



# Modification of cupronickel alloy surface with octadecylphosphonic acid self-assembled films for improved corrosion resistance



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## ABSTRACT

The aim of this work was to form protective and durable films of octadecylphosphonic acid on the surface of CuNi alloy. In order to achieve this goal several parameters of the film preparation procedure were examined: temperature and duration of adsorption as well as the drying temperature. It was found that these parameters had significant impact on the corrosion protection efficiency and durability. The best corrosion protection was obtained when both adsorption and drying were conducted at elevated temperatures. The maximum protection efficiency was 96% for the first and 82% for the 14th day of exposure to corrosive medium.

## 1. Introduction

Cupronickel alloys (CuNi) are often used in marine applications as a construction material, especially for naval vessels, pipelines or desalination plants, because of their good corrosion resistance. However, in such aggressive environment corrosion of CuNi alloys cannot be neglected and application of the corrosion protection is necessary [1]. Commonly, corrosion inhibitors are added to corrosive medium to prolong the service life of copper based structures [2,3].

Marine environment is sensitive to toxic compounds and many commercial corrosion inhibitors are ecologically unsuitable for seawater application. Recently, the application of self-assembled monolayers (SAMs) has been introduced as potential ecologically suitable solution for increasing a corrosion resistance of different metals and their alloys [4–7]. SAMs have been also proposed as an efficient method for biofouling control [8].

The most studied SAM systems are thiols on non-oxidized metal surfaces and silanes on oxide surfaces. However, the disadvantages of these two systems are their oxidation in time and instability in various aqueous and biological media [9–11]. The promising replacement for the thiols and silanes are phosphonate acids since they are relatively stable and can be attached to a wide range of oxide surfaces [12–17].

Most of the studies on phosphonic acids SAMs are focused on their physical properties, characterization of SAM structure and initial corrosion protection [12–15,17], but there are far less studies that examine the efficiency and durability of corrosion protection [18–20], which is very important for their practical application. Moreover, many studies have been conducted on pure metals while studies on alloys are much scarcer. According to our knowledge, only Kruszewski et al. [8]

investigated phosphonic acids layers on cupronickel alloy, however, in their paper, only initial corrosion protection was examined.

In order to achieve efficient corrosion protection SAM should be strongly bonded to the surface, dense, well ordered and defect free. This is not an easy task to achieve on heterogeneous polycrystalline surface of metals and alloys [21,22]. In our previous investigations corrosion protection of cupronickel alloy by SAMs of stearic acids, it was found that much better and longer lasting corrosion protection was obtained when instead of monolayer the multilayer films were formed [23]. Therefore, the aim of this work, is to examine if multilayer films of octadecylphosphonic acid (ODPA) can provide efficient and long-lasting protection to CuNi alloy in 3% NaCl solution. Multilayer films can be formed by the use of solutions with higher organic acid concentration compared to those usually used for monolayer preparation [24–29]. Although thicker than monolayer, multilayer films should also be compact, as porous layers dissolve more easily in aqueous media, thus weakly contributing to corrosion protection efficiency. It has been shown [30] that the thickness, structure and molecular packing of self-assembled films of long chain organic acids depend on the parameters such as temperature, concentration of organic acid and film formation duration. For multilayer films it has been also shown that temperature and time have significant effect on their structure [24–29]. For that reason, the intention of this work is to study the influence of these parameters on the protective properties of ODPA films against CuNi alloy corrosion.

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**Table 1**  
Composition of cupronickel alloy.

Element	Cu	Ni	Mn	Fe
Wt.%	67.3	31.0	1.0	0.7

## 2. Materials and methods

### 2.1. Materials

Investigations were performed on cupronickel alloy rod with a 1.3 cm diameter which was obtained from Goodfellow Inc. UK. The composition of cupronickel alloy is given in Table 1. In order to prepare working electrodes, CuNi rod was cut-out in 0.5 cm thick samples and on their back side a copper wire was soldered. At the end they were embedded into epoxy resin and the exposed surface of working electrode was 1.33 cm<sup>2</sup>. Octadecylphosphonic acid (ODPA, 97%) was obtained from Sigma-Aldrich Corp. USA, while sodium chloride (p.a) and ethanol (96% p.a.) were obtained from Lach-ner d.o.o. Croatia. Solutions were prepared with deionised water (conductivity 0.055 μS cm<sup>-1</sup>).

### 2.2. Sample preparation

The electrodes were abraded with emery paper grade 800, 1200 and 2500 and polished with α-Al<sub>2</sub>O<sub>3</sub> particle size 0.1 μm, degreased with ethanol in ultrasonic bath and rinsed with deionised water.

ODPA film formation on the surface of the alloy was conducted according to the experimental procedures presented in Table 2. They consist of three steps [31]: substrate oxidation which is conducted in order to obtain reproducible oxide layer, ODPA adsorption from ethanol solution and drying of the sample. In order to optimize the preparation method different parameters were investigated: a) the influence of adsorption time (samples A-25 °C, 20 h and A-25 °C, 72 h); b) adsorption temperature (samples A-25 °C, 20 h and A-40 °C) and c) the influence of drying temperature (samples D-25 °C, D-50 °C and D-80 °C).

Acid adsorption occurred in 0.01 mol dm<sup>-3</sup> octadecylphosphonic acid ethanolic solution. Samples were dipped into the solution for the required time of adsorption. For comparison, a blank sample was prepared, on which native oxide layer was formed during 24 h at 80 °C (CuNi). The oxidation and drying were conducted in an air convection oven.

### 2.3. Surface studies

Contact angle (CA) measurements, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were performed with the aim of surface layer characterization. The contact angle measurements on bare cupronickel and the ODPA treated samples were conducted using a goniometer DataPhysics Contact Angle System OCA 20, with a drop of 2 μL water under the ambient atmospheric conditions. All the measurements were conducted in at least ten points. SEM morphology analysis was performed with VEGA 3 SEM TESCAN at an acceleration voltage of 10 kV. FTIR measurements were carried out

**Table 2**  
The investigated ODPA film preparation procedures.

Sample	Oxidation		Adsorption		Drying	
	Temperature	Time	Temperature	Time	Temperature	Time
CuNi	80 °C	24 h	–	–	–	–
A-25 °C, 20h	80 °C	24 h	25 °C	20 h	25 °C	5 h
A-25 °C, 72h	80 °C	24 h	25 °C	72 h	25 °C	5 h
A-40 °C/D-25 °C	80 °C	24 h	40 °C	20 h	25 °C	5 h
D-50 °C	80 °C	24 h	40 °C	20 h	50 °C	5 h
D-80 °C	80 °C	24 h	40 °C	20 h	80 °C	5 h

by attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR), using a Spectrum One FTIR spectrometer from Perkin Elmer, with the scan range from 4000 to 650 cm<sup>-1</sup>, having a resolution of 0.5 cm<sup>-1</sup>, and the results shown in this paper were averages of 25 scans.

### 2.4. Electrochemical measurements

The electrochemical investigations were conducted in a three electrode cell (250 cm<sup>3</sup>), in a solution simulating seawater, 3% NaCl. A platinum foil and saturated calomel electrode were used as the counter and reference electrode, respectively. The polarization measurements were performed in a wide (± 150 mV vs. open circuit potential) and narrow (± 20 mV vs. open circuit potential) potential range, at a potential scan rate of 0.166 mV s<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) was performed at E<sub>ocp</sub> (open circuit potential) in the frequency range 100 kHz–10 mHz with a 10 mV<sub>rms</sub> amplitude. The obtained impedance spectra were interpreted on the basis of equivalent electrical circuits using ZSimpWin software. In general, χ<sup>2</sup> value was always below 5·10<sup>-4</sup>. The electrochemical measurements were performed using a Bio-Logic SP-300 potentiostat. All the measurements were conducted in triplicate.

## 3. Results and discussion

### 3.1. FTIR analysis

Protective films of ODPA were formed on the metal oxide surface of CuNi using dip-coating method described above. FTIR spectroscopy was used to confirm phosphonic acid film formation and to analyse the alkyl chain ordering in the film.

Characteristics of the methylene (CH<sub>2</sub>) stretching region of the FTIR spectrum indicate whether or not an ordered film is present on the surface. A well-ordered film has been characterized as having alkyl chains in an all trans configuration on the substrate with characteristic peaks at ν<sub>CH2asymm</sub> ≤ 2918 cm<sup>-1</sup> and ν<sub>CH2symm</sub> ≤ 2850 cm<sup>-1</sup>. Shifts of these peaks to higher wavenumbers indicate a disordered film with gauche interactions in the alkyl chain [15,32–35]. Although, FTIR has been mainly used to characterize monolayer films, it was also applied in characterization of self-assembled and Langmuir-Blodgett multilayer films [36–40].

The spectra presented in Fig. 1 exhibit adsorption peaks characteristic for well-ordered films for all studied samples.

Still, by taking in account the complexity of studied films, it cannot be completely ruled out that at some spots film could be less ordered, especially at the film/pore boundary.

For phosphonic acid, the IR stretch values in the P–O region, which correspond to 1300–900 cm<sup>-1</sup>, can provide information about the type of bonding of the head group with the substrate. However, preliminary ellipsometric measurements conducted on samples treated with 1 mM ODPA (A-40 °C/D-25 °C procedure) showed that the thickness of the film around 17 nm while the thickness of film formed in 10 mM ODPA solution is higher but could not be accurately determined with ellipsometry as the films become blurry with the increase in thickness. Thus the ODPA layers obtained in our study where not monolayers but multilayers and FTIR spectra given in Fig. 1 cannot be used for accurate determination of ODPA bonding to CuNi surface as the vibrations of upper layers probably dominate in the obtained spectra. Studies on ODPA adsorption [8] on CuNi alloy point towards bidentate bonding of ODPA molecules on the surface of the alloy. Fontes and al. [26] found that H-bonds may form between headgroups in adjacent ODPA bilayers when samples are annealed in the temperature range between 60 °C and 110 °C. In their work formation of H-bonds was observed as the shift of peaks in P–O region towards lower wavenumbers. In our work, shift of P=O stretching vibration towards lower wavenumbers (around 1242 cm<sup>-1</sup>) was observed with the increase of drying temperature.

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