

Cupric tannate: A low copper content antifouling pigment

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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 (Argentina), 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.

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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].

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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

The composition of cupric tannate was determined by current analytical techniques. Physical and chemical characteristics of

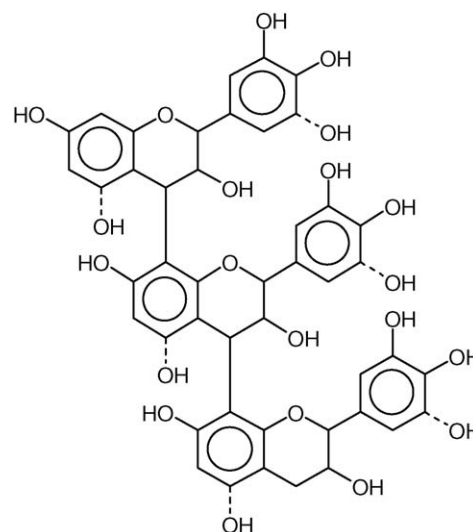


Fig. 1. Proposed basic structure of quebracho tannin.

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% $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in $\text{NH}_4\text{Cl}/\text{NH}_3$ (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 liters 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.

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