Improving the corrosion properties of amorphous Ni-P thin films using different additives

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Highlights

- Effects of various additives on the corrosion resistance of Ni-P films is studied.
- Thinner, more uniform, and smoother Ni-P thin films are formed with additives.
- Excellent improvement of the corrosion resistance is observed.

Abstract

Ni-P amorphous coatings are considered as important engineering alloys. In this paper, the effects of various additives on the properties of Ni-P thin films were investigated, including saccharine, glycine, pyridinium propyl sulfonate, coumarin, sodium citrate, and cerium sulfate. Potentiodynamic polarization and electrochemical impedance spectroscopy tests, scanning electron microscopy, X-ray fluorescence and diffraction, and atomic force microscopy were employed to study the properties of the samples. It was found that a proper concentration of these additives, except saccharine, noticeably improved the corrosion resistance, especially at high potentials (about 25% increase in instantaneous corrosion efficiency and about 300% in corrosion efficiency at high potentials) and decreased the surface roughness (by about 10 to 55 %) of Ni-P thin films. Thinner, more uniform, and less porous coatings were formed in the presence of additives. Except saccharine, all the additives enhanced the P content of Ni-P films, which thus kept their amorphous structure; saccharine highly suppressed the incorporation of P inside the Ni lattice and a mixed amorphous-crystalline structure was stabilized.

Keywords: Ni-P coatings, additives, electrodeposition, corrosion efficiency

1- Introduction

Cu and its alloys, in bulk or electrodeposited form, are considered important materials in industry due to their high electrical and thermal conductivity, mechanical workability, low chemical reactivity, and atmospheric corrosion resistance. Such properties make these materials suitable for many applications, including electronics, telecommunications, and heat exchangers. However, their poor corrosion properties, especially in the presence of aggressive ions like chlorides, limit their usage [1–4]. As a result, there are several studies related to the

1 improvement of the corrosion properties of Cu and its alloys using different
2 approaches including protective coatings [2,5] and corrosion inhibitors [1,6–8].

3 The preparation of thin film coatings using electrochemical methods is attractive due
4 to their simplicity, the opportunity to work generally at ambient temperature, the
5 uniform and controllable deposition rate, the possibility to form multilayers, the
6 ability to coat large surfaces in almost any shape and geometry, and the low cost
7 [9,10]. Electrodeposition is one of the most frequently used methods, which can
8 promote the appearance, extend the lifetime, and improve the performance of the
9 substrate by producing metallic (metals, alloys, composites) single or multi-layers
10 through a highly controllable procedure [11]. Compared to other methods of forming
11 thin films (such as physical deposition processes [12]), electrochemical techniques
12 are more economical, and thus, they are widely used to cover a wide range of
13 applications like electrical contacts, corrosion and wear resistance, decorative
14 purposes, photovoltaic devices, and so on [9,13]. The electrodeposition of iron group
15 metals (Ni, Co, and Fe) in particular attracts interest due to their unique magnetic
16 and thermophysical properties [5].

17 Ni-P coatings are considered important engineering alloys due to their interesting
18 combination of properties, i.e. good corrosion and wear resistance, good
19 solderability, high electrical conductivity, smooth and uniform surface morphology,
20 low friction coefficient, electrocatalytic activity, and paramagnetic characteristics;
21 they can be obtained through simple electrochemical methods [5,14–17]. These
22 alloys can be also employed as the under-layer for other top coatings [18]; they are
23 especially important in microelectronics due to their usage as diffusion barriers
24 between copper and gold and for the corrosion protection of contacts [5]. Cu/Ni-
25 P/Au multi-layer films are used in electronics and microelectronics in applications
26 such as switches, relays, circuit breakers, SIM cards, electrical contacts, and
27 contactors, because they present a combination of high electrical conductivity,
28 corrosion resistance, and wear resistance [19–22]. Compared to Ni coatings, Ni-P
29 films present a bright, shiny, and smooth look [15], and are less susceptible to
30 oxidation [23]. It is well known that phosphorus cannot be electrodeposited as a pure
31 phase, but its co-deposition with iron group metals is possible. The electrodeposition
32 mechanism of Ni-P coatings is based on the reduction of Ni ions and PO_3^{3-} ions. In
33 fact, Ni^{2+} ions are reduced on active surface sites of the cathode and then diffuse to
34 a proper site of the lattice. The co-deposited P atoms hinder the Ni diffusion, and
35 thus impede crystalite nucleiation. Therefore, the amount of P in the alloy affects its
36 crystallographic structure; increasing the P content changes the microstructure from

1 crystalline to nano-crystalline and finally to an amorphous state. According to the
2 literature, there is not a specific content but a range of P contents for the crystalline
3 to amorphous transition of Ni-P coatings [15]. However, coatings with P contents
4 higher than 8% present usually an amorphous structure [14]. Given that the P content
5 largely determines the properties of Ni-P coatings shows the importance of the
6 chemical composition of the electrodeposition bath. it is well known that
7 introducing even a small amount of certain compounds as additives to the electrolyte
8 significantly affects the properties and appearance of deposits [24]. The refinement
9 of the microstructure, with a decrease of the internal stress and the surface roughness,
10 an increase of the brightness , and the improvement of the corrosion resistance and
11 mechanical properties of the coatings are some of the reported benefits of additives
12 [11,16,17,23,25–29]. Organic compounds are the most commonly used additives,
13 and they are called carriers, brighteners, complexing agents, leveling agents, and so
14 on, based on their purpose; carriers are those that are added to refine the grain size
15 and increase the luster [25]. There are several studies regarding the effects of using
16 saccharine [23], glycine [26], coumarin [29], sodium citrate [30] as organic
17 additives. Moreover, similar benefits have been also reported by adding rare metal
18 salts to the deposition electrolyte [31]. Based on these studies, utilizing even small
19 quantities of these compounds can highly enhance the properties of the obtained
20 coatings, and thus, their usage is highly recommended.

21 There are several studies regarding the improvement of the corrosion resistance of
22 Ni-P films, including the preparation of ternary alloys and composite coatings.
23 **Implementing additives are not as challenging as forming ternary alloys [32] and**
24 **there is no concern about their agglomeration as it occurs for nano-particles [33].**
25 **Therefore,** additives are easier to use, more economical, and more practical for **the**
26 **mentioned** purpose. To the best of our knowledge, among all the published papers
27 related to the utilization of additives, there is no study regarding the comparison of
28 the effects of different additives on the corrosion resistance of Ni-P coatings on
29 copper. Moreover, almost all studies have used high deposition times, and thus,
30 investigated the effects of additives on thick layers. As a result, there is no work
31 about the effect of several additives on the properties of thin Ni-P films and finding
32 their optimum concentration.

33 In this paper, the effect of different additives has been investigated and compared
34 for thin Ni-P layers formed on copper, which is especially interesting for
35 microelectronics. The additives include saccharine that is the most commonly used
36 carrier, brightener, and stress reducing agent; coumarin as brightener; pyridinium

ions as auxiliary brightener [25]; glycine that is the smallest amino acid [26] as complexing and buffering agent [34]; sodium citrate used as complexing, buffering and leveling agent [11]; and cerium sulfate as a rare metal salt [31]. However, it should be noted that while a combination of additives is usually applied for the deposition of single ions, e.g. Cu [24], Ni [25], their synergistic effect [11] could limit their influence on the electrodeposition of Ni-P alloys. Therefore, we present only the effect of individual mentioned additives in the following.

2- Experimental procedure

Industrially available smooth Cu films were used as the substrate for Ni-P electrodeposited coatings. All samples underwent a chemical pretreatment: 30 s in a diluted basic solution (1 mL of 30% NH_4OH solution in 200 mL of demineralized water), 30 s in demineralized water, and 30 s in a 10% H_2SO_4 solution to eliminate oxides, if there are any, and clean the surface before the deposition process.

A common electrodeposition bath, containing 190 g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ + 10 g/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (as Ni source), 8 g/L H_3PO_3 (as P source), 5 mL/L H_3PO_4 (to enhance the stability of H_3PO_3), and 16 g/L H_3BO_3 (as buffering agent) has been employed as the main bath to form the Ni-P coatings. 5 different concentrations of additives were prepared: saccharine and glycine (0.1, 0.5, 1, 2.5, and 5 g/L), coumarin (5, 10, 50, 100, and 250 mg/L), pyridinium propyl sulfonate (0.1, 0.5, 1, 2, and 4 g/L), sodium citrate (4, 8, 12, 16, and 20 g/L), and cerium sulfate (4, 8, 12, 20, and 30 mg/L). All the chemicals were provided by Sigma-Aldrich with high purity. They were added to the main bath to investigate their effects on the corrosion resistance of Ni-P coatings. The pH of the deposition electrolyte, in the absence and presence of additives, was 1. All the samples are named using the first three letters of their respective additives and their concentration; i.e. Cou.10m represents the Ni-P coating formed in the presence of 10 mg/L of coumarin as the additive.

A 3-electrode setup cell was used for the coating process: the pretreated Cu films was the cathode or working electrode, a Pt electrode functioned as the anode or counter electrode, and Ag/AgCl (KCl saturated) performed as the reference electrode. All samples were coated at 60 °C using a Solartron 1287 potentiostat at a constant potential of -1 V vs. the reference electrode for 7 minutes, while the solution was stirred at a speed of 650 rpm. These conditions were employed after preliminary experiments (not presented here) to obtain bright, homogeneous and compact Ni-P films. The mass of the coatings was measured by subtracting the mass after and

1 before the deposition process using a precision scale ($\pm 10^{-4}$ g). Three coatings were
2 made for each condition.

3 Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization
4 tests were employed to determine the corrosion properties of the obtained Ni-P films
5 in the absence and presence of different concentrations of the mentioned additives.
6 The same setup as for the coating process was used for the corrosion measurements;
7 the coated samples acted as the working electrode. All tests were performed using a
8 PARSTAT 2273 potentiostat, which was operated by the PowerSuit software after
9 1 h immersion in a 3% NaCl solution. The EIS measurements were done in a
10 frequency range of 10 kHz-10 mHz with a voltage amplitude of 10 mV (peak-to-
11 peak) versus the respective Open Circuit Potential (OCP). The Zview software was
12 used to analyze the obtained EIS data. The potentiodynamic polarization
13 experiments were carried out from -300 mV (vs. OCP) to 500 mV (vs. reference
14 electrode) at a scan rate of 0.5 mV/s. The area exposed to the corrosive medium was
15 measured after the tests and used to normalize the obtained corrosion data. Each test
16 was repeated twice to be sure of its validity.

17 After evaluating the corrosion results, the best samples among each category were
18 chosen for further characterization. A Siemens D5000 diffractometer was used to
19 evaluate the structure of the selected samples. X-ray diffractometry (XRD) with
20 0.04° step size over the 2θ range of $40\text{--}55^\circ$ was done using Cu K α radiation ($\lambda =$
21 0.15406 nm) generated at 40 kV and 30 mA. A scanning electron microscope (SEM)
22 model Philips XL 30 ESEM equipped with an Energy dispersive spectroscopy
23 (EDS) analyzer was used to investigate the surface morphology and chemical
24 composition of the selected coatings. The thickness of the samples was measured at
25 different locations of the samples using the X-ray fluorescence technique
26 (Fischerscope XRAY XDV- μ). A Digital Instruments Dimension 3100 atomic force
27 microscope (AFM) was also employed for a more detailed examination of the
28 morphology and to measure the roughness using Nova software.

30 **3- Results**

31 Figure 1 shows the effects of the additives on the current density during the
32 electrodeposition process. As it can be seen, the current density decreases rapidly at
33 the beginning of the coating procedure and then stays at a stationary value until the
34 end of the process. Moreover, the addition of all chosen additives to the Ni-P
35 electrodeposition bath led to lower current densities during the coating procedure.

1 For example, the current is almost divided by 3 in the case of the addition of sodium
2 citrate, and by 1.5 when cerium sulfate is added to the Ni-P bath. Therefore, even if
3 only the water side reaction is impacted by the additives, the thickness of the Ni-P
4 layers in presence of additives is assumed to be decreased as well. This assumption
5 will be checked later by cross-sectional observations, gravimetric and X-ray
6 fluorescence measurements.

7 Table 1 and Table 2 present the analyzed information from potentiodynamic
8 polarization and EIS tests, respectively. Figure 2 depicts the surface of the samples
9 before and after the corrosion tests. The curves for samples that were considered the
10 best in each category are depicted in Figure 3 and

11 Figure 4. Based on the presented data and irrespective of the presence of additives,
12 applying a Ni-P layer on Cu shifted the corrosion potential to more negative values
13 and decreased the corrosion current density. The use of a proper amount of the tested
14 additives improved the corrosion properties of Ni-P films, especially at high
15 potentials.

16 Figure 7 shows the X-Ray diffraction patterns of the chosen samples in each
17 category, and Figure 8 shows their surface morphology. Figure 9 shows the cross-
18 section and the surface of the Ni-P layer with no additive before and after corrosion.
19 The chemical composition of these samples, obtained using the EDS technique, are
20 summarized in Table 4 and the average thickness of the coatings with their variations
21 determined by X-ray fluorescence on the complete surface of the samples, can be
22 found in Table 5. The thickness of the Ni-P layer from the cross-section image is in
23 a good agreement with the values measured by X-Ray fluorescence. Figure 11 and
24 Table 6 represent the surface morphology and the average roughness values of the
25 samples obtained by AFM. All the samples present a similar surface morphology
26 containing globular fungi-form features. However, thinner and smoother coatings
27 were formed in the presence of additives. This observation implies that the additives
28 have a noticeable effect on the thickness and roughness of the coatings, but their
29 surface morphology is controlled by other parameters, i.e. coating conditions. With
30 the exception of the sample Sac. 2.5 that has only around 2% of P, the P content is
31 around 14% in the others. The X-ray patterns of all samples, except Sac. 2.5, is
32 similar to the substrate, meaning that the Ni-P layers present a completely
33 amorphous structure. In the X-ray pattern of Sac. 2.5, however, there are two broad
34 peaks related to the presence of crystalline Ni; its structure is a mixture of amorphous
35 and crystalline phases.

4- Discussion

The Tafel extrapolation method was employed to extract the summarized data in Table 1, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic and cathodic Tafel slopes (β_a and β_c). The polarization resistance (R_p) was calculated using the Stern-Geary equation [35] :

$$R_p = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c) i_{\text{corr}}} \quad (1)$$

i_{corr} can be used as criterion for comparing the corrosion resistance; a lower i_{corr} means a higher corrosion resistance. It is well-known that a localized corrosion process occurs on Ni-P films with a porous Au top-coat based on the high ratio of cathode area (Au) to anode area (Ni-P) that leads to a high polarization of the Ni-P film [19,36,37]. The current density value at high potential, such as +0.6 V vs. OCP, can also be used to simulate the corrosion resistance of different Ni-P layers. Thus, i values measured at a potential of +0.6 V vs. OCP for all samples are also presented in Table 1.

Based on the analyzed potentiodynamic data, applying the Ni-P layers on Cu shifted the corrosion potential to more negative values, decreased the corrosion current density and increased the polarization resistance - meaning that they can act as a sacrificial anode for the Cu substrate, and thus, eliminate its localized corrosion [31] and improve the corrosion resistance. Moreover, they have higher anodic slopes meaning that the rate of the anodic reaction by the dissolution of metal (Ni for coatings against Cu for the substrate) has decreased. However, the cathodic slope almost did not change, except some samples in Sac. and Gly. Categories, meaning that the same cathodic reaction rate due to the hydrogen evolution is observed during the corrosion process. It can be seen that all the presented Tafel plots have almost similar cathodic branches, and while the substrate undergoes a fast active dissolution, the coatings show a pseudo-passivation behavior in their anodic branch; this layer is broken only for Sac. 2.5 and the Ni-P layer with no additives (around -0.1 V vs. Ag/AgCl), and therefore, they have an accelerated corrosion at high potentials (Figure 3). This feature explains the appearance of these samples after corrosion (Figure 2), where Ni-P and Sac.2.5 are blackened at the edges or completely dissolved, respectively; the other samples kept their primitive shiny gray appearance after the corrosion process.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to detect the ongoing interfacial reactions and characterize the coating corrosion properties. A simple model consisting of a solution resistance (R_s) in series with a parallel circuit of a constant phase element (CPE_{dl}) and a polarization/charge transfer resistance (R_{ct}) and with a Warburg element (Figure 5.a) has been usually employed to fit the EIS data of copper corrosion in chloride containing solutions. The Warburg element represents the fact that the corrosion of copper is controlled by the diffusion of oxygen through the interface at low frequencies [7] due to the formation of a non-protective $CuCl$ film [1]. The fit values for this element were $6059 \Omega \cdot cm^2$ (W-R), $165.9 s$ (W-T), and 0.43 (W-P). There is no Warburg element for Ni-P coatings though and the Randles model (Figure 5.b) is usually reported to be the best fit for the EIS data [14]. This model is the same as the proposed model for the substrate without the Warburg element.

The CPE is used, because the formed double layer does not usually present an ideal capacitance behavior; its impedance is expressed as:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (2)$$

Where Y_0 is the admittance constant, j is the imaginary number, ω is the angular frequency ($\omega = 2\pi f$) and n is the exponent of CPE. The n value, which varies from 0 to 1, depends on the surface roughness and heterogeneity because of the non-uniform current distribution [35]. The n value can determine the nature of the electrochemical element; the element is an ideal capacitance if $n = 1$ and it is a Warburg element if $n = 0.5$ [7].

Similar EIS curves, i.e. Nyquist and Bode plots, show that all coatings undergo the same fundamental electrochemical reaction. The presence of a single semi-circle in the Nyquist plots (and a single peak in the Bode-phase plot) of the coatings indicates that the corrosion process involves a single time constant, which corresponds to the charge transfer reaction, meaning that the dissolution of Ni during the corrosion is the main process. The different radius of the semi-circles is a representative of the different active area where this reaction occurs. The resistance value at low frequencies in the Bode-Z plot and the extracted data using the proposed impedance models (Table 2) can be used to evaluate the corrosion results. They imply that improving the corrosion resistance of the substrate by applying Ni-P electrodeposited coatings is mainly related to the reduced charge transfer at the interface of electrolyte and electrode. It is believed that the dissolution of Ni occurs

in the early stages of corrosion that leaves a P-rich film behind. This film then hinders further dissolution of Ni and decreases the corrosion rate [31].

Using the obtained corrosion resistance from polarization and EIS tests, one can calculate corrosion efficiency (CorE) and porosity density (P.D) of the electrodeposited coatings (Table 3) employing the equations 3 [14] and 4 [38], respectively.

$$(CorE\%) = \left(1 - \left(\frac{R_{PS}}{R_P}\right)\right) * 100 \quad (3)$$

$$P.D = \frac{R_{ps}}{R_p} \times 10^{-\left(\frac{\Delta E}{\beta_a}\right)} \quad (4)$$

ΔE is the difference between the corrosion potential of the coated sample and the substrate, β_a is the anodic slope of the substrate, and R_{ps} and R_p are the polarization resistance of the substrate and the coating extracted from Tafel plots, respectively.

Charge transfer resistance values obtained from EIS tests, according to reference [39], can be considered equal to polarization resistances, and hence they were inserted in equation (3) to measure the corrosion efficiency. An equation similar to

(3) could be employed to calculate the corrosion efficiency at high potentials using the current density values at these potentials (Table 1) bearing in mind that the current density and the polarization resistance have an inverse relationship. The Ni-P layer without additives has a 63.4/55.5 corrosion efficiency % (using Tafel/EIS test data), a really low corrosion efficiency at high potentials (-210%) and 12.8% of porosity, possibly more around the edges given that the edges blacken after the corrosion tests (Figure 2). The blackened parts proved to be Nickel oxide (NiO) based on EDS analysis. The surface and cross-section morphology of the blackened part is presented in Figure 9. It can be seen that more than half of the Ni-P film is corroded and converted to NiO, leaving a cracked surface behind. The fast Ni dissolution that blackened the edge left a high P content film (20 wt. %) with a high internal stress [17], which explains the cracked surface. It should be noticed that the cross-section and surface of the shiny part is intact after corrosion while the P content has increased. Therefore, one can assume the same for other samples using additives that kept their shiny look after corrosion. It is well known that there is a non-uniform distribution of current around the edges during the deposition that can lead to the formation of a non-uniform coating. There is a pseudo-passivation region in its anodic branch (Figure 3) that ends around -0.1 V (vs. Ag/AgCl). This could be due

1 to the localized attack of chlorine ions at the edges of the Ni-P coatings that led to a
2 galvanic corrosion between copper and nickel, and thus, a fast oxidation of Ni that
3 blackens the edges; which also explains the high current, and a negative corrosion
4 efficiency at high potentials. The whole surface of the substrate got slightly tarnished
5 and there is a passivation looking-region in its polarization curve at high potentials,
6 possibly due to the oxidation of the surface or the formation of a chlorine film. Based
7 on Figure 2, introducing the additives has homogenized the current distribution; it
8 can be also concluded that employing a proper content of additives can efficiently
9 improve the corrosion efficiency, especially at high potentials, and highly decrease
10 the porosity content (Table 3). This is especially important for the microelectronic
11 contacts, where a severe corrosion phenomenon is reported at their edges, and the
12 presence of a gold top-coat requires a barrier film with a good corrosion resistance
13 at high potentials due to the galvanic corrosion between gold and the Ni-P sublayer
14 [36,37].

15 4-1- Effect of saccharine as an additive

16 The adsorption of additives on the surface of the cathode is reported to affect the
17 activation energy, charge transfer rate in the electrochemical reactions, and electro-
18 crystallization mechanism. Therefore, introducing additives to an electrodeposition
19 bath affects the deposition procedure, and thus, the properties and structure of the
20 obtained coatings [27]. Saccharine is one of the most used brightening agents in the
21 electrodeposition of nickel. Its effect on the brightness of the coatings comes from
22 its ability to refine the grains and increase the cathode polarization. Amorphous films
23 with lower P content can be obtained in the presence of saccharine, because
24 saccharine adsorbs on the cathode surface, limits the number of deposition sites and
25 obstructs the surface diffusion of Ni. As a result, multi-phase deposits can be formed
26 when saccharine is present in the electrolyte. Moreover, the addition of saccharine
27 can also improve the physical properties of the coating because it can inhibit the
28 discharge of protons on the cathode surface [23], and thus, it suppresses the hydrogen
29 evolution reaction during the deposition process [26]. It is also reported that
30 saccharine decreases the internal stress of Ni-P coatings, however, the segregation
31 of sulphur into the grain boundaries can increase the internal stress again in high
32 concentrations [17]. Our results show that even though the instantaneous corrosion
33 resistance has been improved (especially Sac. 2.5), the general corrosion behavior
34 could not be considered appropriate due to the following reasons. The cathodic
35 slopes are lower in the presence of saccharine meaning a higher cathodic reaction
36 rate. The oxidation current densities at the end of experiments are relatively high

(and thus the corrosion efficiency is low at high potentials). The surface of the coatings have uniformly blackened after the corrosion process, and have completely dissolved at saccharine concentrations above 1 g/L (Figure 2). In the case of Sac. 2.5, the coating has a low P content (1.8 wt. %), and a mixed crystalline-amorphous structure. The crystallinity of coatings should be enhanced with increasing saccharin concentration, since it hinders the incorporation of P. Moreover, the common defects of a polycrystalline layer, like grain boundaries, can act as high-speed pathways for the diffusion of copper to the surface during the corrosion process, especially at high potentials [36]. Therefore, a galvanic corrosion phenomenon between nickel in the crystalline state (anode) and the amorphous state (cathode) could be the reason of the blackening/dissolving of the layer in the presence of low/high concentrations of saccharine. This could be also supported by the fact that saccharine shifted the corrosion potentials compared to the Ni-P one. Moreover, Murugan et al. [37] have reported that eliminating the Ni(crystalline)/Ni-P(amorphous) interface has improved the corrosion performance of stacked layers. This could be easily extended to our results as well. Therefore, employing saccharine as an additive, especially for microelectronics where there is a porous gold topcoat, can lead to the fast corrosion of the barrier layer, and hence, its usage should be avoided for Ni-P thin films.

4-2- Effect of glycine as an additive

Glycine is another brightener that can be introduced to the electrolyte. It can act as a buffering and complexing agent, and thus, improve the corrosion behavior, increase the brightness, and modify the structure [26,27,34]. Regarding our results, glycine as an additive efficiently improved the corrosion resistance of Ni-P thin films; however, a further increase of its concentration had a negative effect, i.e. the corrosion efficiency decreased by 10%-15% by increasing its concentration from 0.1 to 5 g/L based on the Tafel (EIS) data. In comparison to the film with no additives, the coatings possessed a higher anodic slope (β_a) representing a slower anodic dissolution of nickel ions. However, the β_a value decreased with increasing glycine concentration, meaning a faster dissolution of Ni in the presence of more glycine. This result is in agreement with the data of Guo *et al.* [40], who used cyclic voltammetry to study the deposition of Ni-Mn films with glycine as complexing agent and showed that the dissolution of Ni occurs faster in the presence of glycine. The Ni-P coatings present lower cathodic slopes meaning a higher hydrogen evolution rate. The obtained polarization and charge transfer resistances from the corrosion tests show that glycine in low concentrations, i.e. 0.1 g/L, can improve the

corrosion efficiency of Ni-P thin films. As it can be seen in Figure 2, the coated samples have kept their appearance after corrosion tests up to a glycine concentration of 2.5 g/L. At higher concentrations, the surface blackened and the film dissolved mostly at the edges. The EDS analysis showed that glycine, similar to saccharine, can reduce the P content: it decreased from 14.6% at 0.1 g/L glycine to only 6.4 % at 2.5 g/L of glycine. Therefore, the same galvanic corrosion phenomenon, however in less extent compared to the saccharine samples, occurred and the surface of the samples blackened in high concentrations. By taking the corrosion efficiency at high potentials into account, it can be concluded that the coatings undergo a fast dissolution at high potentials in concentrations above 1 g/L of glycine.

4-3- Effect of pyridinium propyl sulfonate as an additive

Pyridinium propyl sulfonate (PPS) is an active sulphur containing organic compound that is reported to have a powerful effect on the brightening of Ni deposits. It was classified as an auxiliary brightener, and it is effective when it is used in a low concentration (0.1- 4 g/L) [25]. Its usage for Ni-P coatings, however, is not reported so far. Based on the extracted data from corrosion tests, the use of PPS as an additive in low concentrations, i.e. 0.1 g/L, leads to an improvement of the corrosion performance of Ni-P thin films. However, its effect was diminished by increasing the concentration; the corrosion efficiency decreased about 15% by the increase of PPS concentration from 0.1 to 4 g/L. This is especially evident for the corrosion efficiency at high potentials, where almost a 100% drop can be seen as the concentration increased. Moreover, exfoliation of the coatings during the corrosion process occurred in concentrations above 1 g/L (Figure 2). Pyridinium presents a cationic nature when it is added to acidic solutions [41,42]. Therefore, it competes with metal ions during the deposition procedure and can suppress the cation reactions. As a result, the use of high concentrations of PPS can degrade the coating quality, including an easy exfoliation by weakening the bond strength between the substrate and the coating [43].

4-4- Effect of coumarin as an additive

Coumarin is reported to lead to coatings with a shiny look, good conductivity, and proper mechanical properties. However, it is known to highly increase the internal stress and brittleness, and hence, its concentration should be kept as low as possible (0.005 – 0.2 g/L) [25,29,44]. Moreover, its toxic nature is another reason to use it only in low concentrations [45]. Table 1 to Table 3 show that coumarin even used in very small quantities has improved the corrosion behavior. The corrosion efficiency

of Ni-P thin films increased by about 25% (about 300% at high potentials) by adding 5 mg/L of coumarin; the Ni-P films kept their appearance after the corrosion tests (Figure 2). Meanwhile, the addition of 5 mg/L of coumarin increased the P content by 3.4% and such high P content gave Cou.5m an amorphous structure. However, no meaningful relation between the additive concentration and the corrosion resistance can be observed, possibly due to the small range of tested concentrations compared to the other additives.

4-5- Effect of sodium citrate as an additive

Sodium citrate can act as brightening, leveling, and buffering agent in electrodeposition electrolytes, and thus, eliminates the need for other additives [11]. However, it is mainly known as a complexing agent, and thus, the deposition occurs from Ni ions in complex form, not free ions. Higher bath stability, higher deposition rate, lower roughness, and better corrosion resistance are the reported effects of using sodium citrate as an additive for coatings [16,30,46]. Our results show that sodium citrate, which is relatively inexpensive, has interestingly improved the corrosion behavior of Ni-P films and their appearance was intact after the corrosion process. Moreover, 4.8% more P content was incorporated inside the Ni-P layer in its presence (4 g/L) that explains its amorphous structure. However, increasing the concentration from 4 to 20 g/L slightly decreased the corrosion efficiency.

4-6- Effect of cerium sulfate as an additive

Finally, it has been reported that a slight addition of rare earth metals, such as Ce, Yb, and La, into deposition electrolytes refines the microstructure, decreases the grain size and improves the corrosion resistance of the obtained coatings. Rare metals tend to adsorb and form a thin film on the surface of the substrate - preferentially on crystal defects such as dislocations and grain boundaries - due to their unique 4f electron configuration, strong adsorption capacity, low electronegativity, and large atomic radius. Therefore, they decrease the amount of catalytic sites, hinder the electron transfer among ions, reduce the surface energy and increase the nucleation rate, which refines the deposited coatings. Moreover, it was demonstrated that rare metals are not incorporated inside the deposited film, and thus, they are not consumed during the process [31]. Our results show a better corrosion efficiency, both instantaneous and at high potential, and better appearance after the corrosion tests in the presence of cerium sulfate compared to its absence. The corrosion resistance notably increased by increasing its concentration to 8 mg/L; a further increase of concentration decreased the efficiency. This result is in

accordance with Huang et al. [31], who suggested that a small amount of Ce ion addition decreases the defect density of coatings; however, they will also hinder the deposition of ions and lower the deposition rate. Therefore, they diminish the coating quality and corrosion resistance in high concentrations. As conclusion, the effect of the addition of rare earth metals on the properties of the deposited coatings completely depends on their concentration.

4-7- Comparison of the effects of each additive added in the selected concentration on the properties of thin Ni-P coatings

As a conclusion of the experiments described above, Sac. 2.5, Gly. 0.1, Pyr. 0.1, Cou. 5m, Cit. 4, and Ce. 8m were chosen as the best samples in each category with regard to the corrosion resistance. Figure 6 presents the corrosion efficiency of these samples; instantaneous and at high potentials.

By measuring the coating mass and its chemical composition, one can employ the following equation to calculate the coating efficiency [47]:

$$CE \% = \frac{mF}{It} \sum \frac{c_i}{n_i} \quad (5)$$

Where m is the coating mass (g), F is Faraday's constant (96485 C/mol), I is the total current (A), t is the deposition time (s), c_i is the mass fraction of the element (Ni, and P), and n_i is the number of transferred electrons.

The measured mass, thickness, and coating efficiency of the chosen samples in each category are presented in Table 5. It is obvious that introducing the additives to the electrolyte decreased the coating efficiency from 3.5% (Sac. 2.5) to 5% (Cou. 5m). Therefore, it can be concluded that employing the additives leads to coatings with higher corrosion efficiency and lower coating efficiency, respectively. Moreover, all the coatings are amorphous, except Sac. 2.5 that has a mixed crystalline-amorphous structure. Figure 9 shows the cross-section of the Ni-P layer with no additive: it can be seen that a uniform compact coating has been formed. As it was suspected, the addition of these compounds have decreased the average coating thickness, i.e. from about 1 μm for Sac.2.5 to 1.7 μm for Gly.0.1 compared to the thickness of the Ni-P layer with no additives (Table 5). However, the thickness variation has also decreased, meaning that a more uniform coating was formed in the presence of additives (1.01 μm for Ni-P vs. 0.16 μm for Gly.0.1). Furthermore, again except Sac. 2.5, they have higher P content, lower roughness, and better stability at high potentials compared to the Ni-P layer with no additives. However, all the additives, including saccharine, decreased the porosity content, leading as the same time to an

improvement of the instantaneous corrosion resistance. Table 6 shows that employing additives, except saccharine, can decrease the surface roughness from 31 nm (Cou.5m) to 186 nm (Pyr.0.1) with respect to their absence (341 nm). It is well known that coatings with higher quality and better properties form on smoother substrates, and the roughness of the substrate has an important impact on the physical properties of multilayer coatings [48,49]. Therefore, the ability of these additives to smooth the surface is especially important for electrical contacts where there is a gold top-coat. The porosity content of this top-coat is known to be the most important parameter determining the lifetime of microelectronic devices. It was reported that decreasing the substrate roughness from 0.4 μm to 0.2 μm decreased the electrographic porosity index of the gold layer by about ten times [50].

In order to investigate the relationship between the P content, the corrosion efficiency and coating efficiency of the amorphous Ni-P layers, the P content of the samples with glycine and cerium sulfate as additives was measured using the EDS technique. Figure 10 depicts the P content, corrosion efficiency and coating efficiency of coatings with glycine and cerium sulfate as function of their concentration. While there is a similar trend for the corrosion efficiency and P content, there is no trend for the coating efficiency as function of the concentration of additives. Therefore, the P content definitely plays an important role in determining the corrosion behavior of amorphous Ni-P layers.

5- Conclusions

In this paper, we have investigated the effects of different additives on the properties of Ni-P thin films. Based on our results, it can be concluded:

- The P content plays an important role for the corrosion resistance of amorphous Ni-P films: a higher P content improves the corrosion resistance.
- In the presence of additives, thinner and more uniform coatings with similar surface morphology are formed. However, they decreased the coating efficiency.
- Employing the proper concentration of additives effectively enhanced the corrosion efficiency of Ni-P thin films.
- Saccharine improved the instantaneous corrosion resistance; however, an accelerated corrosion at high potentials was observed so that its usage should be avoided in electronics. Moreover, Saccharine decreased the incorporation

of P inside the Ni lattice and thus a mixed crystalline amorphous structure was formed when saccharine was in the electrolyte.

- Glycine and PPS, especially in low concentrations, proved to be effective additives to improve the corrosion efficiency of Ni-P layers, decreased the roughness and increased the uniformity of the coatings. A further increase of their concentration, however, had a negative effect on corrosion properties of Ni-P layers.
- Coumarin and cerium sulfate can be considered as interesting additives, because even a low concentration of them (mg/L) noticeably enhanced the properties of amorphous Ni-P thin films.
- Sodium citrate proved to be an effective (and economical) additive to improve the properties of Ni-P coatings; its impact depended only slightly on its concentration.

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Tables

Table 1. Analyzed data from Potentiodynamic polarization tests

Sample		i_{corr} ($\mu\text{A.cm}^{-2}$)	E_{corr} (mV) vs. Ag/AgCl	Average Tafel slope (mV. dec ⁻¹)		R_p ($\text{k}\Omega.\text{cm}^2$)	i (mA.cm ⁻²) at +0.6 V vs. OCP
				β_a	β_c		
Substrate (Cu)		3.32	-200	66	195	6.4	5.12
Ni-P		1.69	-302	108	184	17.5	15.86
Saccharin	Sac.0.1	1.49	-274	202	143	24.3	7.24
	Sac.0.5	1.24	-288	236	136	28.6	3.46
	Sac.1	1.32	-256	105	125	23.6	16.92
	Sac.2.5	0.83	-246	266	119	42.9	3.32
	Sac.5	1.11	-241	84	167	24.8	13.65
Glycine	Gly.0.1	0.94	-296	230	156	42.7	0.10
	Gly.0.5	1.15	-324	191	152	32.5	0.08
	Gly.1	1.27	-302	188	138	27.4	18.85
	Gly.2.5	1.42	-284	172	159	25.1	19.73
	Gly.5	1.51	-286	162	166	25.1	15.12
PPS	Pyr.0.1	0.82	-298	188	188	50.4	0.22
	Pyr.0.5	0.84	-310	196	186	49.0	0.72
	Pyr.1	1.85	-263	159	251	26.0	1.74
	Pyr.2	2.22	-285	215	230	21.9	3.98
	Pyr.4	1.72	-266	149	256	23.6	6.05
Coumarin	Cou.5m	0.83	-310	187	169	46.9	0.68
	Cou.10m	1.51	-290	156	222	29.6	1.74
	Cou.50m	0.86	-300	161	190	44.1	0.83
	Cou.100m	0.84	-290	194	190	49.7	1.01
	Cou.250m	1.00	-303	156	176	36.3	0.35
Sodium Citrate	Cit.4	0.74	-296	170	180	51.6	0.09
	Cit.8	0.72	-309	174	155	49.7	0.05
	Cit.12	0.80	-312	164	163	45.2	0.08
	Cit.16	1.02	-295	168	200	38.4	0.19
	Cit.20	0.74	-308	151	142	43.2	0.23
Cerium Sulfate	Ce.4m	0.96	-292	182	192	42.6	1.29
	Ce.8m	0.75	-284	200	192	57.2	0.69
	Ce.12m	0.88	-300	150	198	41.8	1.58
	Ce.20m	0.82	-290	170	172	45.3	0.67
	Ce.30m	1.19	-287	202	210	37.5	1.15

Table 2. Analyzed data from EIS tests

Sample		R_s ($\Omega.cm^2$)	CPE_{dl}		R_{ct} ($k\Omega.cm^2$)
			$CPE-T$ ($\mu F.cm^{-2}.s^{n-1}$)	$CPE-P$	
Substrate (Cu)		20.3	129.8	0.80	0.02
Ni-P		12.0	42.4	0.89	13.7
Saccharin	Sac.0.1	47.7	30.2	0.94	14.4
	Sac.0.5	61.9	33.0	0.87	21.2
	Sac.1	16.2	26.5	0.89	20.2
	Sac.2.5	118.8	24.8	0.90	44.8
	Sac.5	15.2	16.4	0.89	25.1
Glycine	Gly.0.1	91.9	24.5	0.95	40.0
	Gly.0.5	65.0	31.4	0.94	25.2
	Gly.1	14.2	23.6	0.92	23.8
	Gly.2.5	14.9	25.2	0.91	21.3
	Gly.5	17.3	28.0	0.91	20.2
PPS	Pyr.0.1	16.6	28.9	0.95	40.2
	Pyr.0.5	14.5	33.6	0.93	38.5
	Pyr.1	18.5	46.5	0.90	23.9
	Pyr.2	12.8	66.0	0.91	16.0
	Pyr.4	13.6	61.5	0.90	19.3
Coumarin	Cou.5m	16.3	24.4	0.95	38.7
	Cou.10m	19.1	23.2	0.94	27.4
	Cou.50m	14.0	26.8	0.94	36.6
	Cou.100m	15.7	36.2	0.92	43.5
	Cou.250m	17.1	36.1	0.94	27.5
Sodium Citrate	Cit.4	64.4	27.5	0.95	40.0
	Cit.8	67.1	25.9	0.95	35.3
	Cit.12	56.7	26.4	0.94	29.6
	Cit.16	66.5	28.1	0.94	32.1
	Cit.20	69.3	29.2	0.93	30.7
Cerium Sulfate	Ce.4m	12.6	27.2	0.94	38.7
	Ce.8m	13.1	25.5	0.95	46.6
	Ce.12m	14.2	26.4	0.94	31.8
	Ce.20m	13.0	28.9	0.95	36.7
	Ce.30m	14.0	40.8	0.92	33.4

Table 3. Corrosion efficiency and porosity density of the obtained Ni-P coatings

Sample		Corrosion efficiency (%)		Corrosion efficiency at high potentials (%)	Porosity density (%)
		Tafel	EIS		
Ni-P		63.4	55.5	-209.8	12.8
Saccharin	Sac.0.1	73.7	57.6	-41.4	3.5
	Sac.0.5	77.6	71.2	32.4	4.8
	Sac.1	72.9	69.8	-230.5	1.9
	Sac.2.5	85.5	86.4	35.2	0.7
	Sac.5	74.2	75.7	-166.1	1.1
Glycine	Gly.0.1	85.0	84.8	98.0	4.3
	Gly.0.5	80.3	75.8	98.4	14.9
	Gly.1	76.6	74.4	-268.2	8.2
	Gly.2.5	74.5	71.4	-285.4	4.8
	Gly.5	74.5	69.8	-195.3	7.8
PPS	Pyr.0.1	87.3	84.8	95.7	3.9
	Pyr.0.5	86.9	84.2	85.9	6.1
	Pyr.1	75.4	74.5	66.0	2.2
	Pyr.2	70.8	61.9	22.3	5.7
	Pyr.4	72.9	68.4	-18.2	2.7
Coumarin	Cou.5m	86.4	84.2	86.7	6.3
	Cou.10m	78.4	77.7	66.0	5.0
	Cou.50m	85.5	83.3	83.8	4.8
	Cou.100m	87.1	86.0	80.3	3.0
	Cou.250m	82.4	77.8	93.2	6.4
Sodium Citrate	Cit.4	87.6	84.8	98.2	3.5
	Cit.8	87.1	82.7	99.0	5.8
	Cit.12	85.8	79.4	98.4	7.0
	Cit.16	83.3	81.0	96.3	4.6
	Cit.20	85.2	80.1	95.5	6.4
Cerium Sulfate	Ce.4m	85.0	84.2	74.8	3.7
	Ce.8m	88.8	86.9	86.5	2.1
	Ce.12m	84.7	80.8	69.1	5.0
	Ce.20m	85.9	83.4	86.9	3.3
	Ce.30m	82.9	81.7	77.5	3.6

Table 4. Chemical composition of the chosen samples in each category obtained by EDS technique

Element Sample	Ni (wt. %)	P (wt. %)
No additives	89.5	10.5
Sac. 2.5	98.2	1.8
Gly. 0.1	85.4	14.6
Pyr. 0.1	82.6	14.4
Cou. 5m	82.2	13.9
Cit. 4	84.7	15.3
Ce. 8m	81.2	14.6

Table 5. Mass, area, thickness, and coating efficiency of the chosen samples

Sample	m (mg)	A (cm ²)	t (μm)	CE %
No additives	14.7	3.46	2.74±1.01	13.2
Sac. 2.5	5.3	4.03	1.77±0.39	9.7
Gly. 0.1	4.7	4.03	1.08±0.16	7.1
Pyr. 0.1	6.3	3.83	1.38±0.52	8.6
Cou. 5m	5.0	4.18	1.40±0.38	6.6
Cit. 4	4.0	3.85	1.54±0.42	8.9
Ce. 8m	6.3	3.92	1.64±0.45	7.5

Table 6. Average roughness of the chosen samples obtained by AFM

Sample	Average Roughness Sa (nm)	Root mean square Sq (nm)
No additives	341	410
Sac. 2.5	343	407
Gly. 0.1	207	246
Pyr. 0.1	155	219
Cou. 5m	310	383
Cit. 4	213	249
Ce. 8m	191	238

Figures

Figure 1. Current density-coating time curves for Ni-P coatings in the presence of (A) saccharine, (B) glycine, (C) PPS, (D) coumarin, (E) sodium citrate, and (F) cerium sulfate as additive.

Figure 2. Coated samples before and after the corrosion tests.

Figure 3. Potentiodynamic polarization curves for the substrate (Cu), Ni-P with no additives, Sac. 2.5, Gly. 0.1, Pyr. 0.1, Cou. 5m, Cit. 4, and Ce. 8m.

Figure 4. (a) Nyquist, (b) Bode-Z, and (c) Bode-Phase curves for the substrate (Cu), Ni-P with no additives, Sac. 2.5, Gly. 0.1, Pyr. 0.1, Cou. 5m, Cit. 4, and Ce. 8m.

Figure 5. Proposed ECs for fitting the EIS data for (A) Cu substrate, and (B) Ni-P coated samples with and without additives.

Figure 6. Corrosion efficiency, instantaneous and at high potentials, for Ni-P with no additives, Sac. 2.5, Gly. 0.1, Pyr. 0.1, Cou. 5m, Cit. 4, and Ce. 8m.

Figure 7. X-Ray diffraction patterns of (A) Cu substrate, (B) Ni-P coating without additives, (C) Sac. 2.5, (D) Gly. 0.1, (E) Pyr. 0.1, (F) Cou. 5m, (G) Cit. 4, and (H) Ce. 8m.

Figure 8. SEM images of (A) Ni-P without additives, (B) Sac. 2.5, (C) Gly. 0.1, (D) Pyr. 0.1, (E) Cou. 5m, (F) Cit. 4, and (G) Ce. 8m.

Figure 9. Cross-section and surface SEM images of Ni-P without additives, (A) before corrosion, (B) shiny part after corrosion, and (C) dark region after corrosion.

Figure 10. Effects of the concentration of glycine (A) and cerium sulfate (B) as additives on the corrosion efficiency ($\bullet$), coating efficiency ($\blacktriangle$), and P content ($\blacksquare$) of Ni-P layers.

Figure 11. AFM images of (A) Ni-P without additives, (B) Sac. 2.5, (C) Gly. 0.1, (D) Pyr. 0.1, (E) Cou. 5m, (F) Cit. 4, and (G) Ce. 8m.