Progress in Organic Coatings 55 (2006) 311–315

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Cupric tannate: A low copper content antifouling pigment

Miriam Pérez, Guillermo Blustein, Mónica García, Beatriz del Amo, Mirta Stupak *

CIDEPINT, Centro de Investigación y Desarrollo en Tecnología de Pinturas, 52 e/121 y 122, 1900 La Plata, Argentina

Received 31 March 2005; received in revised form 9 June 2005; accepted 2 November 2005

Abstract

Fouling organisms attached to man-made surfaces submerged in seawater constitute a major worldwide technical and economical problem. Protection against biofouling is essential for efficient service of boats and ships. Due to recent and imminent restrictions of the use of traditional toxic antifouling paints, there is a growing need for new alternative compounds that ensure a good performance without polluting the marine ecosystem.

The aim of this work is to develop a new antifouling formulation using compounds of natural origin, i.e. tannates, in combination with a minimum concentration of a known bioactive pigment, i.e. copper.

Laboratory assays have shown that cupric tannate has a narcotic effect on biofouling larvae. In the field, after 12 months of immersion in Mar del Plata harbor (Argentine), none of the tested painted panels showed macrofouling organisms. This result was obtained with a large decrease in copper content in the order of 40 times relative to conventional cuprous oxide based paints.

Because copper tannate is not lethal at low concentrations, this pigment has an excellent potential as an antifouling agent.

Keywords: Antifouling paints; Cupric tannate pigment; Low copper content

1. Introduction

Fouling organisms attached to man-made surfaces submerged in seawater constitute a major worldwide technical and economical problem. Biofouling is a complex sequence of events influenced by several chemical, physical and biological processes. A surface that is immersed in the marine environment will be immediately covered by dissolved chemical compounds that adsorb on the surface and evolve to a macromolecular film [1,2]. This is followed by a process of biofouling where the macromolecular film on the surface is colonized by microorganisms, algal spores and invertebrate larvae.

Protection against biofouling is essential for efficient service of boats and ships. Historically, the attempts to protect hulls of sea-going vessels against fouling organisms go back at least to Roman times when hulls were covered with lead or bronze [3]. The most successful modern techniques have involved coating ship hulls with metal-containing antifouling paints. These paints protect against fouling by continuously releasing a toxic compound into the surrounding seawater. Due to the banning of TBT (tributyltin) by an increasing number of countries, copper and copper based antifouling paints are coming into use again [4].

Some species of marine algae and several species of marine invertebrates produce a wide variety of chemically active metabolites in their surroundings, potentially as an aid to protect themselves against other settling organisms. These active metabolites, also known as biogenic compounds, have antibacterial, antialgal and antifungal properties, which are effective in the prevention of biofouling [5–10]. A potent antimacrofouling activity against mussels and barnacles has been reported for extracts of several sponges and soft corals [11–16].

Tannins are naturally occurring phenolic compounds which precipitate proteins, they are important in industry, food and environmental sciences [17,18]. In general, tannins have high relative molecular weight (>500) and have many phenolic groups. Phenolic compounds are among the most widely distributed plant secondary products and are found in many plants [19,20].

The anticorrosive properties of tannins were known at last 50 years ago when they were first suggested for the treatment of rusted steel [21]. Subsequently a number of tannin-based products appeared on the market and found a certain amount of success as pre-treatment primers for use of rusted steel without requiring complete removal of the corrosion product [21,22].

---

* Corresponding author. Tel.: +54 221 483 1141/44; fax: +54 221 427 1537. *E-mail address:* biofouling@cidepint.gov.ar (M. Stupak).

0300-9440/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2005.11.014

Tannins and tannic acid are mixtures of polyhydric phenols and are classified according to their source plant. Their chemistry is complex, but the feature relevant to this discussion is the existence of numerous reactive dihydric or trihydric phenol nuclei around the molecule. These neighbouring di- or trihydroxy groups can readily complex with metal ions [23].

On the other hand, the antifouling properties of tannins were claimed as early as 1881 [24]. Sieburth and Conover [25] showed that phlorotannins from *Sargassum natans* paralyzed the tentacles of hydroids, and killed bacteria, nematodes and copepods. Phlorotannins are phenolic compounds specific to brown algae. Some authors suggested ecological functions of phlorotannins as antimicrobial, antipathogenic or antifouling substances [26–31]. In addition, Scalbert [32] reviewed the antimicrobial properties of tannins against many types of fungi, bacteria, and yeasts. In contrast, information is very scarce about the effect of condensed vegetable tannins (oligomers and polymers of flavan-3-ol-nuclei) and their effect on biofouling. Sawant et al. [33] suggested that methanol extracts of *Derris scandens* (Dicotyledonae) possess both antibacterial and antialgal properties. In a previous paper [34] the narcotic effect of chestnut, quebracho and mimosa tannin was demonstrated on *Balanus amphitrite* in laboratory trials and the antifouling effect of these compounds was also shown in the sea.

However, because non-toxic antifouling paints cannot as yet be produced on an industrial scale, there is a growing need for the development of alternative formulations that ensure good performance without polluting the marine ecosystem. In this sense, the challenge is to identify and promote the use of more environmentally friendly antifouling products [35,36].

The aim of this paper is to describe and evaluate the effect of soluble matrix antifouling paints formulated with cupric tannate on fouling organisms.

2. Experimental

2.1. Antifouling pigment preparation

Antifouling pigment was synthesized using quebracho tannin (condensed tannin) (Fig. 1). Tannin solution was prepared by dissolving 10 g quebracho tannin in 500 ml of hot water. This solution together with a solution of 40 ml cupric sulphate (1.0 M) were dropped simultaneously into a glass beaker containing 500 ml of 0.04 M sodium hydroxide solution with stirring at 60 °C to precipitate the metallic tannate. Finally, pH was adjusted to 5.5 by means of a 40% (w/v) potassium hydroxide solution.

Once the pigment precipitated, it was filtrated employing a Büchner funnel, washed with distilled water and dried in air at room temperature. The final product was stable at room temperature with regard to atmospheric oxidation.

2.2. Pigment characterisation

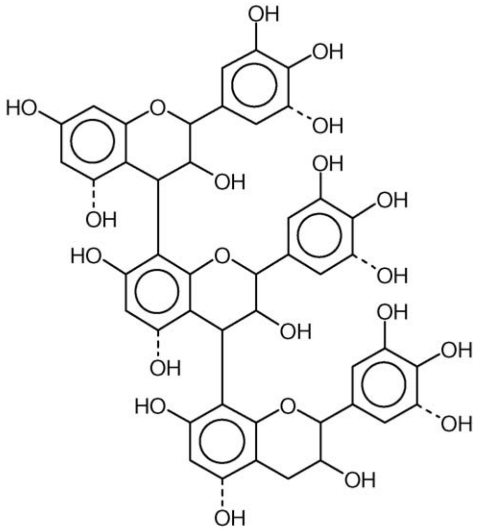

Fig. 1. Proposed basic structure of quebracho tannin.

The composition of cupric tannate was determined by current analytical techniques. Physical and chemical characteristics of this pigment such as density, and pH and solubility in artificial seawater were also determined at room temperature.

Soluble tannate concentration in artificial seawater was determined by a colorimetric technique. The dissolved tannate was precipitated with 5% $Al_2(SO_4)_3 \cdot 18H_2O$ in NH_4Cl/NH_3 (2 M:2 M) buffer medium and then it was dissolved in nitric acid solution (4:1 by volume). Aluminium cation was finally complexed with citric acid in ammoniacal medium. The concentration of tannate was determined by comparison with standard tannate solutions prepared in similar conditions. Copper concentration in seawater was obtained by atomic absorption spectrometry.

2.3. Cupric tannate solution preparation

In order to establish the tolerance limits of larvae to cupric tannate, a series of dilutions from a saturated solution ranging between 1 and 100% were prepared.

Saturated solution was obtained as follows: 10 g of tannate-based pigment was incorporated into a glass beaker containing 1000 ml of artificial seawater. Then, the suspension was stirred during 24 h to achieve equilibrium solubility. Finally, the saturated solution was obtained from the suspension by filtration employing a Büchner funnel.

2.4. Composition, manufacture and application of paints

Colophony (WW rosin) was used as binder and oleic acid as plasticizer; moreover, aluminium stearate was employed as rheological agent. Paint was formulated with a pigment volume concentration (PVC) of 37% (Table 1) and cupric tannate as antifouling pigment. The paint was prepared in a laboratory scale ball mill (3.3 litters jars); the operating conditions of the ball mill were chosen so as to achieve an efficient dispersion. The ball mill was loaded with the vehicle followed by metallic tannate, calcium carbonate and aluminium stearate which were dispersed during 24 h.

Table 1
Soluble matrix paint composition

Components	% by volume[a]
Cupric tannate	16.00
Calcium carbonate	2.96
Colophony (WW rosin)	26.80
Oleic acid	5.80
Solvent[b]	48.44

[a] Paints were prepared with a 2.0 wt.% content aluminium stearate.

[b] Solvent employed was a mixture of xylene/white spirit (1:1 % by weight).

In order to determine the effect of paint leachates on larval survival under laboratory conditions, antifouling formulations were applied on glass slides. Then, paints were put into crystallizing vessels containing 1000 ml of artificial seawater for 1–3 days to obtain solutions with increasing pigment concentrations.

Settling tests were performed using crystallizing vessels (diameter 50 mm). The inside was painted with three layers of the test paints. A drying time of 24 h was allowed for each layer. After drying, the painted crystallizing vessels were filled with artificial seawater to remove any possible toxic residues from the paint itself. After three days, the crystallizing vessels were replenished with 50 ml of fresh artificial seawater and biological assays were carried out. Observations were made under stereomicroscope at suitable interval times.

Sandblasted acrylic tiles (8 cm × 16 cm; Rm: 21 μm) were used for field trials. Paints containing cupric tannate were applied by brush on tiles previously degreased with toluene. Three coats of paint were applied and were allowed to dry 24 h between each application, resulting in a final dry thickness of 150 ± 5 μm. Then, coated panels were hung in a marina in Mar del Plata harbor to a depth of 50 cm below the water line. Three replicates of paint were randomly sampled every month following increasing exposure periods up to 12 months. In addition, two paints were used as controls, one of them was a traditional cuprous oxide based paint and the second one, a paint without toxic pigment. A series of unpainted acrylic tiles was used to establish fouling community development.

2.5. Biological tests

Plankton samples were taken from Club de Motonáutica (38°08′17″S–57°31′18″W), Mar del Plata, Argentine, using a 25 μm zooplankton net. Nauplii and cyprids of *B. amphitrite* (Cirripedia, Balanidae) and larvae of *Polydora ligni* (Polychaeta, Spionidae) were isolated under stereomicroscope in the lab. Organisms were incubated in natural light at room temperature (18–20 °C) and suitable aeration. Larvae were fed with *Skeletonema costatum* culture.

Thirty larvae were used for each bioassay. In all bioassays artificial seawater (ASTM D 1141/75) was used. Larvae were added using a Pasteur pipette to small crystallizing vessels containing a volume of 50 ml of solution.

Larval behaviour was evaluated by estimating phototactic response, appendage mobility and recovery in fresh artificial seawater after exposure to tannate solutions.

Table 2
Cupric tannate composition

Components	% by weight
Tannate	69.9
Copper (Cu^{2+})	13.2
Potassium (K^+)	2.4
Sodium (Na^+)	0.3
Loss at 100 °C	14.2

3. Results and discussion

Pigment composition is presented in Table 2, these values are shown in % by weight because precipitated compound is a non-stoichiometric one. The natural tannin used in the experiments is constituted by several products, the compound shown in Fig. 1 is one of the most relevant.

Physical and chemical properties are shown in Table 3. The pH value obtained (6.48) suggests a good performance of both antifouling properties [37] and paint matrix dissolution. Moreover, tannate and copper concentrations were adequate to inhibit larval activity.

The antifouling effect of cupric tannate was evaluated using two different biological tests. Firstly, tests to evaluate the toxicity of the pigment in solution and in leachates from paints were carried out. Secondly, field tests to estimate the tendency for fouling organisms or their larvae to attach directly to the paint surface were conducted.

Laboratory assays indicated that *B. amphitrite* and *P. ligni* larvae were rapidly affected by exposure to solutions of increasing concentrations of cupric tannate in seawater (Fig. 2). Larval behaviour was similar in all cases, i.e. larvae lost their phototactic response, became immediately quiescent, immobilized their appendages and stopped their swimming movements. When larvae lost their activity they fell to the bottom of the vessels with the result that the number could readily be counted at suitable time intervals. The 50 inactivity time (It_{50}) was estimated, i.e. the time required for 50% of the test organisms become inactive [38].

As seen in Fig. 2, the effect of larval immobilization is clear even at very low concentrations of cupric tannate, in the order of 1–10% v/v of saturated solution, and above these concentrations larval response was almost immediate. Larvae exposed to concentrations below 5% v/v could recover and their development was followed when they were transferred to clean artificial seawater. These laboratory results indicate that cupric tannate has narcotic activity with *B. amphitrite* and *P. ligni* larvae. As opposed to a toxic compound, when a narcotic compound is applied to a test organism or tissue, physiological function is

Table 3
Physical and chemical properties of the cupric tannate

pH[a]	Density (g/cm^3)	Solubility[a]	
		Tannate (ppm)	Copper (Cu^{2+}) (mM)
6.48	1.13	0.2	0.82

[a] In artificial seawater.

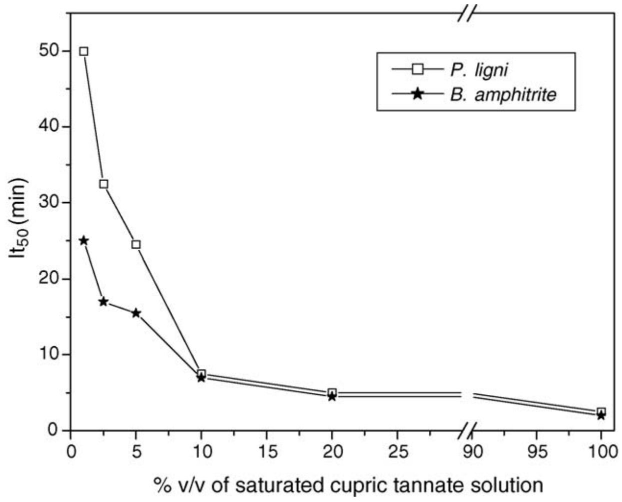

Fig. 2. Fifty percentage inactivity (It_{50}) time for *P. ligni* and *B. amphitrite* larvae in dilutions from a cupric tannate saturated solution.

usually temporarily depressed, and recovery can be rapid when the test material is removed to narcotic-free surroundings.

This pigment concentration was taken into account in antifouling paint preparation in order to reach an adequate leaching rate that ensures antifouling control and marine ecosystem protection.

The exposure of larvae to leachates from the tannate paints showed a similar behaviour, i.e. lost of phototactic response and reduction in appendage activity up to complete immobilization. Results of experiments indicated a higher sensitivity of *B. amphitrite* nauplii to pigment leachate in comparison with *P. ligni*. As the concentration of antifouling pigment in solution increased the effects were faster and more evident (Fig. 3).

After laboratory assays using cupric tannate in solution, series of antifouling paints were submerged and tested in the sea. In previous studies, the effect of the film on larval settlement was carried out in the lab and it could be observed that after exploring the paint surface, most of cyprids closed their valves hermetically and stopped swimming. The remaining ones avoided the paint and rapidly swam off. In all cases, when larvae were transferred to fresh artificial seawater, they recovered rapidly and completed their metamorphosis into an adult form (unpublished data).

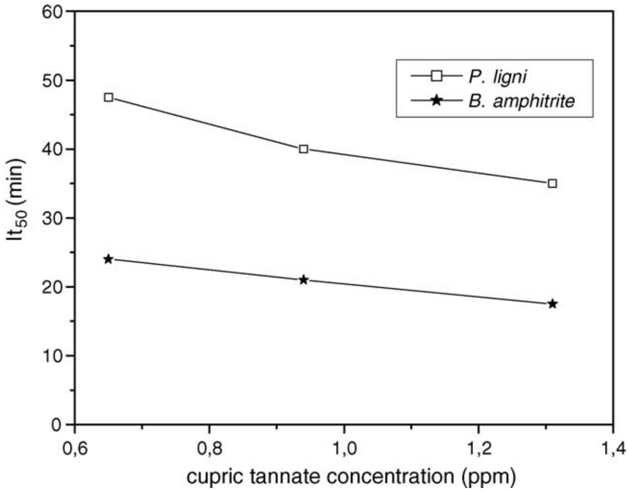

Fig. 3. Fifty percentage inactivity (It_{50}) time for *P. ligni* and *B. amphitrite* larvae in leachates from cupric tannate paints.

Fig. 4. Series of panels exposed in Mar del Plata harbor, above: cupric tannate paint, below: control acrylic panel, 12 months of immersion.

Field trials carried out in Mar del Plata harbor demonstrated that these paints have an antifouling performance as good as cuprous oxide based paints. After 12 months of immersion, no macrofouling species were recorded and only a low density of diatom species with a weak bond to paint film was present. Moreover, significant differences were also detected between tested and control panels: on acrylic panels without paint a heavy attachment of macro and microorganisms was observed (Fig. 4).

In a previous paper [39], a good performance was obtained with formulations based on core-shell pigments. A large copper content decrease in the order of 35 times in relation to traditional antifouling paints was achieved. In these trials, the use of cupric tannate as antifouling pigment allowed a higher reduction in copper content in the order of 40 times in comparison with cuprous oxide based paints.

Our results show that this new pigment, cupric tannate, is not lethal at low concentrations and consequently is a promising compound for antifouling formulations. In addition, Laks et al. [40] demonstrated that copper complexed, condensed tannin-containing bark extracts have efficacy as wood preservatives when evaluated by standardized wood preservatives laboratory testing procedures. On this basis, further studies will take into consideration the evaluation of the effect of cupric tannate pigment on submerged wooden structures.

Finally, this novel antifouling compound combines the narcotic effect of quebracho tannin with a minimum concentration of a conventional bioactive pigment. It is important to note that cupric tannate produces less marine pollution and allows a considerable decrease in the costs of paint composition.

4. Conclusions

Cupric tannate pigment at low concentrations shows a narcotic effect in lab trials on *B. amphitrite* and *P. ligni* larvae.

After 12 months of exposure in the sea, cupric tannate coated panels accumulated only light fouling. Fouling consisted of a thin slime of diatoms and no macrofouling species were observed on any of the panels.

Paints formulated with this pigment have a reduction in copper content in the order of 40 times in comparison with cuprous oxide based paints. This feature should allow a considerable decrease in the costs of paint composition and produces less marine contamination.

Acknowledgments

The authors would like to thank the Comisión de Investigaciones Científicas de la provincia de Buenos Aires (CIC) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) for their support. They also wish to thank to the Club de Motonáutica de Mar del Plata for the permission to use their marine testing site and the anonymous reviewers for their useful comments.

References

[1] M. Wahl, Mar. Ecol. Prog. Ser. 58 (1989) 175.
[2] M. Pérez, M. Stupak, CIDEPINT-Anales (1996) 95.
[3] D.M. Yebra, S. Kiil, K. Dam-Johansen, Prog. Org. Coat. 50 (2) (2004) 75.
[4] N. Voulvoulis, D. Scrimshaw, J. Lester, Chemosphere 47 (2002) 789.
[5] S.M. Al-Ogily, E.W. Knight-Jones, Nature 265 (1977) 728.
[6] T.M. Schmitt, M.E. Hay, N. Lindquist, Ecology 76 (1) (1995) 107.
[7] S.V. Dobretsov, Biofouling 14 (2) (1999) 153.
[8] B. Da Gama, R. Pereira, A. Carvalho, R. Continho, Y. Yoneshigue-Valentin, Biofouling 18 (1) (2002) 13.
[9] G.M. Nylund, H. Pavia, Mar. Biol. 143 (2003) 875.
[10] P. Bhadury, P. Wright, Planta 219 (4) (2004) 561.
[11] D. Standing, I. Hooper, D. Costlow, J. Chem. Ecol. 10 (1984) 823.
[12] D. Rittschof, I. Hooper, E. Branscomb, J. Costlow, J. Chem. Ecol. 11 (1985) 551.
[13] M. Sears, D. Gerhart, D. Rittschof, J. Chem. Ecol. 16 (1990) 791.
[14] P. Keifer, R. Schwartz, M. Koker, R. Hughes Jr., D. Rittschof, K. Rinehart, J. Org. Chem. 56 (1991) 2965.
[15] P.R. Willemsen, Int. Mar. Biodet. 34 (1994) 361.
[16] S. Dobretsov, P.Y. Qian, J. Exp. Mar. Biol. Ecol. 299 (2004) 35.
[17] Ch. Ho, Phenolic compounds in food: an overview, in: M.J. Comstock (Ed.), Phenolic Compounds in Food and their Effects on Health II, ACS Symposium Series, 1992.
[18] K. Chung, T. Wong, Ch. Wei, Y. Huang, Y. Lin, Crit. Rev. Food Sci. Nutr. 38 (6) (1998) 421.
[19] M. Cowan, Clin. Microbiol. Rev. 12 (4) (1999) 564.
[20] T. De Bruyne, L. Pieters, H. Deelstra, A. Vlietinck, Biochem. Syst. Ecol. 27 (1999) 445.
[21] E. Knowles, T. White, J. Oil Colour Chem. Ass. 41 (1958) 10.
[22] G. Matamala, W. Smeltzer, G. Droguett, Corros. Sci. 48 (2) (2000) 1351.
[23] J.A. Jaén, E. García de Saldaña, C. Hernández, Hyperfine Interact. 122 (1999) 139.
[24] E. Jones, U.S. Letters Patent No. 251,054, 1881.
[25] J. Sieburth, J.T. Conover, Nature 208 (5005) (1965) 52.
[26] S.C. Lau, P.Y. Qian, Mar. Ecol. Prog. Ser. 159 (1997) 219.
[27] S.C. Lau, P.Y. Qian, Biofouling 16 (1) (2000) 47.
[28] K. Nagayama, Y. Iwamura, T. Shibata, I. Hirayama, T. Nakamura, J. Antimicrob. Chemother. 50 (6) (2002) 889.
[29] G. Toth, H. Pavia, Mar. Biol. 140 (2) (2002) 403.
[30] A. Hemmi, T. Honkanen, V. Jormalainen, Mar. Ecol. Prog. Ser. 273 (2004) 109.
[31] S. Wikström, H. Pavia, Oecologia 138 (2004) 223.
[32] A. Scalbert, Phytochemistry 30 (1991) 3875.
[33] S.S. Sawant, S. Sonak, A. Garg, Indian J. Mar. Sci. 24 (1995) 229.
[34] M. Stupak, M. García, M. Pérez, Int. Biodeterior. Biodegrad. 52 (2003) 49.
[35] E. Armstrong, K. Boyd, A. Pisacane, C. Peppiatt, J. Burgess, Biofouling 16 (2–4) (2000) 215.
[36] J. Burgess, K. Boyd, E. Armstrong, Z. Jiang, L. Yan, M. Berggen, U. May, A. Granmo, D. Adams, Biofouling 19 (2003) 197.
[37] M. Pérez, M. García, V. Vetere, M. Deyá, B. del Amo, M. Stupak, Pigment Resin Technol. 30 (1) (2001) 34.
[38] V. Vetere, M. Pérez, M. García, M. Deyá, M. Stupak, B. del Amo, Surf. Coat. Int. 82 (12) (1999) 586.
[39] M. Pérez, M. García, B. del Amo, G. Blustein, M. Stupak, Surf. Coat. Int. Part B, Coat. Trans. 86 (2003) 259.
[40] P. Laks, P. McKaig, R. Hemingway, Holzforschung 42 (5) (1988) 299.