



## Modified tannin extracted from black wattle tree as an environmentally friendly antifouling pigment



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### ABSTRACT

The use of modified black wattle tannin as an antifouling pigment is reported in this work. A mixture of tannin adsorbed in activated carbon (soluble fraction of tannin) and low soluble fraction of tannin was used as an antifouling pigment. The soluble rosin resin was used as a paint matrix. <sup>13</sup>C NMR analysis confirm the modification of black wattle tannin through the cleavage of tannin interflavonoid bonds. FTIR spectra indicate the presence of tannin in the formulated antifouling coating even after 7 months of its exposure in a marine environment. Water contact angle analysis shows the hydrophilic characteristic of the tannin antifouling coating surface. Immersion tests at Badalona Port in the Mediterranean Sea shows the high antifouling efficiency of the TAN coating, comparable to commercial paint, until 7 months. The use of a natural black wattle tannin, without its complexation with metals, can eliminate the release of metals and other toxic biocides to the marine environment.

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### 1. Introduction

Hulls and submersed vessels and structures are subject to the attachment of organisms on their surface (Redfield and Hutchins, 1952). The accumulation of these organisms forms a layer called marine biofouling, its thickness depending on the organism species, water environment and season (Callow and Callow, 2002; Wahl, 1989). Barnacles, mussels, hydroids, molluscs, tubeworms and algae are the most common types of fouling organisms found in submersed structures and hulls (Callow and Callow, 2002). The presence of fouling attached to ship hulls increases the friction with water, raising fuel consumption (Callow and Callow, 2002; Senda, 2009). Maintenance costs of hulls, turbines, heat exchangers and ducts of hydroelectric plants are also affected by fouling (Lewandowski and Beyenal, 2009). Economically, fouling causes serious financial loss to industry and, therefore, control of this organism accumulation is mandatory (Callow and Callow, 2002).

The most common method for protecting immersed structures against fouling is the use of antifouling paints (Pérez et al., 2006). In the past, several toxicants such as arsenic and mercury oxide were added to resin matrixes, but in the 1950s concern about health problems led to the elimination of these products from the market

(Readman, 2006). The development of the tributyltin (TBT) compound introduced one of the most effective products ever made in the antifouling market (Goldberg, 1986). Its high durability and efficiency resulted in considerable savings in the maintenance costs of ship hulls (Goldberg, 1986). However, TBT was considered one of the most toxic biocides purposely released in the marine environment (Goldberg, 1986). Studies have shown that TBT impairs the embryogenesis and larval development of oysters, even at very low concentrations (i.e. 0.05 µg L<sup>-1</sup>) (Alzieu, 2000; His and Robert, 1983). As a consequence, the use of organotin compounds (including TBT) on ships was forbidden by the International Maritime Organisation (IMO, 2001).

New alternatives to TBT were development and, currently, the most common antifouling pigment is copper oxide (Callow and Callow, 2002). Copper has been used since the 1800s, even though its utilisation depends of local legislation (Callow and Callow, 2002). However, copper is categorised as toxic for the marine environment when its concentration exceeds some threshold limits (Flemming and Trevors, 1989). Others biocides, such as Diuron<sup>®</sup> and Irgarol<sup>®</sup> 1051, are used together (co-biocides) with copper pigment, even though they are harmful to phytoplankton organisms (Devilla et al., 2005). The use of Diuron<sup>®</sup> is not allowed in the United Kingdom while Irgarol<sup>®</sup> 1051 is limited to small watercrafts (Chesworth et al., 2004). Metallic pyrithiones are also used as co-biocides. However, these compounds show high toxicity for some fish species (skeletal deformities were reported) (Arai et al.,

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2009). Inside this scenario, research on environmentally friendly antifouling agents and coatings has received increasing attention.

Many natural compounds with antifouling properties were found in natural products, as reported by several authors. Etoh et al. (2002) isolated shogaols from roots of ginger that are three times more active than copper sulphate. The behaviour of *trans*-8-shogaol is similar to that of tributyltin fluoride (TBTF) against the adhesion of blue mussels (Etoh et al., 2002). Etoh et al. (2003) also isolated neocurdiol, isoprocurcumenol and 9-oxoneoprocumenol from *Curcuma aromatica* and *Curcuma zedoaria*, using them as antifouling agents against blue mussel. Watts (1995) reported the application of natural or synthetic capsaicin mixed with epoxy resin as an antifouling agent. In fact, the large-scale extraction of natural antifouling agents has become one of the main challenges in the development of ecologic antifouling paint formulations (Qian et al., 2010).

Tannins are natural polyphenolic compounds associated with the defence mechanism of plants (Hagerman and Robbins, 1987). Large amounts of these compounds are typically found in the bark, roots, wood and seeds of many trees (Hillis, 1997; Rahim and Kassim, 2008). Tannins can be classified as condensed, hydrolysable and procyanidins (Amarowicz, 2007; Bate-Smith and Swain, 1962). Condensed tannins are formed by flavonoid units that release anthocyanidins in a controlled medium (i.e. alcohol solutions at high temperatures in the presence of strong acids) (Amarowicz, 2007; Hagerman Ann et al., 1997). Hydrolysable tannins are constituted by gallic acid and its derivatives, which can be esterified to polyols (Hernes et al., 2001). Procyanidins, which are found only in brown algae, are based on phloroglucinol (Amarowicz, 2007; Hernes et al., 2001). Tannins are applied in several fields, for example in surface preparation (Peres et al., 2014a, 2014b), corrosion (Matamala et al., 2000; Rahim et al., 2007, 2008), the leather tannin industry (Onem et al., 2014), adhesives (Pizzi, 1982) and polymers (Szcurek et al., 2014).

The antifouling properties of *Sargassum* procyanidin were reported by Sieburth and Conover (1965). Chet et al. (1975) evidenced that tannic acid acts as repellent of bacteria in immersed surfaces. The presence of bacteria in immersed surfaces is frequently associated with the attachment of fouling species (Chet et al., 1975; Wahl, 1989). Lau and Qian (2000) studied the inhibitory effect of procyanidins, phloroglucinol and tannic acid on the settlement of Barnacles (*Balanus amphitrite amphitrite*). The toxicity and inhibitory effect on the fouling settlement were tested for three larval stages, results depending on the fouling specie and chemical characteristics of the phenolic compounds (Lau and Qian, 2000). Chung et al. (1998) reported an inhibition in the growth of some microorganisms due to the iron-chelating effect of tannic acid. The tannic acid removes iron ions in solution, which are essential for the growth of some aerobic microorganisms (Chung et al., 1998). Slabbert (1992) also described the chelating effects of condensed tannins with several metals, including iron, copper, aluminium, cobalt, vanadium, zinc and nickel. According to Slabbert (1992), the condensed tannins are able to form chelates with metals due to the presence of –OH groups in ortho position on the flavonoid B-ring. Some works reported the utilisation of tannates as antifouling agents in coating formulations (Bellotti et al., 2012a, 2012b; Pérez et al., 2006, 2007; Stupak et al., 2003). Tannates are organometallic compounds derived from the reaction of tannins and metallic salts (Slabbert, 1992). Pérez et al. (2006, 2007) used the copper and aluminium tannates (from quebracho tannin) in the formulation of antifouling coatings. Bellotti et al. (2012a, 2012b) reported the utilisation of zinc tannates obtained from the reaction of tara and quebracho tannins with zinc nitrate. Stupak et al. (2003) found that aluminium tannate (from quebracho, chestnut and mimosa tannins) has a narcotic effect on nauplii of *Balanus amphitrite*. Due to the high solubility of tannin in water, the syntheses of tannates

with zinc, copper and aluminium are necessary to decrease tannin solubility (Bellotti et al., 2012a).

The aim of this study is to investigate the use of a modified black wattle tannin (extract from *Acacia mearnsii*) as an environmentally friendly antifouling agent. The tannin was been modified in an alcoholic medium at high temperatures with the presence of hydrochloric acid, following by adsorption of its soluble fraction in activated carbon. The adsorbed and low soluble fractions of black wattle tannin were used as pigment. The antifouling coatings were formulated with a natural soluble matrix (rosin). This method avoids the utilisation of metals, enabling the utilisation of pure tannin, which contributes to the formulation of an environmentally friendly coating.

## 2. Experimental procedure

### 2.1. Materials

Black wattle tannin (TANAC, Brazil), HCl (Synth, Brazil), absolute ethanol (Synth, Brazil) and activated carbon powder (Delaware, Brazil) were used in the preparation of antifouling pigment. Coatings were prepared using rosin grade WW (RB Sul, Brazil) as matrix, oleic acid (Sigma–Aldrich, USA) as plasticiser and methyl ethyl ketone (MBN chemicals, Brazil) as solvent. The commercial antifouling coating Micron<sup>®</sup> Premium (Akzo Nobel, USA) was used as a control of the antifouling activity and the two-component epoxy primer Intergard 269 (Akzo Nobel, USA) was used as an anticorrosive primer and blank.

### 2.2. Black wattle tannin modification and antifouling pigment preparation

The modification of black wattle tannin was based on Swain and Hillis work (Swain and Hillis, 1959), even though it was with some variations. Firstly, 10 g of black wattle tannin was dissolved in 180 mL of absolute ethanol followed by addition of the 10 mL of deionised water. The mixture was stirred magnetically until homogenisation and 10 mL of concentrated hydrochloric acid was added carefully (drop-by-drop) to the mixture. After the complete addition of the hydrochloric acid, the mixture was heated at 70 °C until the almost complete evaporation of the alcoholic solution. Then, 200 mL of deionised water was added followed by vigorous stirring. After dissolution of the soluble fraction of black wattle tannin, 20 g of activated carbon powder was added and stirred for 1 h. At the end of the adsorption process, the pigment formed by the soluble tannin fraction (adsorbed in activated carbon) and low soluble tannin fraction was filtered in a Büchner funnel and dried for 24 h at 60 °C.

Chemical structure modification of the tannin after hydrolysis was verified by <sup>13</sup>C NMR and FTIR spectroscopies. <sup>13</sup>C NMR spectra were performed using a 300 MHz Bruker AMX300 spectrometer operating at 75.5 MHz. The soluble fraction of black wattle tannin was diluted in DMSO-*d*<sub>6</sub> and the internal standard was tetramethylsilane. FTIR spectra were recorded using an FTIR 4100 Jasco spectrophotometer coupled with an attenuated total reflection accessory (Specac model MKII Golden Gate Heated Single Reflection Diamond ATR). Spectra were obtained after 32 scans at a resolution of 4 cm<sup>-1</sup>, in a spectral range of 600–4000 cm<sup>-1</sup>, in transmittance mode.

### 2.3. Antifouling coating preparation

Initially, 48 g of rosin flakes and 3 g of oleic acid were dissolved in 50 mL of MEK. Then, the dissolved rosin was added in the jacketed reactor of a Dispermat N1 (VMA-Getzmann GmbH of Reichshof, Germany) disperser equipped with a Cowles disc. The

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