Vol. 22, No. 2(2023) Proc2331
Revista Mexicana de Ingeniería Química

Effect of complexing/buffering agent on the characteristics of a high phosphorous electroless nickel coating

Efecto del agente complejante/amortiguador sobre las características de un recubrimiento autocatalítico de níquel con alto fósforo

J.I. Ruiz-Vela[1], E.E. Rodríguez-Vázquez[1], Y. Gudiño-Pérez[2], R. Sánchez-Ramírez[3], J.J. Montes-Rodríguez[1]*
[1] *Centro de Ingeniería y Desarrollo Industrial, Av. Playa Pie de la Cuesta No. 702, Des. Hab. San Pablo, 76125, Querétaro, Qro., México.*
[2] *Tecnológico Nacional de México, I.T. de Querétaro, Av. Tecnológico esq. Mariano Escobedo s/n, Col. Centro, 76000, Querétaro, Qro., México.*
[3] *Universidad Tecnológica de Querétaro, Av. Pie de la Cuesta No. 2501, Col. Unidad Nacional, 76148, Querétaro, Qro., México.*

Received: June 1, 2022; Accepted: May 13, 2023

Abstract

It is well known that phosphorous content in the coatings produced by electroless nickel plating plays an important role to obtain high wear and corrosion resistance. A coating with more than 10 wt.% phosphorous is considered superior to stainless steel and almost as resistant as hard chromium. Many industrial applications require these combinations of properties. The formulation of electroless nickel plating solutions is the base to obtain a coating with an adequate content of phosphorous. The aim of this work was to study the effect of several complexing/buffering agents on the characteristics of a high phosphorous electroless nickel coating, in order to formulate a solution able to produce nickel coatings with a phosphorous content between 10 and 12 wt.%. Four complexing/buffering agents were used: ammonium citrate, propionic acid, lactic acid, and acetic acid. Lead acetate was selected as a stabilizer and its replenishment was determined experimentally. In order to know the effect of each compound solutions combining two and three of them were prepared and tested. The phosphorous content and the plating rate were measured, and the surface finishing and brightness were also evaluated. Finally, the useful life of the best formulation was tested up to 5.6 metal turnovers.

Keywords: electroless, nickel, high phosphorus, buffering agent, complexing agent.

Resumen

En los recubrimientos autocatalíticos de níquel, el contenido de fósforo juega un papel importante para obtener altas resistencias al desgaste y la corrosión. Un recubrimiento con más del 10 % en peso de fósforo se considera superior al acero inoxidable, y casi tan resistente como el cromo duro. Muchas aplicaciones industriales requieren esta combinación de propiedades. La formulación de soluciones para niquelado autocatalítico es la base para obtener recubrimientos con un contenido adecuado de fósforo. El objetivo de este trabajo fue estudiar el efecto de varios agentes complejantes/amortiguadores sobre las características de un recubrimiento autocatalítico de níquel alto en fósforo, para lograr producir recubrimientos de níquel con contenidos de fósforo entre 10 y 12 % en peso. Se utilizaron cuatro agentes complejantes/amortiguadores: citrato de amonio, ácido propiónico, ácido láctico y ácido acético. Se seleccionó acetato de plomo como estabilizador, y se determinó experimentalmente su reposición. Para conocer el efecto de cada compuesto se prepararon y ensayaron soluciones combinando dos y tres de ellos. Se midió el contenido de fósforo y la tasa de recubrimiento, y también se evaluaron el acabado superficial y el brillo. Finalmente, se probó la vida útil de la mejor formulación, hasta 5.6 rotaciones de metal.

Palabras clave: autocatalítico, níquel, alto fósforo, agente amortiguador, agente complejante.

Corresponding author. E-mail: `jmontes@cidesi.edu.mx`

https://doi.org/10.24275/rmiq/Proc2331
ISSN:1665-2738, *issn-e*: 2395-8472

1 Introduction

The corrosion of steel components and structures is an electrochemical phenomenon (León-Bello & Amaya-Malpica, 2008) that causes a large number of problematic situations derived from structural affectations, maintenance, and repair costs, in addition to other environmental effects (Balan-Ortiz *et al*., 2017), so it is relevant to avoid, as far as possible, its occurrence. In this sense, the application of protective coatings is an alternative widely employed, as a way to avoid or delay the appearance of corrosion in steels of various types used in multiple applications.

In the beginning of the 1980s electroless nickel (Ni) plating was introduced in the industry, due to the outstanding combination of properties of its coatings it was well accepted and utilized in many applications (Mainer *et al*., 2013; Tahery, 2003). High hardness, excellent corrosion resistance, uniformity of the deposit, good brightness, and fast plating rate are some of the characteristics of the electroless nickel. One of the advantages offered by this process is the phosphorous (P) content in the coating, which allows having a variety of properties. In the industry, electroless nickel coatings are classified as low (2-4 wt.%), medium (5-9 wt.%) and high phosphorus (more than 10 wt.%) (ASTM International, 2015). In general, in industrial applications with severe service conditions a high phosphorous electroless nickel is recommended. High phosphorous coatings have demonstrated high corrosion resistance, even better than stainless steel, and high resistance, almost as hard as chromium (Huang *et al*., 2019). High phosphorous electroless nickel has important applications in the petroleum industry, where it is used on valves, special tools, risers, pumps, and production pipes, due to its abrasion and corrosion resistance (Mainer *et al*., 2013).

The composition of the plating solution is one important factor that determines the phosphorous content in the coating. The main components in the plating solution are: (i) a source of nickel ions, (ii) a reducing agent, (iii) complexing/buffering agents, and (iv) a stabilizer. If hypophosphite is being used as a reducing agent, decreasing the ratio $Ni^{2+}/H_2PO_2^-$ will diminish the phosphorus content in the coating. Complexing agents with a high stability constant (pKa) reduce the plating rate but increase the phosphorus content. Stabilizers affect the plating rate, phosphorous content, and internal stresses, being its main function to avoid the spontaneous decomposition of the plating solution (Mallory & Hajdu, 1990; Tahery, 2003). According to this, the selection of each component for the formulation of the solutions is an important aspect if certain phosphorous content is required.

Acetic and propionic acids have been used in the formulation of electroless nickel baths, but they have low stability constants, so that some researchers use them as buffers only (Janssen *et al*., 2013; Jin *et al*., 2010); however, others have said that they also have a complexing effect (Mallory & Hajdu, 1990). In the literature is very common to find lactic acid in the formulation of electroless nickel baths: due to its pKa it can be used for medium to high phosphorous coatings (Ashtiani *et al*., 2017; Park & Kim, 2019). Ashtiani *et al*. (2017) tested three different complexing agents in electroless nickel solutions under the same conditions: sodium citrate, sodium acetate and lactic acid; they found that the last one produced the highest phosphorous content. Ammonium and citrate ions have also been used, however, there is little information about acidic electroless nickel solutions with ammonium citrate. Wang *et al*. (2003) used an alkaline electroless nickel solution with these ions, and they found that by increasing the citrate concentration up to 0.35 mol the phosphorous content increases in the nickel plate to 13%, approximately; in addition, they found the presence of a complex formed by citrate and ammonium.

The aim of this work was to formulate a high phosphorous electroless nickel solution, using lactic acid, ammonium citrate, acetic acid, and propionic acid. The strategy followed was, at first, to determine the best stabilizer to be used between thiourea and lead acetate, and at the same time, the amount required to replenish was also established. Then, for the selection of the complexing/buffer agents solutions combining two, three and four compounds were prepared and tested. Based on the plating rate, phosphorous content and surface finishing the formulation was selected. With the experiments carried out it was possible to determine the role of propionic and acetic acids and select one formulation for a high phosphorous electroless nickel solution. The coatings produced by the selected solution were compared with the coating produced by a brand solution offered in the market through corrosion test and hardness test after heat treatment. Finally, the solution was tested up to 5.6 MTO (Metal TurnOver), analyzing the phosphorous content in the coating and the visual appearance.

This paper first presents everything related to the experimentation, indicating the materials used and the processes carried out. Then the results obtained are shown, as well as their analysis and discussion. Finally, the most relevant conclusions reached from the present investigation are exposed.

2 Experimental procedure

The substrate used in the experiments was a low carbon, low allow steel sheet with 0.697 mm in thickness. Its preparation before plating consisted of cleaning with acetone, electrolytic cleaning with an alkaline solution at 55°C for 1 minute, rinse with current water, acid pickling with hydrochloric acid 1:1 in water for 1 minute, and rinse with distilled water. All the tests were done with a relation of 2.4 dm^2/L of plating solution. Plating rate was determined with the following expression (Karthikeyan & Ramamoorthy, 2014; Omar *et al.*, 2018):

$$R = \frac{(w_t - w_0) * 10000}{\rho * S * t} \tag{1}$$

where R is the plating rate in μm/h, w_0 is the initial mass of the substrate in g, w_t is the final mass of the substrate in g, ρ is the density of the Ni-P plate (7.9 g/cm^3), S is the area of the substrate in cm^2 and t is the time in h. This equation considers some assumptions that it is necessary to indicate (Parkinson, n.d.): 1) the density of the Ni-P coating corresponds to a P content of 10%, approximately, which is consistent with the contents obtained for this element in the coatings and, 2) the thickness of the coating is uniform.

In order to determine the necessary amount of stabilizer, experiments were carried out with different additions of two stabilizers. A base plating solution consisting of 6 g/L nickel, 25 g/L sodium hypophosphite, 28 g/L of 85% lactic acid, and 2.2 g/L propionic acid was used, at 89 ± 2°C and pH 4.7 ± 0.1 for two hours. Additionally, stock solutions (SS) with 100 ppm of lead acetate and thiourea were prepared. A volume of 150 mL of base solution was used on each experiment with the additions showed in Table 1; pH was controlled with ammonium hydroxide and the concentrations of nickel and hypophosphite were replenished during the tests. At the end of the experiment the walls and bottom of the cell were visually inspected, if nickel was deposited on them another experiment was repeated increasing the volume added of stabilizer.

To formulate the high phosphorous electroless nickel solution four compounds were used as complexing/buffering agents: lactic acid (LA), propionic acid (PA), citrate ammonium (CA) and acetic acid (AA). The combination of lactic acid and propionic acid in electroless nickel solutions has been used by many authors to produce high phosphorous coatings: the concentrations used are 28 to 33 g/L for lactic acid and 2.2 g/l for propionic acid (Ashtiani *et al.*, 2017; Baskaran *et al.*, 2006; Chen *et al.*, 2003; Cheon *et al.*, 2010). In this research, lactic acid 85% with a concentration of 32 g/L, and propionic acid with 2.2 g/L were used. On the other hand, citrates and acetates are two ions that can produce around 10% of phosphorous coatings with concentrations from 10 to 40 g/L and 11.5 to 23 g/L, respectively (Elhaloui *et al.*, 2015; Miao *et al.*, 2018). To investigate the effect of a low concentration of citrate ions, in combination with other complexing/buffering agents, citrate ammonium with 8.7 g/L was selected as the third compound in the bath. Finally, acetic acid was used with a concentration of 30.1 g/L, obtaining 29.6 g/L of acetate ion in the bath, which is higher than that in the previous reference, to ensure a high content of phosphorous in the coating in baths with only one or two agents. The composition of each solution tested is shown in Table 2. The stabilizer was lead acetate, 2 mL of 100 ppm SS were added initially and then 1.5 mL every 15 min, nickel concentration was 6.0 g/L and sodium hypophosphite 30 g/L. Each solution was tested for 2 hours making additions of nickel and hypophosphite to replenish their concentrations; ammonium hydroxide was used to keep the pH in the 4.7-4.8 range, and the temperature was 89 ± 2°C.

Table 1. Experiments with different additions of stabilizers.

Test number	Thiourea (mL of SS)*	Lead Acetate (mL of SS)*
Initial Addition	2	2
1	0.5	—
2	1	—
3	3	—
4	—	1
5	—	1.5
6	—	2

* Every addition was made 15 minutes after the previous step (Test).

Table 2. Combinations of complexing/buffering agents tested.

Solution	Compounds	Nomenclature
1	Acetic acid (AA) - Citrate ammonium (CA)	AA-CA
2	Acetic acid (AA) - Lactic acid (LA)	AA-LA
3	Acetic acid (AA) - Propionic acid (PA)	AA-PA
4	Citrate ammonium (CA) - Lactic acid (LA)	CA-LA
5	Citrate ammonium (CA) - Propionic acid (PA)	CA-PA
6	Lactic acid (LA) - Propionic acid (PA)	LA-PA
7	Acetic acid (AA) - Citrate ammonium (CA) - Lactic acid (LA)	AA-CA-LA
8	Acetic acid (AA) - Citrate ammonium (CA) - Propionic acid (LA)	AA-CA-PA
9	Acetic acid (AA) - Lactic acid (LA) - Propionic acid (PA)	AA-LA-PA
10	Citrate ammonium (CA) - Lactic acid (LA) - Propionic acid (PA)	CA-LA-PA
11	Acetic acid (AA) - Citrate ammonium (CA) - Lactic acid (LA) - Propionic acid (PA)	AA-CA-LA-PA

In order to increase the phosphorous content in the coating, AA-CA-LA-PA solution was also tested with a concentration of 33 and 35 g/L of sodium hypophosphite with the same conditions described above. Coatings on the same substrates and with the same conditions were prepared with the solution Nichem HP 1151 from Atotech®; the time lapsed was enough to get a thickness similar to the produced by the solutions formulated in this work.

The brightness of the coatings was visually evaluated comparing the coatings. A scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) probe was used to determine qualitatively the phosphorous content, and to inspect the superficial morphology of the coating. For the corrosion test, a weight loss technic was used, and a solution with the same compounds of a salt spray test (ASTM International, 2014) was selected to ensure a corrosive media; the concentrations used were: 20% acetic acid and 60 g/L of sodium chloride. The coated samples were submerged for various days, and their weight loss was measured.

A heat treatment at 400°C for 1 h was applied on samples produced by the formulation selected in this study and by the brand solution, in accordance with standard practices for this kind of coatings (ASTM International, 2015; Parkinson, n.d.). After that, both samples were cut and metallographically prepared for hardness test with Knoop indenter and a load of 100 gf. The service life of the formulation selected was tested up to 5.6 MTO; the plating rate, phosphorous content and superficial appearance were evaluated

3 Results and discussion

The results of the stabilizer experiments are shown in Figures 1 and 2. In first place, a difference in the precipitation of nickel on the cell is observed, additions of 0.404 mg of thiourea per gram of plated nickel, and 1.249 mg of lead acetate per gram of plated nickel, resulted in the occurrence of nickel particles in the bottom of the cell; the other additions schedules did not showed precipitation of nickel. The plating rate and the phosphorous content were affected by the type of stabilizer. Lead acetate showed lower plating rates than thiourea, however this last one produced lower phosphorous contents (see Figure 1). The effect of these stabilizers has been studied in other works and the results presented here agree with them in general terms. Baskaran *et al*. (2006) worked with electroless solutions with similar composition to those used here, with thiourea and lead acetate as stabilizers; they found that the former produced less phosphorous in the coating but higher deposition rates, in comparison to lead acetate. From their work, it can be assumed that they operated their baths with 0.8 ppm of thiourea for 60 minutes without replenishment of stabilizers, obtaining a plating rate of 25 μm/h.

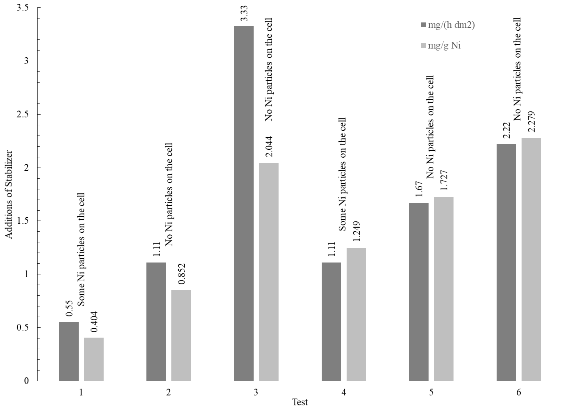

Figure 1. Amounts of stabilizer added, its ratio to the mass of nickel produced and their results of bath breakdown.

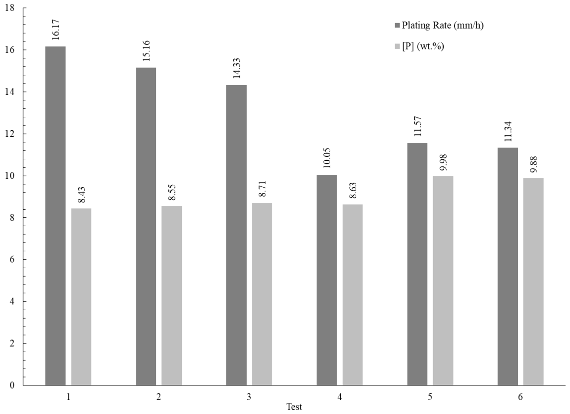

Figure 2. Plating rate and phosphorus content obtained from the experiments of stabilizer selection.

The initial concentration of thiourea in the baths tested in our study was 1.33 ppm, obtaining between 16.17 and 14.33 μm/h, however, additions every 15 minutes were made in order to prevent the decomposition of the electroless solution. As the amount of added thiourea was increased the plating rate decreased. Thiourea can decrease the activation energy of the nickel reduction reaction, but can inhibit it at concentrations above 1 ppm; lower concentrations increase the plating rate (Lin & Hwang, 2002). The results shown in Figure 1 are evidence of a consumption or loss of stabilizer during bath operation; the initial amount of thiourea can not be enough to prevent the bath decomposition, in the conditions tested at least 1ml of Thiourea stock solution, meaning an addition of 0.67 ppm in the concentration of the plating bath, each 15 minutes was required to prevent the bath decomposition.

Lead acetate as stabilizer also inhibits the reduction of nickel in the range of 0.5 to 2.0 ppm and stops it with a concentration beyond 3 ppm (Baskaran *et al*., 2006). The initial concentration of the solutions tested was 1.33 ppm with a minimum addition of 1.5 mL of SS every

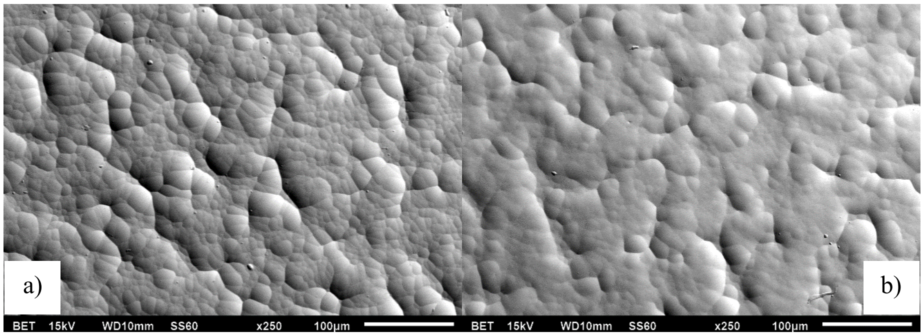

Figure 3. SEM images comparing the surface of coatings produced with a) thiourea and b) lead acetate baths.

15 minutes, equivalent to an addition of 1 ppm to avoid the bath decomposition. However, the phosphorous content produced by these baths was superior to those obtained with thiourea. This is attributed to the adsorption of thiourea on the substrate, hindering the access of the hypophosphite ions, thus inhibiting the oxidation of hypophosphite or the production of atomic hydrogen (Baskaran *et al*., 2006).

It was mentioned that the function of the stabilizer is to avoid the spontaneous decomposition of the plating solution, which can be observed with the precipitation of nickel particles in places out of the substrate surface (Baskaran *et al*., 2006; Lin & Hwang, 2002; Xie *et al*., 2011). In the literature there is a test based on the reaction of the plating solution with palladium chloride ($PdCl_2$): it measures the time taken by the solution to decompose getting a dark color (Xiao *et al*., 2008; Xie *et al*., 2011). This test applies to the initial composition of the plating solution and does not offer information about the consumption of the stabilizer during the plating. In addition, it has been pointed out that this test indicates the stability of the solution to highly catalytic foreign nuclei rather than finely divided nickel precipitates (Xie *et al*., 2011). During the development of the tests, it was observed that in baths with enough concentration of stabilizers, the spontaneous precipitation of nickel particles and the plating on container surfaces was inhibited, leading to a decrease in the additions of the nickel replenishment solution and better control in the composition of the bath. In this work the inhibiting effect of the stabilizers was used as an advantage: if the solution is to be used industrially, the reduction of plate out is a benefit because the waste of nickel and the problems of rough surfaces are diminished. The approach used in this work is a practical way to determine the stability of the plating solution through the operation time.

Since the main objective of this work was to develop a solution with a phosphorous content above 10%, lead acetate was selected for the rest of the experiments. In addition, lead acetate showed another advantage. In Figure 3 there is a comparison between the appearance of the surfaces produced with thiourea and lead acetate, which were inspected with electron scanning microscopy; lead acetate coating has a smoother and brighter appearance.

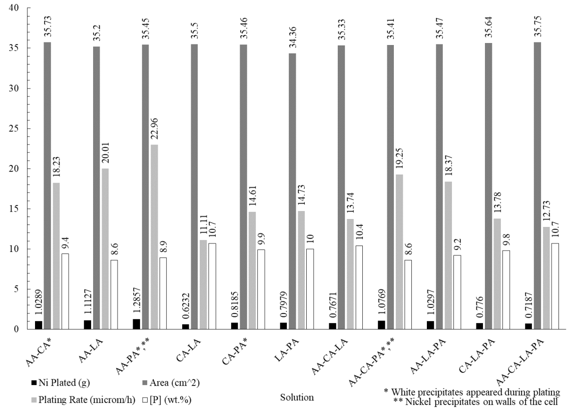

Figure 4. Results of mass of nickel produced, plating rate, and phosphorous content obtained from the combinations of complexing/buffering agents tested.

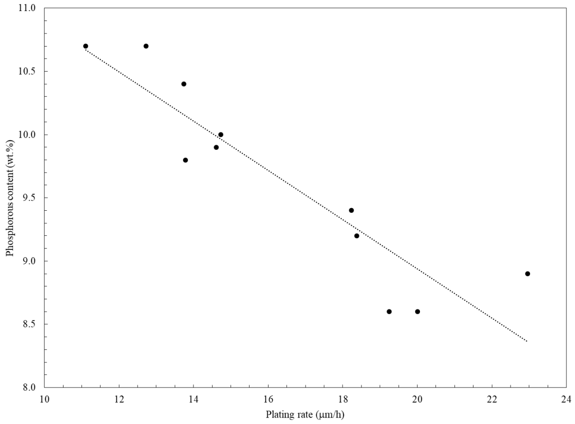

Figure 5. Plating rate vs. phosphorous content for the combinations of agents tested.

The results obtained by the combination of the four complexing/buffer agents are shown in Figure 4, while Figure 5 shows a graph of phosphorous content against plating rate; it can be observed that the higher the phosphorous content the lower the plating rate. Complexing agents reduce the plating rate by sequestering nickel ions and

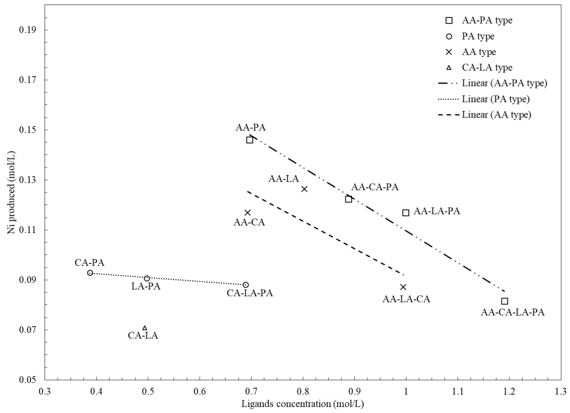

Figure 6. Ligands concentrations vs. amount of nickel produced with the solutions tested.

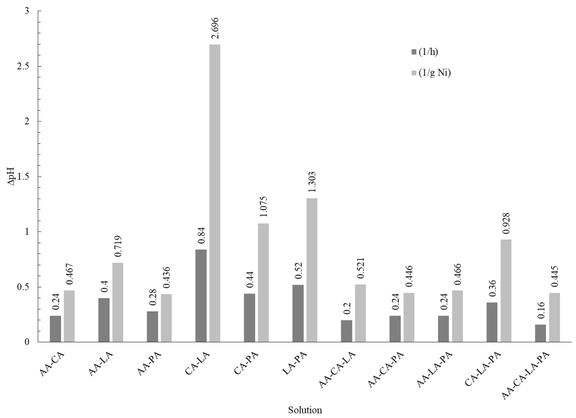

Figure 7. Changes in pH per time and per amount of nickel produced for all the combinations of agents tested.

decreasing the reduction sites used by them, thus allowing an increment in the phosphorous content in the coating due to an increase in the reduction sites for this element (Mallory & Hajdu, 1990; Sahoo & Das, 2011).

Some researchers (Mallory & Hajdu, 1990) have determined that the plating rate and the phosphorous content depend on the complexing agent stability constant (log K). Cui *et al*. (2005) found a correlation between the phosphorous content and the plating rate with the concentration of ligands in the electroless nickel. They defined as ligands the structures -COOH and -NH_2 present in the molecule of the complexing agent. Using this approach, Figure 6 shows a graph of ligands concentration versus the plating rate, expressed in Ni mol/L, for the compositions used in this work and the results obtained. Three correlations were found: 1) all the solutions containing propionic acid without acetic acid, 2) solutions containing propionic acid and acetic acid at the same time and, 3) solutions containing acetic acid without propionic acid. The results also indicate that the plating rate can be changed depending on the basis of the solution: AA, PA or AA-PA; the solution CA-LA without AA nor PA showed the lowest plating rate. On the other hand, solutions containing AA-PA showed higher plating rates than solution with PA or AA as basis, despite the fact that they were formulated with the same additives and concentrations.

Binary combinations demonstrated that acetic acid (AA) and propionic acid (PA) are good pH controllers; the combination AA-PA showed the lowest change of pH per gram of deposited nickel, (see Figure 7). In contrast, it showed the highest plating rate and low phosphorous content indicating a poor complexing effect. Also, combinations AA-CA-PA and AA-LA-PA have the highest plating rates from all the ternary combinations tested, with the lowest changes in pH. Combinations AA-CA, AA-PA and AA-CA-PA produce solutions with low changes in pH and white precipitates during the plating, evidence of lack of complexing effect, since another function from the complexing agent is to prevent the precipitation of nickel salts (Mallory & Hajdu, 1990). On the other hand, the combination CA-LA produced one of the biggest phosphorous content, the lowest plating rate, and the greatest change of pH, meaning that CA and LA are better complexing agents. Ternary combinations confirmed the same observations: AA-CA-LA and CA-LA-PA contained more complexing agents, promoting lower plating rates, and higher phosphorous contents, but greater changes in pH per gram of deposited nickel, in comparison with the other ternary combinations. The additions of acetic acid to the binary combinations increased the plating rate, indicating an "un-complexing" effect; when acetic acid was added to the CA-LA combination, an increase in its ligands concentration occurred, as can be seen in Figure 6, which according to other authors should decrease the plating rate and increase the amount of phosphorus in the coating however the opposite was observed. The complexing effect of acetic acid was not observed when added to the ternary combination CA-LA-PA; in this case, the plating rate was decreased, and the phosphorous content increased. With propionic acid something similar happened, its addition increased the deposition rate in the combinations AA-CA and CA-LA, but decreased it in the combination AA-LA. This is evidence that the pair of lactic acid and propionic acid has a potentiated complexing effect. This is observed again with the addition of propionic acid to AA-CA-LA, which increased the plating rate. However, when propionic acid is added to CA-LA it worked only as a pH controller and "un-complexing" agent. Based on these results propionic acid and acetic acid cannot be only classified as pH controllers, because they have a complexing effect too, that is activated depending on the composition of the bath. The function of the citrate ammonium and lactic acid is well defined, because they always worked as complexing agents, promoting an increase in the phosphorous content in the coating and lowering the plating rate. However, their function is potentiated by adding propionic and acetic acids, as observed in the combination AA-CA-LA-PA, which produced one of the highest phosphorous content but a little

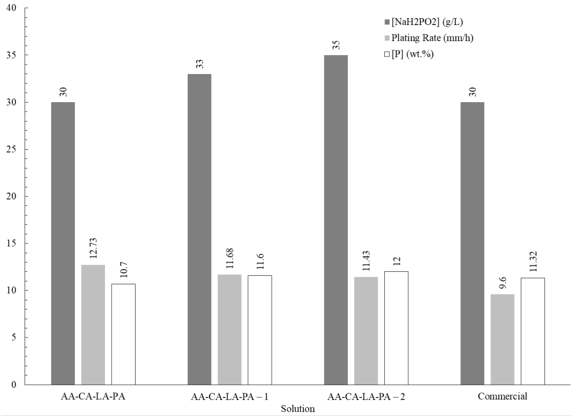

Figure 8. Results of plating rate and phosphorus content for the tests with the combination AA-CA-LA-PA with different concentrations of hypophosphite, and the commercial solution.

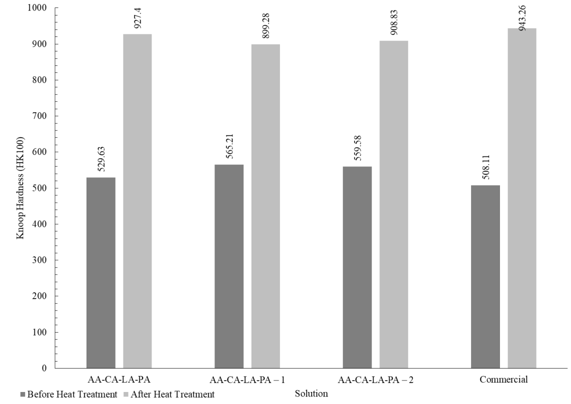

Figure 9. Hardness results before and after heat treatment.

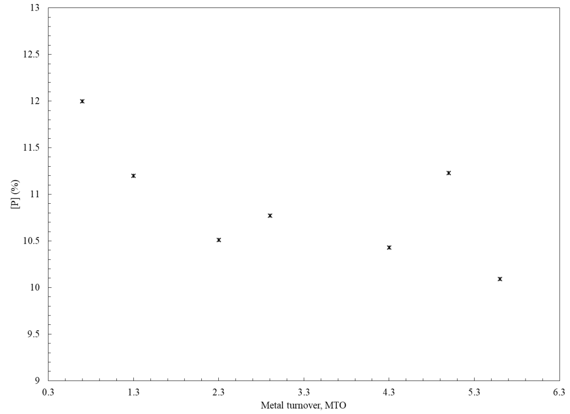

Figure 10. Metal turnover (MTO) vs. phosphorous content in coatings produced by AA-CA-LA-PA-2 solution.

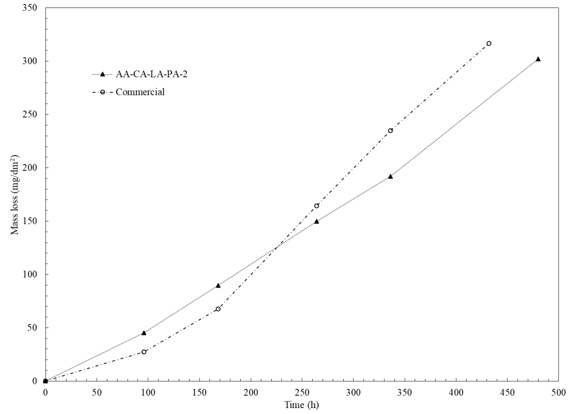

Figure 11. Corrosion results for AA-CA-LA-PA-2 and commercial solutions.

increase in the plating rate. Therefore, the best combination resulted from the bath using the four compounds.

For the formulation of a 10 to 12% of phosphorous plating solution, the combination AA-CA-LA-PA was selected; however, it was necessary to increase its hypophosphite concentration in order to increase the phosphorous content in the coating. Figure 8 shows the hypophosphite concentration used, the plating rate and the phosphorous content obtained, in comparison to previous AA-CA-LA-PA combination; in addition, the same results are showed for the commercial solution.

With the increment in the concentration of hypophosphite the coating increased its phosphorous content. Hardness in the coatings produced by the combinations AA-CA-LA-PA, AA-CA-LA-PA-1 and AA-CA-LA-PA-2 are in the range of 899.28 to 927.4 HK100 (see Figure 9), and are very near to the coating produced by the commercial solution. The standard ASTM B733 is a specification for electroless nickel-phosphorous coatings which requires a minimum hardness of 850 HK for the class 2 of heat treated coatings between 260 to 400°C (ASTM International, 2015). With this reference value, it is concluded that the three AA-CA-LA-PA combinations tested meet this requirement. The service life was tested up to 5.6 MTO, evaluating the phosphorous content and the appearance of the coating. Figure 10 shows a graph where it can be observed that the phosphorous content is in the range of 10 to 12%, but decreases with the time, which is a common behavior in the electroless nickel solutions (Tahery, 2003). Commercial solutions offer services life in the range of 6 to 8 MTO (Atotech Deutschland GmbH., 2015; Enthone España, S.A., n.d.).

The coatings produced with different MTO did not showed superficial defects nor brightness loss. This characteristic is attributed to the use of four complexing/buffering agents, since another of their functions is to increase the tolerance of the electroless nickel solution to orthophosphites (Mallory & Hajdu, 1990), which can produce superficial defects and other problems (Colburn, 2020; Mallory & Hajdu, 1990; Tahery, 2003). Evidence that supports this statement is the fact that some solutions

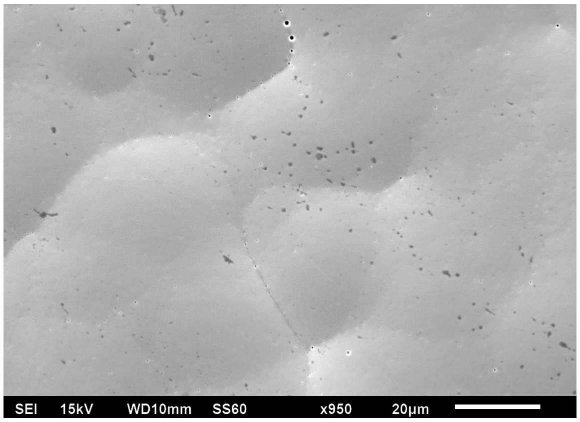

Figure 12. SEM image showing pores in the coating produced by the AA-CA-LA-PA-2 solution.

presented white precipitations during the tests (see Figure 4); this phenomenon is known as whiteout and is caused by the precipitation of orthophosphites (Colburn, 2020). Whiteout is a chemical problem seen in the plating solution, due to losses of complexing agent and/or high pH among other causes, which provoke the insolubility of nickel phosphite; in extreme cases whiteout may lead to roughness and porosity (Durkin, 2005).

Finally, the results of the corrosion test are presented in Figure 11. It can be seen in this figure that, in general, the AA-CA-LA-PA-2 and the commercial solutions have the same behavior. However, it is important to note that the coating produced with the commercial solution showed a slower loss of mass at the beginning of the test (first 168 hours), then the loss mass rate increased, even more than that of the solution AA-CA-LA-PA-2. The corrosion resistance of electroless nickel coatings depends on the phosphorous content, thickness and surface quality factors, such as porosity level (Omar *et al*., 2018). Both samples had almost the same thickness: 24 mm for the A-C-L-P-2 combination and 25 mm for the commercial solution, and also their phosphorous contents were very similar (see Figure 8); so the quality of the surface was the main difference among the tested samples. The presence of pores on the coating can be detrimental for the corrosion resistance of this kind of coatings, and their presence on the coating from AA-CA-LA-PA-2 was confirmed (see Figure 12). Commercial solutions could be formulated with more additives such as organic substances, that can increase the corrosion resistance or reduce the porosity of the coatings produced (Sahoo & Das, 2011).

Conclusions

The formulation of an electroless nickel solution able to produce coatings with 10 to 12% of phosphorous content was possible using the combination of four complexing/buffering agents. Lead acetate as stabilizer produced coatings brighter and with more phosphorous than thiourea while propionic and acetic acids are buffers mainly, however they also have a complexing effect in the electroless nickel solution. It was possible to correlate the concentration of the ligands (-COOH and -NH_2) present in the solution with the plating rate, as long as the solutions have the same basic components.

The electroless nickel solution formulated with four agents was able to support up to 5.6 MTO, producing the desired level of phosphorus without visual defects on the coating. This solution meets the hardness requirements of ASTM B733-15 standard for a heat treated coating class 2. The corrosion resistance of the coating produced by the formulation developed is comparable to those produced by the commercial solution tested. However, further research work is necessary to improve this characteristic, as well as to do additional testing.

Acknowledgment

The authors thank *Centro de Ingeniería y Desarrollo Industrial* for the facilities granted for carrying out this research.

References

ASTM International (2014). *Standard Test Method for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)* (ASTM B368-09, Reapproved 2014). ASTM International. https://www.astm.org/

ASTM International (2015). *Standard Specification for Autocatalytic (Electroless) Nickel-Phosphorus Coatings on Metal* (ASTM B733-15). ASTM International. https://www.astm.org/

Ashtiani, A.A., Faraji, S., Iranagh, S.A. and Faraji, A.H. (2017). The study of electroless Ni-P alloys with different complexing agents on Ck45 steel substrate. *Arabian Journal of Chemistry 10*(2), S1541-S1545. https://doi.org/10.1016/j.arabjc.2013.05.015

Atotech Deutschland GmbH. (2015). *Nichem HP 1151*, (Data Sheet, ver. 09). Atotech Deutschland GmbH.

Balan-Ortiz, C.A., Luna-Brito, Pérez-López, M.T. and Camacho-Chab, R.J. (2017). Statistical analysis of electrochemical noise records obtained from the process of corrosion of reinforced steel embedded in concrete. *Revista Mexicana de Ingeniería Química 16*(1), 291-303. http://rmiq.org/iqfvp/Pdfs/Vol.%2016,%20No.%201/mat1/RMIQTemplate.pdf

Baskaran, I., Sankara-Narayanan, T.S.N. and Stephen, A. (2006). Effect of accelerators and stabilizers on the formation and characteristics of electroless Ni-P deposits. *Materials Chemistry and Physics 99*(1), 117-126. https://doi.org/10.1016/j.matchemphys.2005.10.001

Chen, Z., Xu, X., Wong, C.C. and Mhaisalkar, S. (2003). Effect of plating parameters on the intrinsic stress in electroless nickel plating. *Surface and Coatings Technology 167*, 170-176. https://doi.org/10.1016/S0257-8972(02)00911-8

Cheon, S.-Y., Park, S.-Y., Rhym, Y.-M., Kim, D.-H., Koo, Y.-S. and Lee, J.-H. (2010). Electroless nickel plating on fibers for the highly porous electrode. *Journal of Electrochemical Science and Technology 1*(2), 117-120. https://doi.org/10.5229/JECST.2010.1.2.117

Colburn, A. (2019, May 1). Solving Problems with Electroless Nickel Solution Whiteout. Products Finishing. Available at: https://www.pfonline.com/articles/solving-problems-with-electroless-nickel-solution-whiteout-. Accessed: June 27, 2020.

Cui, G., Li, N., Li, D. and Chi, M. (2005). Study of optimized complexing agent for low-phosphorus electroless nickel plating bath. *Journal of The Electrochemical Society 152*(10), C669-C674. https://doi.org/10.1149/1.2001487

Durkin, B. (2005). Effectively Problem Solving an Electroless Nickel Plating Operation. 2005 SUR/FIN Proceedings. Available at: https://www.nmfrc.org/pdf/sf2005/sf050204.pdf

Elhaloui, A., Anik, T., Ebn Touhami, M., Shaim, A., Iyach, K., Touir, R., Sfaira, M., Mcharfi, M. and Hammouti, B. (2015). Investigation of ammonium acetate effect on electroless Ni-P deposits. *Journal of Materials and Environmental Science 6*(7), 2028-2036.

Enthone España, S.A. (n.d.). ENPLATE NI 425 (Technical Data Sheet, ver. 0304/3). Cookson Electronics.

Huang, Z., Nguyen, T.T., Zhou, Y. and Qi, G. (2019). A low temperature electroless nickel plating chemistry. *Surface & Coatings Technology 372*, 160-165. https://doi.org/10.1016/j.surfcoat.2019.05.019

Janssen, B.A., Bera, H., Weißbrod, S. and Schafsteller, B. (2013, January 30). *Electroless Nickel Plating Bath Composition* (Europe Patent EP2551375A1). European Patent Office.

Jin, Y., Yu, H., Yang, D. and Sun, D. (2010). Effects of complexing agents on acidic electroless nickel deposition. *Rare Metals 29*(4), 401-406. https://doi.org/10.1007/s12598-010-0138-8

Karthikeyan, S. and Ramamoorthy, B. (2014). Effect of reducing agent and nano Al_2O_3 particles on the properties of electroless Ni-P coating. *Applied Surface Science 307*, 654-660.

León-Bello, F. and Amaya-Malpica, M.G. (2008). Surface Galvanic Action on a Carbon Steel Matrix Microcell Consisting on Ferrite and Pearlite Grains. *Revista Mexicana de Ingeniería Química 7*(1), 29-33. http://rmiq.org/iqfvp/Pdfs/Vol%207%20no%201/RMIQ_Vol7No1_4.pdf

Lin, K.-L. and Hwang, J.-W. (2002). Effect of thiourea and lead acetate on the deposition of electroless nickel. *Materials Chemistry and Physics 76*(2), 204-211. https://doi.org/10.1016/S0254-0584(01)00516-8

Mainer, F.B., Cindra-Fonseca, M.P., Tavares, S.S.M. and Pardal, J.M. (2013). Quality of electroless Ni-P (nickel-phosphorous) coatings applied in oil production equipment with salinity. *Journal of Materials Science and Chemical Engineering 1*(6), 1-8. http://dx.doi.org/10.4236/msce.2013.16001

Mallory, G.O. and Hajdu, J.B. (Eds.) (1990). *Electroless Plating: Fundamentals and Applications*. American Electroplaters and Surface Finishers Society, Orlando, Florida, U.S.A.

Miao, N., Jiang, J. and Wu., W. (2018). Influences of bath chemistry and plating variables on characteristics of electroless Ni-P films on Si wafers from alkaline citrate solutions. *Journal of Nanomaterials 2018*, Article ID 1817542, 11 pages. https://doi.org/10.1155/2018/1817542

Park I.-C. and Kim, S.-J. (2019). Effect of stabilizer concentration on the cavitation erosion resistance characteristics of the electroless nickel plated gray cast iron in seawater. *Surface and Coatings Technology 376*, 31-37. https://doi.org/10.1016/j.surfcoat.2018.08.098

Parkinson, R. (n.d.). *Properties and Applications of Electroless Nickel*. Nickel Development Institute. https://www.nickelinstitute.org/media/1769/propertiesandapplicationsofelectrolessnickel_10081_.pdf

Omar, R., Aboraia, M.S., Oraby, E.A., Gubner, R. and Rizk, A.E. (2018). The effect of sodium citrate as a complex agent on the corrosion properties of the electroless Ni-P coating. *Materials Research Express 5*(12), 126511. https://doi.org/10.1088/2053-1591/aae0b9

Sahoo, P. and Das, S.K. (2011). Tribology of electroless nickel coatings - A review. *Materials & Design 32*(4), 1760-1775. https://doi.org/10.1016/j.matdes.2010.11.013

Tahery, R. (2003). Evaluation of electroless nickel-phosphorous (EN) coatings. Doctor of Philosophy Thesis, University of Saskatchewan, Saskatchewan, Canada.

Wang, X.-C., Cai, W.-B., Wang, W.-J., Liu, H.-T. and Yu, Z.-Z. (2003). Effects of ligands on electroless Ni-P alloy plating from alkaline citrate-ammonia solution. *Surface and Coatings Technology 168*(2-3), 300-306. https://doi.org/10.1016/S0257-8972(03)00013-6

Xiao, Z., Wang, W., Ye, L., Sha, Y. and Tu, S. (2008). Effect of Cd^{2+} as a stabilizer in the electroless nickel plating system. *Surface and Coatings Technology 202*(20), 5008-5011. https://doi.org/10.1016/j.surfcoat.2008.05.002

Xie, Z., Yu, G., Hu, B., Lei, X., Li, T. and Zhang, J. (2011). Effects of $(NH_4)_2SO_4$ on the characteristics of the deposits and properties of an electroless Ni-P plating solution. *Applied Surface Science 257*(11), 5025-5031. https://doi.org/10.1016/j.apsusc.2011.01.016