is leached from the film. The leaching rate is normally determined in laboratory tests, using painted panels that are immersed in artificial seawater (ASW).³ Commonly, two main types of binders are employed: insoluble and soluble ones. Insoluble matrix paints use high-molecular-mass binders such as epoxies, vinyls, acrylics, or chlorinated rubber. Since these binders are not soluble, as the antifouling agents are released, a honeycomb structure is left behind and seawater must diffuse through the pores to dissolve the next toxicant particle.⁴ Pores are normally plugged with particulate material, and the release of toxicants is restrained. Some of the biocides employed with insoluble binders were arsenic–copper compounds and compounds such as triphenyl lead (TPL), tributyl tin (TBT), triphenyl tin (TPT), etc.^{1,2,4–6} Soluble matrix paints, on the other hand, use binders such as rosin and its derivatives with antifouling pigments such as copper or zinc oxide.^{4,7} Because the rosin dissolution rate could be high, it is usually blended with co-binders or plasticizers to obtain suitable paint solubility and good mechanical properties. These paints do not ensure protection for more than 12–15 months, because of the constant erosion that they undergo during their service life.^{1,7}

Most of the aforementioned biocides are no longer used, because of their high toxicity (TPL, TBT, TPT); however, others, such as copper oxide, are still commercially available, despite the uncertainties on their environmental impact.^{1,2,6,8–12}

Modern antifouling coatings must not only prevent fouling settlement but also fulfill regulations imposed by the International Marine Organization (IMO) to stop environmental damage. IMO has forbidden the production of TBT-antifouling paints since January 1, 2003, and the employment of organotin based paints has been forbidden since January 1, 2008.^{1,4} These regulations have created, during the past decade, the necessity of developing new antifouling pigments that are safe for the environment and humans. Among these new pigments, special attention must be paid to tannins and their derivatives. Tannins are synthesized by plants as part of their defense mechanism against pathogens attack, especially microorganisms and fungi.^{13,14}

Tannins are polyphenolic compounds and may be classified as hydrolyzable and nonhydrolyzable or condensed. Hydrolyzable tannins usually possess a D-glucose core with the hydroxyl groups partially or completely esterified with phenolic groups (gallic acid in gallotannins and ellagic acid in ellagitannins). Condensed tannins, which are also known as proanthocyanidins, are polymers with flavonoid units that cannot be cleaved upon hydrolysis. As a consequence of their chemical structure, they flocculate with divalent or trivalent cations and, in some cases, with monovalent cations, forming the corresponding “tannates”. The ability of condensed tannins and “tannates” to react with proteins and other macromolecules explains their antiseptic capacity and its use in the leather industry.¹⁵

Recently, the antifouling activity of a soluble matrix paint with cupric “tannate” as a biocide agent has been reported in laboratory and field tests. No settlement of “macrofouling” organisms occurred after 12 months of immersion in a natural environment.¹⁶ Another tannin-based pigment, aluminum “tannate”, showed results similar to that of cupric “tannate” in laboratory tests. These results suggest that tannins are potentially important as antifouling pigments.¹⁷

Zinc oxide was used in antifouling paints; however, because it is less toxic than cuprous oxide, poorer activity was obtained.^{4,7,9} However, the Zn²⁺ cation can coagulate tannins

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and, because of its size and charge, the zinc “tannate” obtained has suitable solubility.

The objective of this research work was to study the dissolution of quebracho (*Schinopsis bolonsae*) tannin in ASW from paints with zinc “tannate” as biocide and to evaluate their performance in natural seawater. The antifouling compound was precipitated at pH 4 and 8 and the fraction of leached tannin was determined by spectrophotometry using the Folin–Denis reagent (FDr).^{18–21}

Materials and Methods

Precipitation Curves. Zinc “tannate” precipitation was performed at pH 4 and pH 8. Precipitation curves allowed one to study the influence of pH on the solubility of the “tannates”, as well as to optimize the variables for precipitating quebracho tannin with the Zn^{2+} cation. To obtain these curves, 3.000 g of quebracho tannin (UNITAN) was dispersed in distilled water in four different volumetric flasks for 10 min and then 0.50, 1.25, 2.50, and 5.00 mL of 0.65 M zinc nitrate was added to the suspensions in the respective flasks. Distilled water was added to complete a total volume of 25.0 mL. After the addition of zinc nitrate, the suspensions were stirred for 5 min and the pH adjusted to 4.0 or 8.0, using 0.5 M NaOH. The suspensions were stirred for 1 h, the pH was adjusted again, and the systems were allowed to settle down for 24 h to accomplish complete flocculation. Finally, an additional pH adjustment was made under stirring and then the solids were separated by centrifuging and dried at 50 ± 5 °C, until constant weight.

Preparation of Zinc “Tannate”. Zinc “tannate” was prepared, taking into account the suitable ratio of reactants according to the results obtained from the precipitation curve experiments.

To obtain zinc “tannate” at pH 4 (TZn4), 350.0 g of quebracho tannin was dispersed in 2.8 L of distilled water and 146 mL of 0.65 M zinc nitrate was added under constant stirring. Immediately, the pH was adjusted to 4.0 using a 0.5 M sodium hydroxide and the suspension was stirred for 1 h. In the case of zinc “tannate” obtained at pH 8 (TZn8), the procedure was similar but 210.0 g of tannin was dispersed in 1.6 L of distilled water and 175 mL of 0.65 M zinc nitrate was added; the pH value was adjusted to 8 with 0.5 M NaOH and the suspension stirred for 1 h. In both cases, the suspension was kept without stirring overnight and pH was adjusted once more before separating the solids from the supernatants. The solids were washed with distilled water, centrifuged, dried at room temperature under an air current and, finally, in a stove at 50 ± 5 °C.

Characterization of Zinc “Tannates”. The amount of water in zinc “tannates” was determined by indirect gravimetry heating the solids at 105 ± 5 °C. Zinc was determined as zinc oxide by a gravimetric procedure that was used to heat the solids at 800–900 °C. The amount of tannin was calculated as the difference between both values.

The solubility of the “tannates” in ASW (ASTM D 1141) was determined by dispersing 4.000 g of each zinc “tannate” in 200 mL of ASW at 20 ± 2 °C and stirring for 24 h. The solid was separated by filtration; the amounts of tannins, as total polyphenols (TP), and the Zn^{2+} cation were determined in the filtrate. The tannins concentration was obtained spectrophotometrically at 750 nm using the FDr^{16–18} (the band is due to the tannin complexes of molybdate¹⁹). Ultraviolet-visible light (UV–vis) spectra of zinc “tannates” were also obtained in aqueous media with and without FDr. The concentration of Zn^{2+} cation was determined by atomic absorption spectroscopy (AAS).

Table 1. Main Components of Paints (Expressed as a Percentage of Solids by Volume)

paint	Composition (% by volume)						
	Biocide		chalk	vinyl resin	WW rosin	chlorinated rubber	plasticizer
TZn4	TZn8						
1	73.6			15.5	4.9		5.2
2	34.0		8.6		32.3	16.9	6.6
3		34.0	8.6		32.3	16.9	6.6
4	27.0		18.1		45.1		9.8
5		27.0	18.1		45.1		9.8

Formulation and Preparation of Antifouling Paints. Paint 1 was formulated with an insoluble binder; in this case, only the most soluble pigment (TZn4) was used, because the concentration of the active pigment should be high to ensure continuous contact among the particles and minimize the problems of pore blocking. Pores are clogged by the reaction products between tannins and ASW and by particulate matter that is present in a sea environment.

The vinyl resin employed as film forming material (86.0% vinyl chloride, 14.0% vinyl acetate) was mixed with WW rosin (Cicloquímica) in low proportion, to avoid pore blocking. The vinyl resin:rosin ratio was 4:1 by weight. Tricresyl phosphate was used as a plasticizer, at a vinyl resin:plasticizer ratio of 4:1 (by weight). The composition of the paints is given in Table 1.

The vehicle was prepared in a high-speed disperser: vinyl resin was dissolved in a mixture of methyl isobutyl ketone (MIK)/xylene at a 1:1 ratio (by weight). The plasticizer then was added to the mixture. WW rosin was dissolved in xylene in a similar way. The pigments (biocide and chalk) were dispersed in a 3.3 L jar with a fraction of the solvent (4:1 xylene/white spirit) for 24 h. Both vehicles and pine oil were added to the dispersed pigments, and dispersion was continued for another 24 h. After this, 2% (by weight) of castor oil gel was dispersed into the paint. Castor oil gel (15% by weight) was previously activated with xylene, using a shear stress at 40–45 °C, until a stable colloidal structure was obtained.

Soluble matrix paints (paints 2 and 3; see Table 1) were also prepared, using WW rosin as film-forming material. Chlorinated rubber was added as a co-binder in a WW rosin:chlorinated rubber ratio of 1.9:1 (by volume) (see Table 1). The plasticizer was chlorinated paraffin with 42% chloride; the ratio of chlorinated rubber:plasticizer was 2.6:1 (by volume). WW rosin was dissolved in xylene, employing the high-speed disperser; chlorinated rubber was also dispersed in xylene with the plasticizer. The pigments were dispersed in a fraction of the solvent in a ball mill jar. Then, both vehicles and pine oil (0.5% by weight of total paint formula) were incorporated into the jar with the pigments and dispersed for 24 h. Finally, castor oil gel was added in a load of 2% (by weight) of the total paint weight.

The composition of paints 4 and 5 was similar to that of paints 2 and 3, but no cobinder was used. Oleic acid was employed as a plasticizer, instead of chlorinated paraffin.

Determination of Leached Polyphenols, as a Function of Time. Paints were applied on 8 cm × 8 cm sandblasted acrylic panels. Three or four coatings of paints were applied and allowed to dry for 24 h between each application. The total dried film thickness was 120 ± 5 μm. No more than 48 h elapsed before immersion of the painted panels in ASW. Painted panels were submerged in plastic containers with 250 mL of ASW, and the systems were stirred for 3 h each day. The leached “tannate” was determined on a 2-mL aliquot, using the FDr. The original level of the liquid in the containers was restored by adding fresh ASW.

Table 2. Settlement Degree Assessment

settlement degree	efficiency (%)
0, no settlement	100
1, little	80
2, limited	60
3, common	40
4, abundant	20
5, completely covered	0

Solutions were measured 20 min after preparation to ensure that the reaction was completed.

Essays in Natural Seawater. Sandblasted acrylic panels (8 cm × 12 cm) were painted as done previously, to a total dry film thickness of $180 \pm 5 \mu\text{m}$. No more than 48 h elapsed before the painted panels were immersed in a natural sea environment (NSE) at Mar del Plata harbor ($38^{\circ}08'17''\text{S}$ – $57^{\circ}31'18''\text{W}$) in Argentina.²²

Panels were immersed 50–60 cm deep, and the degree of fouling settlement was evaluated monthly, according to the scale presented in Table 2.^{2,23} The values assigned to the settlement degree are dependent in an important way on the observer. However, the results can be compared qualitatively. The behavior of an antifouling paint is considered satisfactory if its qualification is 1 or lower. For settlement degree 0 (no settlement), only bacteria and diatoms could be settled on the panel under study; for settlement degree 1 (little settlement), barnacles and serpulidae could be included. Other organisms such as ascidians, bryozoans, algae, and polychaetes,^{24–27} that are frequently observed in Mar del Plata harbor, could be attached onto the panels. Distances of <1 cm from the edge of the panels were not considered. Uncoated panels were used as control and immersed under the same conditions as the painted ones.

Results and Discussion

The analysis of the precipitation curves revealed that the flocculation of tannins at pH 4 could be achieved with lower amounts of Zn^{2+} cation. The fraction of precipitated tannin did not increase significantly when the amount of zinc nitrate exceeded 60 mg per 3.000 g of tannin dispersed in water (see Figure 1). When the pH was increased to 8, more tannin was precipitated. The mass of tannin bonded to Zn^{2+} cation increased up to the addition of 300 mg of zinc nitrate per 3.000 g of tannin. This behavior could be explained by the C–OH groups being ionized in a higher degree at pH 8 so, more Zn^{2+} cations were

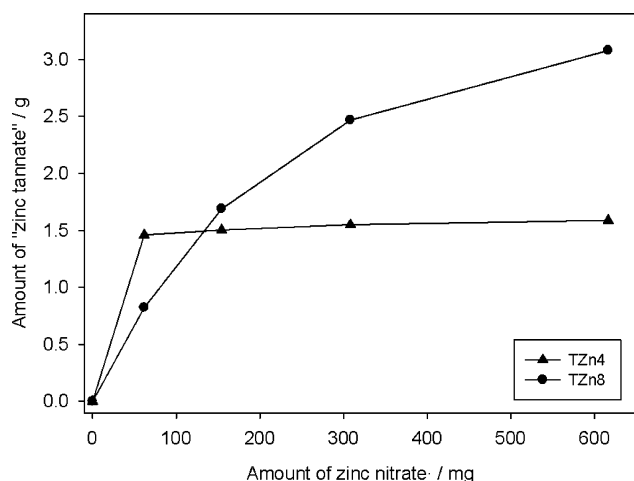


Figure 1. Amount of zinc “tannate” precipitated, as a function of the amount of zinc nitrate added.

Table 3. Composition and Properties of “Zinc Tannates” TZn4 and TZn8

pigment	Solution, in Artificial Seawater		solids density (g/cm ³)
	total polyphenoles, TP (ppm)	Zn ²⁺ (ppm)	
TZn4	3332.0	27.0	1.43
TZn8	323.2	160.0	1.52

combined with the tannin. These results suggested that 20–60 mg of $\text{Zn}(\text{NO}_3)_2$ per gram of tannin is sufficient to effectively precipitate zinc “tannate” at pH 4, while 100–120 mg would be necessary at pH 8.

Chemical analysis of the TZn4 and TZn8 solids showed that the first one contained 86.70% tannin and 0.53% zinc, with the remainder (12.77%) being water; the other one had 71.84% tannin and 6.18% zinc, with the rest (11.98%) being water. Table 3 shows that the concentration of TP in the saturated solution of TZn4 in ASW was higher than that of TZn8 which, in comparison, had the higher Zn^{2+} cation content. This fact may be due to the highest zinc content being observed in TZn8. Probably, the Zn^{2+} cation bonded to quebracho tannin in TZn8 was partially replaced by smaller bivalent cations that are present in seawater, incorporating zinc into the solution.

The spectra in Figure 2 confirmed that the saturated solution of TZn4 contained a higher amount of tannin, because the absorbance of the broad absorption band at 750 nm was higher. This band was also used to quantify TP leached from the tested antifouling paints. The other peak, close to 300 nm, corresponds to the delocalized π -electrons in the benzene structure present in tannins.

The results of the leaching experiments are shown in Figures 3 and 4. After the initial stage, where a high amount of tannin was leached from paint 1 (insoluble matrix), a decrease in the leaching rate was observed, reaching a stationary state after 25 days of immersion. It is thought that the leaching rate decreases as pores are clogged,^{1,4} because the leached tannin is coagulated by small cations such as Ca^{2+} . Paint 2, with the same antifouling pigment but with different resin (soluble matrix), leached lesser amounts of tannin; its leaching rate decreased after 15 days. Paint 3 (with TZn8) kept the leaching rate in low and exhibited constant values almost from the beginning of the essay until 57 days of exposure (Figure 3). In these three cases, the amount of tannin leached after a month of immersion was <2 mg/day. The leaching rate is shown in Figure 4.

The amount of tannin leached from paints 4 and 5 was much less than that from paint 1; however, in both cases, it was higher

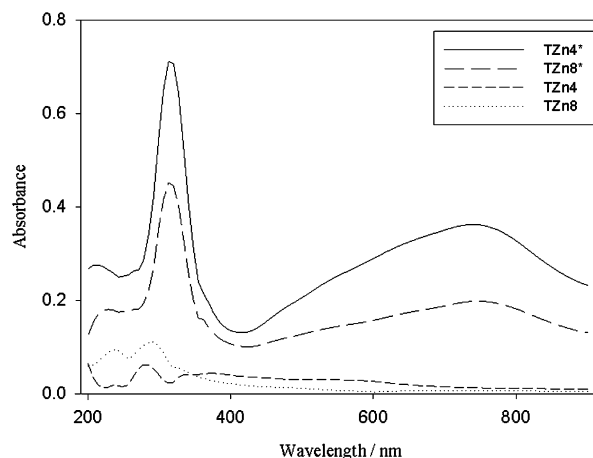


Figure 2. UV–vis spectra of zinc “tannates” in aqueous solution with (denoted by an asterisk, *) and without the Folin–Denis reagent (FDR).

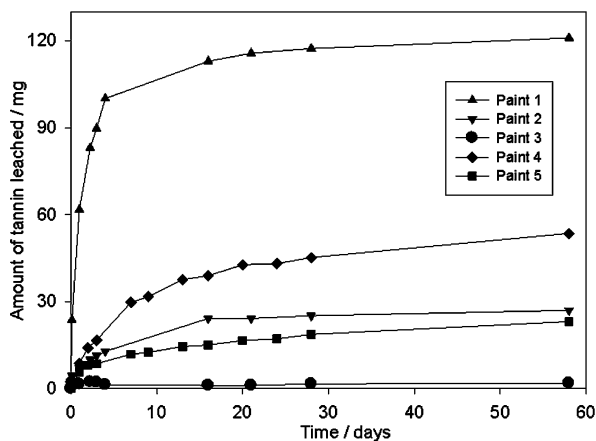


Figure 3. Amount of tannin leached from the paint films.

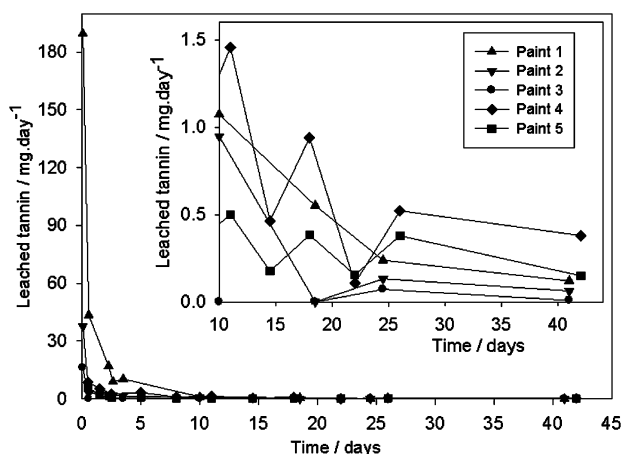


Figure 4. Rate of tannin leaching from the paint films.

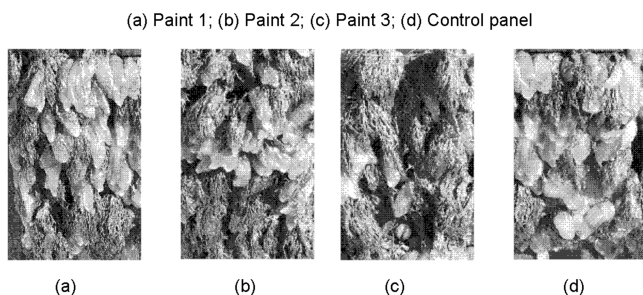


Figure 5. Paints after 2 months of immersion in natural seawater: (a) paint 1, (b) paint 2, (c) paint 3, and (d) control panel.

than the corresponding paints formulated with WW rosin + chlorinated rubber binders. The leaching rate was almost constant during the entire essay, and, after 57 days of immersion, the value was ~ 5 mg/day. These results show that the leaching rate is highly dependent on the resin and is less dependent on the antifouling compound used to formulate the paint.

The amount of tannin leached by soluble matrix paints (paints 2–5) was lower, which may be due to the constant solubilization of the paint film by seawater. Differences in the amount of zinc “tannate” leached from these paints can be attributed to the different solubility of TZn4 and TZn8 (see Table 2).

The observations of the painted panels immersed in NSE are shown in Figures 5a and 6.

Paints 1, 2, and 3 (Figures 5a, 5b, and 5c, respectively) showed a settlement degree of 5 (panel completely covered, efficiency 0%; see Table 2) after 2 months of immersion in

(a) Paint 4; (b) Paint 5

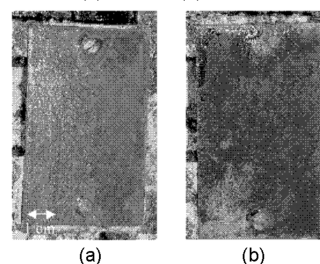


Figure 6. Paints after 4 months of immersion in natural seawater: (a) paint 4 and (b) paint 5.

NSE, with the main fouling organisms being ascidians and bryozoans. These results were similar to that of the blank (see Figure 5d).

The paints based on WW rosin and oleic acid (paints 4 and 5) showed better antifouling behavior and the higher leaching rate at the end of the test. After four months of immersion, the settlement degree was 0; however, the paints showed deterioration, with paint 4 being less deteriorated than paint 5 (see Figures 6a and 6b, respectively). After 6 months, deterioration became important; almost 90% of the paint was washed off from the panels. However, although the blank was completely covered by ascidians, bryozoans, barnacles, and algae, panels 4 and 5 were not fouled.

In outdoor tests, no differences were noticed between paints formulated with the same film-forming material but different zinc “tannate” contents, except in the degree of deterioration of paints 4 and 5. Paint 5 was almost completely dissolved after 6 months of immersion in NSE.

Paints 2 and 5, with different ligands and different antifouling pigment, have similar leaching rates (Figure 3) but different antifouling actions. Paint 2 lasted almost 2 months without fouling, whereas paint 5 lasted 6 months. This may be due to the matrix of the paints; paint 2 has an insoluble co-ligand (chlorinated rubber), but the ligands in paint 5 are soluble. Therefore, in the last case, the paint could be eroded by water currents that, at the same time, are removing the fouling organisms attached to the surface. In the case of paint 2, a honeycomb structure remains and the surface became rougher as the co-ligand is dissolved in NSE. The higher roughness in paint 2 facilitated the settlement of the fouling organisms, thus reducing the lifetime of the coating.²⁸ For the sake of comparison, it must be said that the lifetime of the commercial antifouling paints was in the range of 6–18 months. An experimental paint that contained cupric “tannate” was claimed to last 1 year.^{1,7,16} However, this last paint contained copper as the main antifouling compound, and this metal was shown to contaminate the environment.⁸ Tin-free conventional paints also contain copper, as well as boosters and biocides, such as isothiazolones, which make the comparison difficult. The toxicity of these boosters is not completely known.^{8,9,29,30}

Conclusions

The leaching of tannin in artificial seawater, from paints with zinc “tannates”, could be obtained by determining the total polyphenols (TP). The behaviors of the precipitated “tannates” were different. The one prepared at the lower pH (4) had a leaching rate that was twice that of the “tannate” obtained at pH 8. This feature was observed despite the film forming material that was employed in paint formulation.

In natural seawater environments, paints formulated with WW rosin and oleic acid lasted longer time (6 months) without

fouling than paints with WW rosin and vinyl resin or WW rosin and chlorinated rubber. In this last case, paints lasted equally long in natural seawater (2 months), regardless of the pH used to obtain zinc "tannate" and the leaching rate obtained in the laboratory. This fact suggested that the binders regulate the behavior of the paints.

In the case of WW rosin and oleic acid, differences of the coating erosion were noticed; almost no paint pigmented with TZn8 remained on the panel after 6 months of immersion.

It was also observed that paints with the same leaching rate inhibited fouling settlement in a different way in a sea environment. This fact could be explained by taking the different paint matrixes into consideration.

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