

Article

Assessment of zinc salicylate as antifouling product for marine coatings

Natalia Bellotti, and Roberto Romagnoli

Ind. Eng. Chem. Res., **Just Accepted Manuscript** • DOI: 10.1021/ie5015734 • Publication Date (Web): 30 Aug 2014

Downloaded from <http://pubs.acs.org> on September 8, 2014

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



Assessment of zinc salicylate as antifouling product for marine coatings

Natalia Bellotti^{}, Roberto Romagnoli*

CIDEPINT - Centro de Investigación y Desarrollo en Tecnología de Pinturas(CIC-CONICET) Calle 52 e/ 121 y 122. (B1900AYB) La Plata. Argentina.

KEYWORDS: Zinc salicylate, antifouling coatings, biofouling, biocide, leaching rate.

ABSTRACT

The present research deals with the assessment of a new bioactive product obtained from salicylic acid, zinc salicylate (ZnSal), to be employed in antifouling coatings.

ZnSal was obtained in the laboratory and the procedure to precipitate it was described. Preliminary assays were carried out in the laboratory to assess its potential use in an antifouling formulation. The bioactivity of ZnSal was assessed by means of the *Artemia* larvae test. In a second stage soluble matrix paints were prepared with two different binders: rosin / oleic acid and rosin / styrene-acrylate copolymer. Previous to the immersion in natural environments, the coatings leaching rate in artificial sea water was monitored. Finally, the antifouling efficiency of experimental coatings was evaluated at Mar del Plata harbor, in Argentina. The coating with ZnSal and rosin / oleic acid binder proved to have an acceptable efficiency for more than twelve months.

1. INTRODUCTION

The colonization of hard substrates immersed in natural waters by a wide variety of marine organisms (algae, barnacles, mussels, polychaetes, ascidians, bryozoans, etc.) is commonly referred as “biofouling”. Biofouling causes increased fuel consumption in vessels, due to increased hull friction with water¹; metallic corrosion^{2,3}; pipes and filtration systems blockage⁴; scale formation in water cooling systems; increasing in weight of off-shore sea platforms⁵; etc. Therefore, considering the unfavorable consequences listed above and the economic losses that they produce, the employment of adequate methodologies to prevent biofouling are mandatory^{5,6}.

Antifouling (AF) coatings are commonly employed to prevent fouling settlement. Frequently, they are formulated with a self-polishing copolymer and one or more antifouling agents (biocides), such as Cu_2O and/or organic compounds (Irgarol 1051, Diuron, Seanine, etc.). They may contain ZnO to improve the coating performance⁶. Soluble matrix AF coatings containing the same biocides but with rosin as the binder are also commercialized^{6,7}. These coatings dissolve in sea water and the protection did not last more than 12-18 months, because of the constant erosion that they undergo during their service life^{8,9}. At present, there is a great interest on replacing currently biocides used by others more compatible with the environment^{10,11,12}. In this sense, this research was focused on the assessment of ZnSal as an alternative AF agent. Taking into account that zinc is less toxic than copper¹³, the resulting coating would be more eco-friendly than those formulated with Cu_2O .

Some salts of organic acids have been employed as eco-friendly antifouling agents and they may be easily synthesized in the laboratory^{14,15,16}. Particularly, ferric benzoate proved to be effective in inhibiting barnacle and most fouling organisms

1
2
3 settlement during 2 month at Mar del Plata harbor¹⁵. On this basis, it was decided to use
4 ZnSal as AF agent. Salicylate is found ubiquitously in plants and has been used for
5 medicinal purposes since ancient times because of its antibacterial activity¹⁷. Zinc
6 compounds, as zinc oxide, have been used in antifouling paints to increase their
7 efficiency^{6,9}.
8

9
10
11
12
13
14
15 In the first place, the aim of this research was to synthesize ZnSal as potential
16 antifouling agent. Afterards, preliminary screening was carried out in the laboratory to
17 assess its bioactivity for possible application in the of AF coatings. The tests with
18 *Artemia* nauplii have the advantage of their rapidity and low cost as well as a good
19 predictive potential; as a consequence, they constitute a valid alternative to tests with
20 other crustacean like barnacles (*Balanus Amphitrite*)^{12,18,19}. Finaly, AF coatings with a
21 soluble matrix and ZnSal were formulated. The leaching rate these coatings in artificial
22 sea water (ASW) was monitored periodically. Their biocidal activity was assessed in
23 natural sea water (NSW), at Mar del Plata harbor (38°08'17''S-57°31'18''W), and
24 qualified according to ASTM D 3623 – 78a and ASTM D6990-05^{20,21}. AF coating with
25 rosin / oleic binder and pigmented with ZnSal proved to be efficient against fouling
26 settlement during one year.
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41

42 2. MATERIALS AND METHODS

43 2.1 Salicylic salt abstention and characterization

44
45
46
47
48 ZnSal was synthesized in the laboratory after studying the solution / precipitate
49 equilibrium, as a function of the pH, in the sodium salicylate / zinc nitrate system. In
50 order to obtain the precipitation curve of the ZnSal a solution containing: 75 mL of
51 salicylic acid 0.01M, 5 mL of zinc nitrate 0.05M and 5mL of hydrochloric acid 0.05M
52 was prepared, placed in a beaker and titrated with 0.05 M sodium. The pH of the
53
54
55
56
57
58
59
60

1
2
3 solution was measured with a glass electrode. Sodium hydroxide solution was
4
5 standardized using potassium acid phthalate as primary pattern.
6
7

8 The synthesis of ZnSal was started from ammonium salicylate due to the low
9
10 solubility of salicylic acid in water (1.8 g / L at 20 °C) which would limit the amount of
11
12 ZnSal to be obtained. Therefore, 700 mL of 0.9 M ammonium salicylate was placed in a
13
14 container and 800 mL of 0.4 M zinc nitrate were added drop wise under continuous
15
16 stirring at room temperature. The precipitation pH must be adjusted to 6.8 according to
17
18 results from the precipitation curve of ZnSal. The next day, pH was readjusted, the
19
20 precipitated was centrifuged, washed with distilled water (DW), air dried at room
21
22 temperature and milled.
23
24

25
26 The amount of free water in ZnSal was determined by indirect gravimetric,
27
28 heating the solid at $105 \pm 5^\circ\text{C}$. Zinc was determined as zinc oxide by a gravimetric
29
30 procedure heating the solid at 900°C . The organic fraction was calculated as the
31
32 difference between the mass of dried ZnSal and the zinc content; from this data the
33
34 stoichiometry of ZnSal was obtained. The FTIR spectrum of ZnSal was obtained using
35
36 the potassium bromide disc technique and a Perkin-Elmer Spectrum One FTIR
37
38 Spectrometer. The density of the pigment, needed for coating formulation, was
39
40 determined according to ASTM D 153-84²².
41
42
43
44

45 46 **2.2 Bioassay**

47

48
49 LC_{50} , the concentration which kills 50% of the *Artemia* nauplii population
50
51 within 24 hours, was determined using a short term toxicity test¹⁹.
52

53
54 *Artemia persimilis* eggs, commercially available, were hatched in artificial sea water
55
56 (ASW), at $22 \pm 2^\circ\text{C}$ during 24 hours, under gentle aeration with an aquarium pump²³.
57
58
59
60

1
2
3 The ASW was prepared according to ASTM D1141-98²⁴. After 48 hours a homogenous
4 population of instar II-III nauplii were obtained and used for the test. A saturated
5 solution of ZnSal in ASW was prepared and the concentration of salicylate ions was
6 measured by UV-vis spectrophotometry at 297 nm²⁵. This concentrated solution was
7 diluted to obtain different concentrations of the salt (typically: 1000, 500, 250, 125, 75
8 ppm) to perform the test with the *Artemia* larvae, following the same procedure outlined
9 in previous published research^{12,18}. After an incubation period of 24 h, dead larvae were
10 counted and LC₅₀ values were calculated by Probit analysis²⁶.
11
12
13
14
15
16
17
18
19
20

21 **2.3 Formulation and preparation of coatings**

22
23
24
25 Two coatings, with two different binders, were formulated to carry out this
26 research (Table 1). Coating 1 contained WW rosin as film forming material and oleic
27 acid as plasticizer; aluminum stearate was added as rheological agent²⁷. Coating 2 was
28 formulated with styrene-acrylate copolymer (SAC) as co-binder being 1.9/1 the ratio
29 rosin/SAC by volume (Table 1). In this case, the plasticizer was chlorinated paraffin
30 with 42% of chloride. This plasticizer is commonly recommended for the styrene-
31 acrylate copolymer and is also compatible with the rosin resin²⁸. Coatings were
32 elaborated following a procedure described in the literature^{12,18}.
33
34
35
36
37
38
39
40
41
42

43
44 Control coatings were also elaborated with the same formula of coating 1 and 2,
45 respectively, but replacing ZnSal in volume by TiO₂.
46
47

48 **2.4 Determination of leaching rates in ASW**

49
50
51
52 The leaching rate test in ASW, is a short term test to assess the dissolution of
53 active agent from coatings in laboratory conditions previous to immersion in natural sea
54 water. Coatings were applied on 8 x 8 cm sandblasted acrylic panels. Three or four
55
56
57
58
59
60

1
2
3 coats were applied and allowed to dry 24 hours between each application. The total dry
4
5 film thickness was $120 \pm 5 \mu\text{m}$. Not more than 48 hours elapsed for the painted panels
6
7 to be submerged in a plastic container containing 150 ml of ASW. The leached
8
9 salicylate was determined by UV-Vis spectrophotometry while zinc was determined by
10
11 atomic absorption spectroscopy. The original level of the liquid in the containers was
12
13 restored periodically with distilled water and the pH was adjusted to 8.2.
14
15

16 17 **2.5 Essays in NSW**

18
19
20 Sandblasted acrylic panels (8 x 12 cm) were coated as described before to match
21
22 a total dry film thickness of $180 \pm 5 \mu\text{m}$. No more than 48 hours elapsed before the
23
24 painted panels were immersed in Mar del Plata harbor ($38^{\circ}08'17''\text{S}$ - $57^{\circ}31'18''\text{W}$). The
25
26 coastal area where the trial was performed is subjected, predominantly, to atmospheric
27
28 thermal cycling. The seawater temperatures exhibited seasonality with an average
29
30 maximum of 20°C during February and a minimum of 9.3°C during July. The salinity
31
32 ranged between 32.6 and 34.6 o/oo.
33
34
35

36
37 The biofouling resistance was evaluated according to ASTM D 3623 – 78a and
38
39 ASTM D 6990-05^{30,31}. The range for the fouling rating (FR) was 0 to 100. The FR for
40
41 coatings free of adherent biofouling settlement was recorded as 100. The FR of each
42
43 coating was obtained by discounting from 100 the percentage of the area covered by
44
45 macrofouling. A coating free of macrofouling settlement, but with adherent slime
46
47 (microorganisms such as bacteria, fungi, diatoms and protozoa), was qualified with a
48
49 FR = 99, whichever the percentage of the covered area was. Therefore, fouling rating
50
51 reflects non-fouled area. Distance smaller than 1cm from the edge of the panels were
52
53 not considered. Uncoated panels were used as control and immersed in the same
54
55 conditions as the painted ones. Barnacles, serpulids, ascidians, bryozoans, algae and
56
57
58
59
60

1
2
3 polychaetes are frequent macrofouling organisms at Mar del Plata harbor and may be
4
5 found attached onto the panels^{4,29}. This assay was conducted in triplicate.
6
7

8
9 Microscopic examination of coating 1 (the more efficient coating exposed to
10
11 NSW) during a short time (2 days) was carried out by environmental scanning electron
12
13 microscopy (ESEM) employing a PHLLIPS FEI Quanta 200, in order to assess
14
15 microfouling settlement. The biological structures were preserved with a 2.5%
16
17 glutaraldehyde solution and stored in sea water until their observation^{2,30}.
18
19

20 3. RESULTS AND DISCUSSION

21 3.1 Salicylic salt abstention and characterization

22
23
24
25
26 The precipitated ZnSal was in equilibrium with its own ions at pH 6.8 (Figure
27
28 1). The determination of the pH value is of importance with respect to the synthesis
29
30 procedure to obtain the salicylate derivative with a definite composition. The chemical
31
32 composition of ZnSal was as follows: salicylate, 63.30 %; zinc 24.20 %, being the rest
33
34 (12.50 %) water. According to these results the molar ratio between the salicylate anion
35
36 and the zinc cation was calculated and found to be ~1:1.
37
38
39

40
41 The main absorption bands detected in the FTIR spectrum were in accordance
42
43 with the chemical composition of the ZnSal. The intense band at 3600 cm⁻¹ corresponds
44
45 to the stretching of the OH groups (Figure 2). The asymmetric and symmetric –COO⁻
46
47 stretching produce two strong bands usually present in a sample with carboxilate
48
49 groups, therefore the peaks at 1600 and 1403 cm⁻¹ could be assigned to these ions³⁰. The
50
51 peaks at 1540 and 1456 cm⁻¹ correspond to the stretching of the C=C bond of the
52
53 aromatic ring. The sharp peak at 1235 cm⁻¹ corresponds to the stretching of the C-O
54
55 bonded to the aromatic ring and the peak next to 1093 cm⁻¹ corresponds to the vibration
56
57
58
59
60

1
2
3 of the C-O bond^{32,33}. These observations led to the conclusion that zinc ions would be
4
5 interacting with the carboxylate groups.
6
7

8 The density of ZnSal was 1.80 g/cm³. The solubility of ZnSal in AMA was
9
10 determined by UV spectrophotometry at 297 nm, a wavelength at which ZnSal presents
11
12 an absorption maximum. It was found to be equal to 10143 ppm. The concentration of
13
14 Zn²⁺, in the same solution, determined by atomic absorption, was 1052 ppm.
15
16

17 18 **3.2 Bioassays** 19

20
21 After an incubation period of 24 h, the ZnSal LC₅₀ was found to be 627 ± 56
22
23 mg/l (salicylate) and 7 ± 2.0 mg/l for copper sulphate (positive control). These results
24
25 showed that SalZn has some activity against *Artemia persimili* larvae; however, its
26
27 toxicity is much lower than that of copper sulfate because the dose to achieve LC₅₀ is
28
29 significantly higher for ZnSal.
30
31

32 33 **3.3 Determination of leaching rates in ASW** 34

35
36 Results of leaching experiments are shown in Figure 3 to 5. The reproducibility
37
38 of the test was acceptable and the variation coefficient between measurements was ~
39
40 4%. As a general rule, it can be seen that coating 1, formulated with rosin and oleic
41
42 acid, leached a higher amount of salicylate as it could be observed in the cumulative
43
44 leached mass plot (Figure 3). Coating 1 was observed, principally, during the first
45
46 fortnight of immersion (Figure 3 and 4). It is also remarkable that coating 2 leached
47
48 more salicylate than coating 1 during the first 3 days of the trial. At the end of the trial,
49
50 both coatings showed a leaching rate close to 1.0 µg.cm⁻².day⁻¹ of salicylate. During the
51
52 first days of testing, there was a sharp drop in the leaching rate of coatings 1 and 2
53
54 (Figure 3). This descent could be attributed to the fact that, at the beginning of the
55
56
57
58
59
60

1
2
3 immersion period, the bioactive agent was close to the film surface and, as a
4
5 consequence, it could be leached easily. As time elapsed the biocide must diffuse from
6
7 the inner of the coating to the surface. It is clear that coating 1 offered better diffusion
8
9 path for ZnSal which, in turn, was reflected in the higher values of the leached
10
11 salicylate. After 10 days both coatings presented a similar behavior.
12
13

14
15 At the beginning of the assay, the leaching rate of Zn^{2+} from coatings 2 was
16
17 higher than from coating 1 (Figure 5) but, at the end of the test, both values approached
18
19 to $0.3 - 0.4 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$. As sea water pH is ~ 8.2 , close to the precipitation of zinc
20
21 hydroxide, it was expected that zinc ions tend to precipitate which will increase the
22
23 release of salicylate ions to the medium. This may explain the larger amount of
24
25 salicylate ions leached in relation to zinc ions during the first period of immersion
26
27 before the 20 days.
28
29

30
31 These results were important because they showed that lower amounts of metals
32
33 would be released to the environment during the coatings service life. According to
34
35 bibliographic data, Zn^{2+} ions leaching rate from biocide-free commercial AF paints is
36
37 approximately 20 to 27 times higher than the value determined in this research^{9,34}.
38
39
40

41 **3.4 Essays in NSW**

42
43

44
45 The panels submerged in natural sea water were observed periodically and the
46
47 assay was conducted in triplicate. After six months, coatings 1 and 2 performed
48
49 notoriously better than the controls (Figure 6.a-b). FR of the control panels was found to
50
51 be 15 and it continued decreasing with time. The predominant macrofoulers were
52
53 ascidians, bryozoans, serpulids and algae. These results confirmed the antifouling
54
55 activity of ZnSal which was assessed previously by laboratory test.
56
57
58
59
60

1
2
3 The control coating 1 had a low FR (~10) after one year of exposition but panels
4 with coating 1 exhibited a FR=95 at the same period of time, Figure 6 a. Panels with the
5 control coating were completely covered with ascidians, algae, serpulids, barnacles and
6 bryozoans at the end of the trial and, at the same time, they showed an incipient film
7 wearing since 6 months on. Coating 1 was more resistant than control coating. After 15
8 months of exposition coating 1 showed a high wear and, therefore, panels were removed
9 from the test site, Figure 6 a. The fouling attached onto the panels consisted mostly of a
10 heavy slime and algae. It is encouraging that ZnSal effectiveness in fouling control was
11 maintained even in the case of worn film.
12
13
14
15
16
17
18
19
20
21
22
23

24 Coating 2 resulted to be less efficient than coating 1 with a FR=60 after six
25 months which descended to 30 when nine months of immersion elapsed, Figure 6 b. At
26 the beginning of the immersion period a thick slime layer was deposited quickly onto
27 the panels. After six months the most frequent organisms found attached onto the panels
28 were bryozoans and serpulids. However, film integrity was kept until the ninth month.
29 The panels corresponding to the control coating 2 were almost totally fouled (FR= 5)
30 after six months; mostly with ascidians and serpulids, Figure 6 b. Due to the lower
31 efficiency of the coating 2, the panels were removed at the ninth month. These results
32 showed that the antifouling activity was highly influenced by the nature of the binder.
33 The incorporation of SAC improved film resistance but affected the coating leaching
34 rate causing the antifouling performance to decrease.
35
36
37
38
39
40
41
42
43
44
45
46
47
48

49 Controls for coating 1 and 2 did not contain ZnSal, but less fouling was observed
50 in the first, especially in 6 and 9 months. This should be due to a higher erosion rate
51 associated with a higher content of rosin.
52
53
54
55
56
57
58
59
60

1
2
3 The ESEM micrographs of the control coating 1 and those of the coating 1
4 before and after the exposure to NSW, are shown at the Figure 7. Previous to the
5 immersion both coatings showed a homogeneous and compact film, especially coating
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

The ESEM micrographs of the control coating 1 and those of the coating 1 before and after the exposure to NSW, are shown at the Figure 7. Previous to the immersion both coatings showed a homogeneous and compact film, especially coating 1. After 2 days of immersion in NSW a great degree of colonization was observed on the control coating 1 which exhibited an abundant biofilm with emergence of diatoms and protozoa. Coating 1 did not present biofilm formation but pores appeared as a consequence of binder solubilization. These pores could not be seen on the control coating due to the thick biofilm formed. This result confirmed the fact that ZnSal inhibited the growth of microfouling.

4. CONCLUSIONS

ZnSal showed to be active against *Artemia* larvae and it has a lower toxicity than copper. Coating 1 had longer service life than coatings 2 with a fouling rating above 95 until the twelfth month of immersion.

The coating with ZnSal and rosin / oleic acid binder proved to have an acceptable efficiency for more than twelve months. According to data published, ferric benzoate, ferric and aluminum sorbate were assessed in field test^{15,16} to determine their antifouling efficiency in coatings with a similar binder, but their service life was, approximates, 9 months. In change, similar coatings pigmented with ZnSal proved to have an extended service life. The use of styrene-acrylate copolymer on coating 2, increased the film resistance to wearing, with respect to coating 1, but the antifouling performance was impaired, due to a decreased leaching rate. Results obtained with coating in NSW showed that ZnSal can be used as an effective antifoulant.

FIGURES CAPTIONS

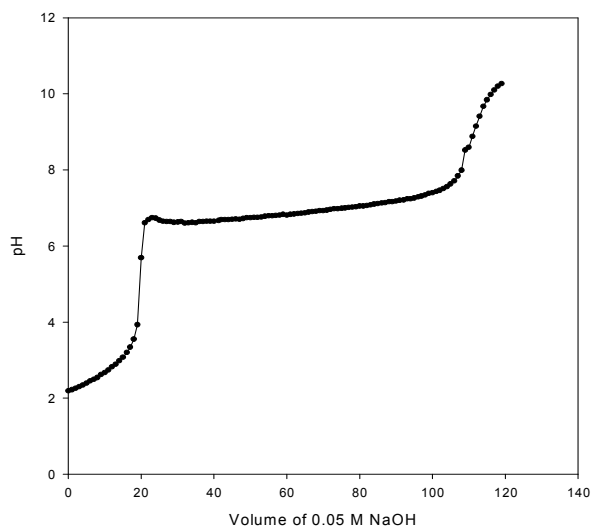
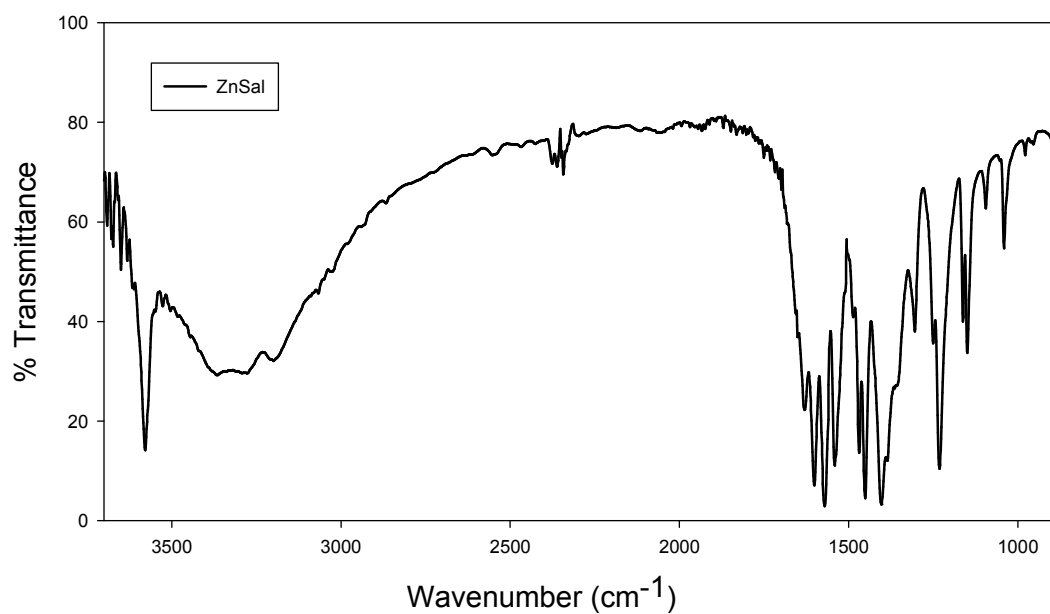
Figure 1. Titration curve of salicylic acid + zinc nitrate with 0.05 M NaOH**Figure 2.** FTIR spectrum of zinc salicylate.

Figure 3. Amount of salicylate leached from coating films.

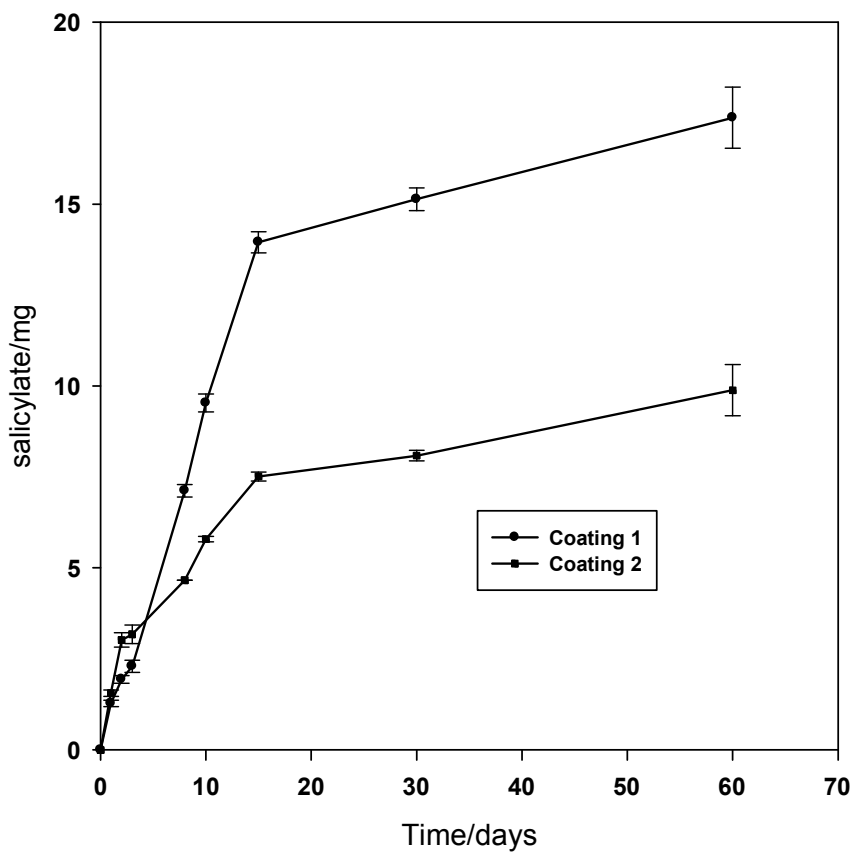


Figure 4. Salicylate leaching rate from coating films.

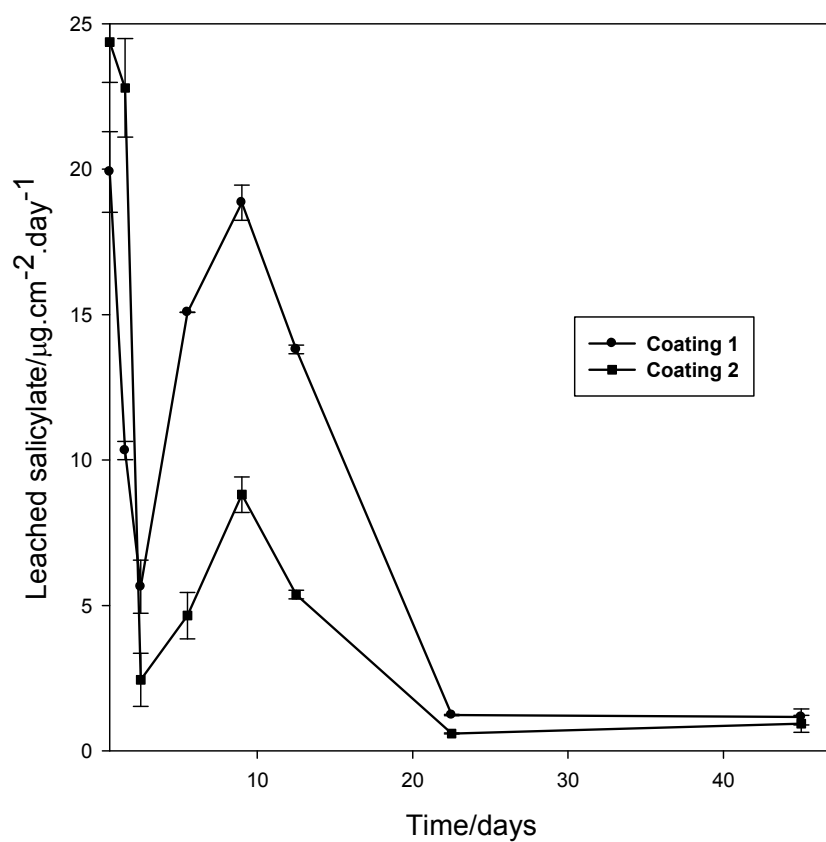
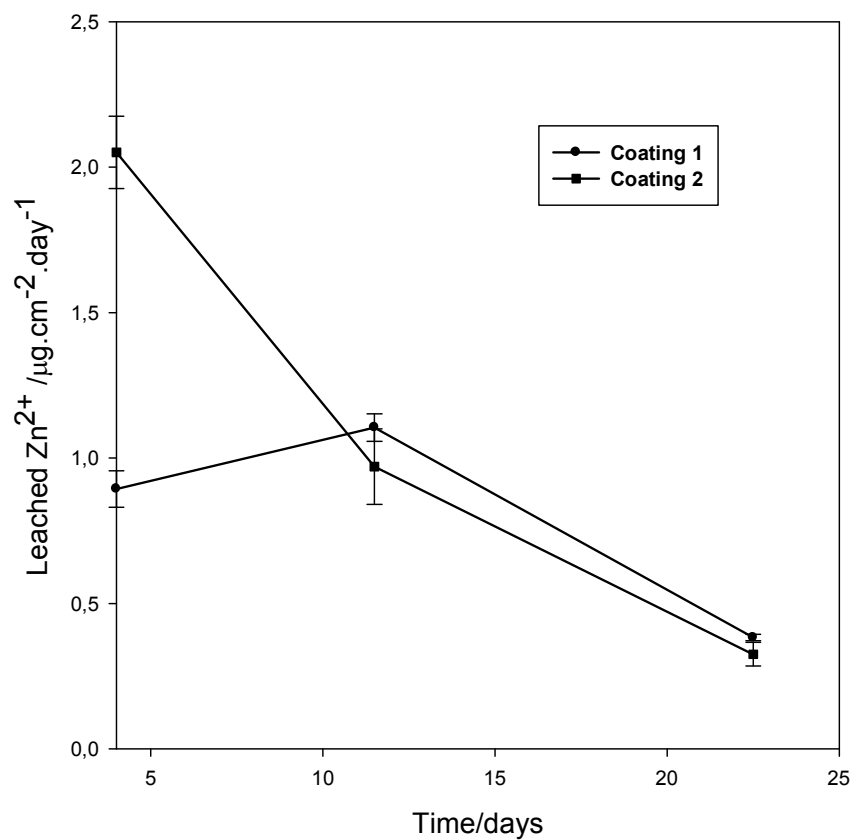
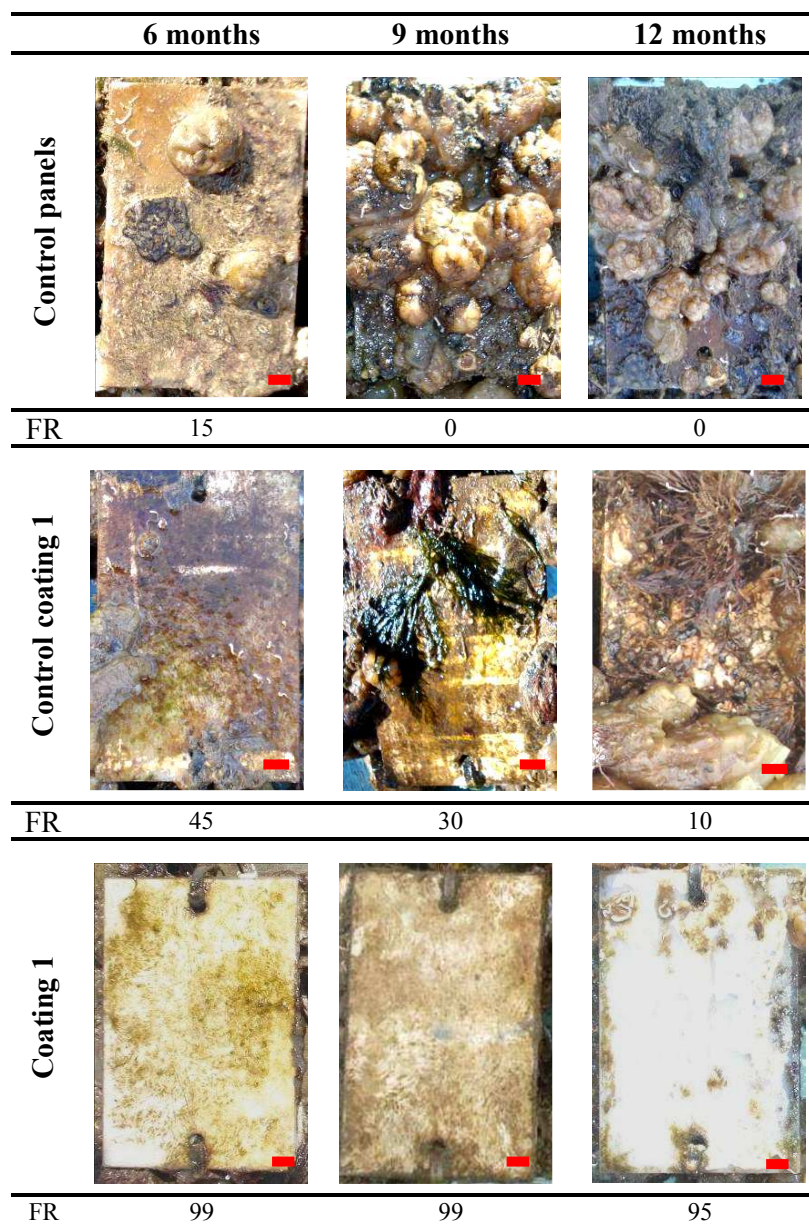


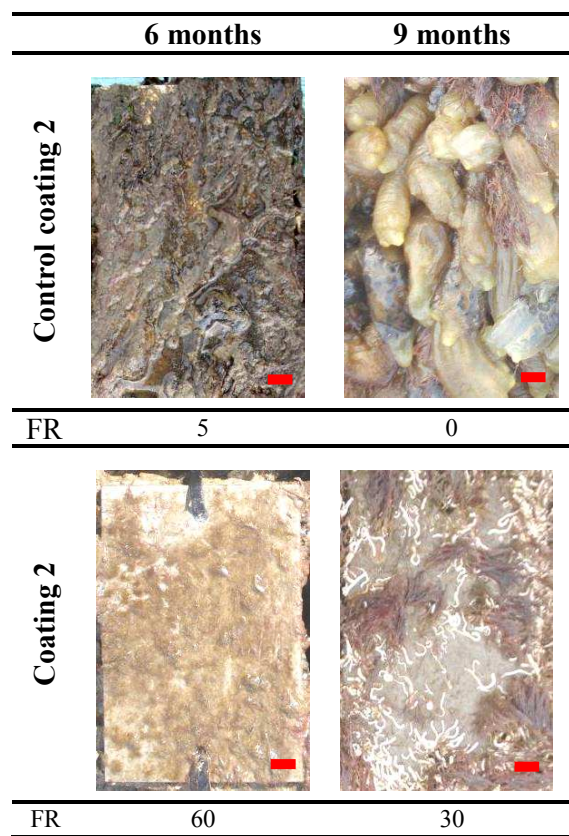
Figure 5. Zinc ions leaching rate from the coating films.



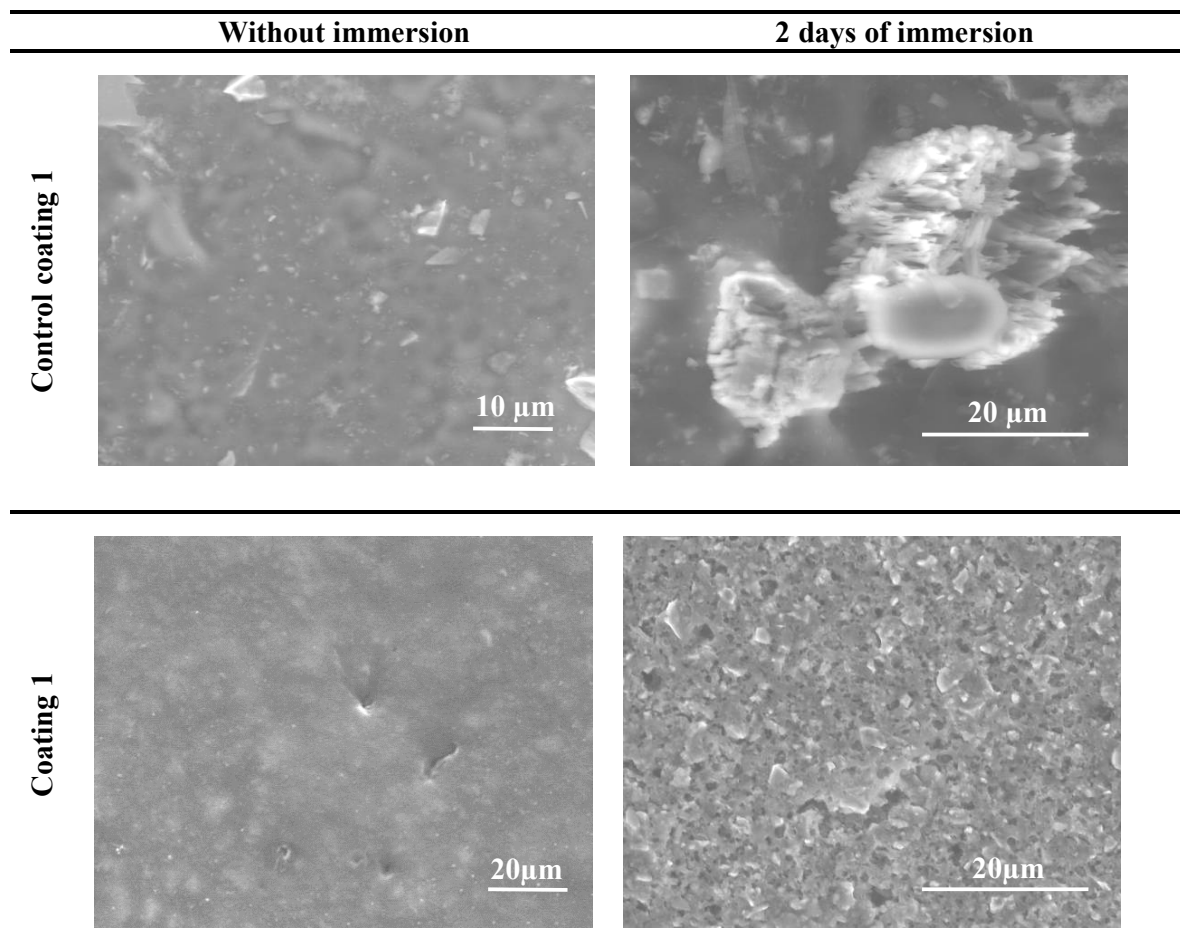
1
2
3 **Figure 6 a.** Photographs of panels (coating 1 and controls) immersed in sea water at
4
5 Mar del Plata harbor, Argentina (bar = 1cm).
6
7
8
9
10



1
2
3 **Figure 6 b.** Photographs of panels (coating 2 and controls) immersed in sea water at
4
5 Mar del Plata harbor, Argentina (bar = 1cm).
6
7
8
9
10



1
2
3 **Figure 7.** ESEM micrograph: panels without and with 2 days of immersion in NSW,
4
5 water at Mar del Plata harbor, Argentina.
6
7



TABLES

Table1. Composition of paints as % of solids by volume

Components	Coating 1 ^a	Coating 2
SalZn	27.0	34.6
Chalk	18.1	8.8
WW rosin	45.1	32.8
SAC	-----	17.2
Chlorinated paraffin	-----	6.6
Oleic acid	9.8	-----

^a Coating 1 was prepared with a 2.0 wt.% content aluminium stearate.

1
2
3 AUTHOR INFORMATION4
5 **Corresponding Author**6
7 *E-mail: pinturashigenicas@cidepint.gov.ar8
9
10 **Notes**11
12 Both authors are CONICET Researchers and UNLP Professors.13
14
15
16 ACKNOWLEDGMENTS17
18
19 The authors wish to thank the Consejo Nacional de Investigaciones Científicas y
20 Técnicas (CONICET), Comisión de Investigaciones Científicas de la Provincia de
21 Buenos Aires (CIC), Agencia Nacional de Promoción Científica y Tecnológica
22 (ANPCyT) and the Universidad Nacional de La Plata (UNLP) for the support to do this
23 research. They also thank to Gastón Guzmán for the analytical determinations.
24
25
26
27
28
29
3031
32 REFERENCES

- 33
-
- 34
-
- 35 (1) Schultz, M.P. Effects of coating roughness and biofouling on ship resistance and
-
- 36 powering.
- Biofouling*
- .
- 2007**
- ,
- 23*
- , 331.
-
- 37
-
- 38
-
- 39 (2) Baier, R.E.
- Adsorption of microorganisms to surfaces*
- ; Wiley-Interscience
-
- 40 Publication: USA, 1980.
-
- 41
-
- 42
-
- 43
-
- 44
-
- 45 (3) Beech, I.B.; Sunner, J. Biocorrosion: towards understanding interactions between
-
- 46
-
- 47
-
- 48 biofilms and metals.
- Curr Opin Biotechnol*
- .
- 2004**
- ,
- 15*
- , 181.
-
- 49
-
- 50
-
- 51 (4) Bastida, R.; Martin, J.P.
- La vida entre mareas: vegetales y animales de las costas de*
-
- 52
-
- 53
-
- 54
- Mar del Plata*
- . Mar del Plata; INIDEP: Mar del Plata, 2004.
-
- 55
-
- 56
-
- 57
-
- 58
-
- 59
-
- 60

1
2
3 (5) Apolinario, M.; Couthino, R. *Advances in marine AF coatings and technologies*;
4
5 Woodhead Publishing: UK, 2009.
6

7
8 (6) Yebra, D.M.; Kiil, S.; Dam-Johansen, K. Antifouling technology—past, present and
9
10 future steps towards efficient and environmentally friendly antifouling coatings. *Prog.*
11
12 *Org. Coat.* **2004**, *50*, 75.
13

14
15 (7) Almeida, E.; Diamantino, T.C.; de Sousa, O. Marine paints: the particular case of
16
17 antifouling paints. *Prog. Org. Coat.* **2007**, *59*, 2.
18
19

20
21 (8) Chambers, L.D.; Stokes, K.R.; Walsh, F.C.; Wood, R.J.K. Modern approaches to
22
23 marine antifouling coatings. *Surf. Coat. Tech.* **2006**, *201*, 3642.
24
25

26
27 (9) Ytreberg, E.; Karlsson, J.; Eklund, B. Comparison of toxicity and release rates of Cu
28
29 and Zn from anti-fouling paints leached in natural and artificial brackish seawater. *Sien.*
30
31 *Total Environ.* **2010**, *408*, 2459.
32

33
34 (10) Konstantinou, I.K. *Antifouling Paint Biocides*; Springer: New York, 2006.
35
36

37
38 (11) Bellotti, N.; Deyá, C.; del Amo, B.; Romagnoli, R. Antifouling Paints with Zinc
39
40 “Tannate”. *Ind. Eng. Chem. Res.* **2010**, *49*, 3386.
41

42
43 (12) Bellotti, N.; del Amo, B.; Romagnoli, R. Quaternary Ammonium “Tannate” for
44
45 Antifouling Coatings, *Ind. Eng. Chem. Res.* **2012**, *51*, 16626.
46
47

48
49 (13) Nriagu, J.O. *Cinc in the environmenta, Part 1: Ecological Cycling*; Wiley: USA,
50
51 1980.
52
53
54
55
56
57
58
59
60

- 1
2
3 (14) Blustein, G.; Romagnoli, R.; Jaén, J.A.; Di Sarli, A.R.; del Amo, B. Zinc basic
4 benzoate as eco-friendly steel corrosion inhibitor pigment for anticorrosive epoxy-
5 coatings. *Coll. Surf. A: Phys. Eng. Aspects*. **2006**, 290, 7.
6
7
8
9
10 (15) del Amo, B.; Blustein, G.; Pérez, M.; García, M.; Deyá, M.; Stupak, M.;
11 Romagnoli, R. A multipurpose compound for protective coatings. *Coll. Surf. A: Phys.*
12 *Eng. Aspects*. **2008**, 324, 58.
13
14
15
16
17 (16) Pérez M.; García M.; Stupak M. and Blustein G. Synthesis and Characterization
18 of Ferric Sorbate and Aluminum Sorbate as Antifouling Pigments for Marine Paints.
19 *Ind. Eng. Chem. Res.* **2014**, 53, 3570.
20
21
22
23
24 (17) Price, C.T.D.; Lee, I. R.; Gustafson, J. E. The effects of salicylate on bacteria. *Int.*
25 *J. Biochen. Cell Biol.* **2000**, 32, 1029.
26
27
28
29 (18) Bellotti, N.; del Amo, B.; Romagnoli, R. Tara tannin a natural product with
30 antifouling coating application. *Prog. Org. Coat.* **2012**, 74, 411.
31
32
33
34
35 (19) Persoone, G.; Wells, P.G. *Artemia Research and its Applications. Vol.1.*
36 *Morphology, Genetics, Strain characterization, Toxicology*; University Press: Belgium,
37 1987.
38
39
40
41
42 (20) ASTM D 3623 – 78a. *Standard test method for testing antifouling panels in*
43 *shallow submergence*; ASTM international: USA, 2004.
44
45
46
47
48 (21) ASTM D 6990-05. *Standard practice for evaluating biofouling resistance and*
49 *physical performance of marine coating systems*; ASTM International: West
50 Conshohocken, PA, USA, 2005.
51
52
53
54
55
56
57
58
59
60

1
2
3 (22) ASTM D 153-84. *Standard test methods for specific gravity pigments*; ASTM
4
5 International: West Conshohocken, PA, USA, 2003.
6
7

8 (23) Persoone, G.; Jaspers, E.; Clasus, C. *Ecotoxicological Testing for the Marine*
9
10 *Environment: Proceedings of the International Symposium on Ecotoxicological Testing*
11
12 *for the Marine Environment, Ghent, Belgium*; State University of Ghent: Ghent,
13
14 Belgium, 1984.
15
16

17
18 (24) ASTM D 1141-98. *Standard practice for the preparation of substitute ocean water*;
19
20 ASTM International: West Conshohocken, PA, USA, 2008.
21
22

23 (25) Snell, F.D.; Snell, C.T. *Colorimetric Methods of Analysis*. D. Van Nostrand
24
25 Company: New York, 1941.
26
27

28 (26) Díaz Baez, M. C.; Bulus Rossini, G. D.; Pica Granados, Y. *Métodos estadísticos*
29
30 *para el análisis de resultados de toxicidad. In Ensayos Toxicológicos y Métodos de*
31
32 *Evaluación de Calidad de Aguas: Estandarización, intercalibración, resultados y*
33
34 *aplicaciones*; Castillo Morales, G., Ed.; IDRC Books: Ottawa, Canada, 2004.
35
36
37

38 (27) Pérez, M.; Blustein, G.; García, M.; del Amo, B.; Stupak, M. Cupric tannate: A low
39
40 copper content antifouling pigment. *Prog. Org. Coat.* **2006**, *55*, 311.
41
42
43

44 (28) Stoye, D.; Freitag, W. *Paints, Coatings and Solvents*. WILEY-VCH: Fed. Rep. of
45
46 Germany, 1998.
47
48

49 (29) Bastida, R.; Capezzani, A.; Torti, M.R. Fouling organisms in the port of Mar del
50
51 Plata (Argentina). I.Siphonaria lessoni: ecological and biometric aspects. *Mar. Biol.*
52
53 **1971**, *10*, 297.
54
55
56
57
58
59
60

1
2
3 (30) Callow, J.A.; Osborne, M.P.; Callow, M.E.; Baker, F.; Donald, A.M.; Use of
4
5 environmental scanning electron microscopy to image the spore adhesive of the marine
6
7 alga *Enteromorpha* in its natural hydrated state. *Coll. Surf. B: Bioint.* **2003**, *27*, 315.
8
9

10 (31) Smith, B. *Infrared Spectral Interpretation*, 1st ed.; CRC Press: New York, 1999.
11

12 (32) Cooper, J.W. *Spectropic techniques for Organic Chemists*, 1st ed.; Wiley-
13
14 Interscience Publication: New York, 1980.
15
16

17 (33) Morrison, R.T.; Boyd, R.N. *Química Orgánica*, Addison-Wesley Iberoamericana:
18
19 Wilmington, DE, 1990.
20
21
22

23 (34) Yebra, D.M., Kiil, S., Dam-Johansen, K. Weinell, C.E., Reaction rate estimation
24
25 of controlled-release antifouling paint binders: Rosin-based systems. *Prog. Org. Coat.*
26
27
28 **2005**, *53*, 256.
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60