Development of process technologies for improvement of electroless nickel coatings properties

A Barba-Pingarrón¹,⁵, A Bolarín-Miró², F Sánchez-de Jesús², L Vargas-Mendoza³, M Trujillo-Barragán¹, P Molera-Sola⁴, M A Hernandez-Gallegos¹ and R Valdez-Navarro¹.

¹Centro de Ingeniería de Superficies y Acabados (CENISA). Departamento de Manufactura y Materiales. División de Ingeniería Mecánica e Industrial. Facultad de Ingeniería. Universidad Nacional Autónoma de México. 2° Nivel. Edificio “T” (Bernardo Quintana). Circuito Exterior. Ciudad Universitaria. Coyoacan, 04510, D.F. arbapin5@gmail.com.

²Cuerpo Académico de Sólidos Particulados. Instituto de Ciencias Básicas e Ingeniería. Universidad Autónoma del Estado de Hidalgo. México

³Departamento de Ingeniería Mecánica. Instituto Tecnológico y de Estudios Superiores de Monterrey. Campus Estado de México.

⁴Departamento de Ciencia de Materiales y Metalurgia. Universidad de Barcelona, España.

Email: arbapin5@gmail.com, abolarin@uaeh.edu.mx, fsanchez@uaeh.edu.mx, lvargas@itesm.mx, trujbar@gmail.com, pmolera@ub.edu, mahg22@yahoo.com.

Abstract. This paper describes research and technology developments that enable to improve nickel electroless coating properties. This work deals with: (a) different methods in order to achieve Ni-P-Mo coatings. (b) Other development is related with coatings with addition of hard particles such as SiC, WC or Al₂O₃. (c) Electroless nickel deposits on PBT and austempered ductile iron (ADI). (d) In addition, nickel coatings were deposited on powder metallic pieces and finally, electroless nickel coatings, in conjunction with layers from thermal spray process were formed. Characterization of all coatings by means of optical microscopy, scanning electron microscopy, micro-hardness, wear and corrosion tests were carried out. Results indicate positive increment in both mechanical and electrochemical properties which enhance field applications in Mexican industry.

1. Introduction.
Electroless (chemical) nickel coatings have been developed in the last 50 years and since then different applications in industrial fields have been reported [1]. Electroless nickel coatings offer interesting features such as: high-versatility of deposition on distinct materials (metals, polymers and ceramics), homogeneous and reproducible thicknesses (no matter shape or geometry of samples),

⁵To whom any correspondence should be addressed
amorphous or crystalline structures deposited as a result of variations in chemical composition baths, availability of heat treatments of coatings in order to achieve enhancement in wear properties and better. Electroless nickel coatings are mainly constituted by combinations of Ni-P at different mixture ratios. These formulations can be obtained either in acidic conditions or in alkaline environment from room temperature up to 100°C [1]. The purpose of this work is to study different routes deposition processes in order to improve mechanical and electrochemical properties which lead further applications.

2. Surface technology treatments

2.1 Development of ternary electroless coatings Ni-P-Mo.

Incorporation of molybdenum to electroless Ni-P coating achieved better wear resistance properties. The Ni-P-Mo bath was alkaline (pH \(-9.5\)), with different percentages of P (9-11%) and Mo (3-8%) using a formulation reported in [2]. Conditions of the deposition were 88°C and 5 hrs. Some coatings, on low carbon steel, were subjected to heat treatment at 300°C, 400°C and 500°C from 30 to 240 minutes. Results show that amorphous coatings change their structure to crystalline as a consequence of heat treatments. Different percentages of crystallinity were observed by Philips XL 20scanning electron microscope (SEM). SEM, in conjunction with EDAX, X-ray diffraction in Siemens 530 Diffractometer, electrochemical tests in HCl solutions, wear measurements (pin on disc) and microhardness evaluations in Shimadzu equipment (100g load), were carried out on different samples. Results indicate that both crystallization and precipitation hardening processes induced a hardness increment from 600 VHN to 1450 VHN. The formation of grains, grain boundaries and the presence of precipitates of compounds Ni-P which are obstacles to dislocation movement explain this hardness improvement. In addition, wear resistance was also modified, with better properties, by similar reasons. However, corrosion resistance did not improve after surface treatments. The presence of grain boundaries, and compounds of Ni, P y Mo (Ni₃P, MoNi₄, for example), originates galvanic sites and reduces corrosion resistance. It has to point out that molybdenum incorporation induces instability in the baths provoking lower deposition rates; therefore, alternatives to solve this problem should be addressed. Figure 1 shows typical morphology of these coatings.

**Figure 1.** Image of Ni-P-Mo coating on AISI 1018 steel. OM.

**Figure 2.** SEM micrograph of electroless Ni-P coating with SiC particles.
2.2 Electroless nickel plating with hard particles incorporated.
Incorporation of hard particles such as SiC, Al₂O₃ or WC into electroless nickel deposits on low carbon steel has been typical procedure studied for several years in CENISA. Proportion of particles used was 0.1 to 6 g/L, 85°C was the temperature and 4 hours the time, using mechanical or air agitation. The bath formulation employed has been reported in [3]. The main focus of incorporate hard particles into coatings relies on the fact that these aggregates induce better wear resistance, as indicated by Taber test results. That behavior is associated to the improvement of microhardness and rugosity generated by the presence of hard particles. In addition, it is also important to develop alternatives of stirring mechanisms of bath that enables homogenous dispersion into the metallic coating.

Concerning results of the characterization techniques described above, it is important to indicate the wear resistance increment. Figure 2 shows clear evidence of the obtained morphology aggregates of a electroless Ni-P coating.

2.3 Electroless Ni-P coatings on PBT
Polymer nickel-plated process represents a feasible chemical route to cover polymeric materials in a satisfactory way. This process involves long-term additional steps compared to traditional metal nickel-plating. One of the major challenges of cover polymers is the surface activation mechanism which directly affects the adherence properties. Results of the following work open a new and innovative trend of PBT metalizing since no references in literature can be found. The PBT nickel-plating procedure consisted of subsequent cleaning steps in conjunction with chemical attack using a solution containing chromic and sulfuric acid, surface sensitization with a SnCl₂ solution, activation mechanism using palladium chloride and finally electroless nickel-plating deposition employing a bath reported in [4] which it is usually carried before of electrolytic nickel plating. Figure 3 obtained in Philips XL20 SEM, shows a representative sample of Ni-P coating on PBT surface. The polymer surface that has been coated shows a uniform thickness and brilliant aspect.

![Figure 3. Scanning electron micrograph of a chemical nickel layer on PBT. (1000 X)](image1)

![Figure 4. SEM micrograph of a Ni-P coating on austempered ductile iron (ADI). 1200 X.](image2)

2.4 Electroless nickel-plating on Austempered Ductile Iron (ADI)
ADI represents a recent engineering material with many industrial applications due to its attractive and adequate mechanical properties similar or even better to those of some alloy steels. Some applications require relatively low-cost material with good wear resistance for machinery devices as shafts, gears, and bearings and ADI is an attractive option [5]. ADI properties results from heat treatment cycles
with final austempering process between 250 to 400°C. Metalizing ADI alloys represents a major challenge since no surface modifications are required after austempering process. Therefore, the present work developed a non-perturbation procedure for cover ADI with Ni-P alloys, using an acid bath formulation (pH 4.3 – 4.6) reported in [6] with a temperature of 85°C and 4 hours. Results show better corrosion properties after electrochemical tests in NaCl solution, without changes in the ADI microstructure. Figure 4, obtained in Philips XL20 SEM, depicts typical morphology of Ni-P coating deposited on ADI.

2.5 Duplex coating systems: Thermal Spray + Electroless nickel-plating on low carbon steel
Flame thermal spray process generates limited industrial coatings applications since morphology and defects of deposited material considerably affect adherence with irregular thicknesses along the sprayed surface. Therefore, the present work shows significant improvement in the corrosion properties of duplex coatings of thermal spray Ni-Cr-Fe-B-Si plus electroless Ni-P coatings. Prior to coating deposition chemical cleaning procedure was carried out in samples. Afterwards, thermal spray process was accomplished by standards procedures as reported elsewhere followed by an electroless nickel-plating. It was used an acid bath formulation (pH 4.3 a 4.6) [7], 85°C and 4 hours, after flame thermal spray procedure, employed operation parameters. This Ni-P layer acts as sealing barrier of defects of the previous coating, as can seen in electron micrograph obtained in Philips XL20 SEM (Figure 5). Therefore, improved adherence of the flame thermal sprayed layer in conjunction with final topcoat barrier provides an enhancement of corrosion properties, as indicated results of electrochemical tests in 3.5% sodium chloride solution.

![Figure 5](image.png)
**Figure 5.** Scanning electron micrograph of duplex flame thermal spray coating + electroless nickel coating on low carbon steel.

![Figure 6](image.png)
**Figure 6.** SEM micrograph of electroless Ni-P coating on iron substrate obtained by powder metallurgy.

2.6 Electroless nickel coatings on powder metallurgy materials.
Figure 6 shows a micrograph obtained in Philips XL20 SEM, of a electroless nickel coating deposited on an iron powder metallurgy sample using an acid bath [8]. Sponge and atomised iron compacts with different porosities were obtained by pressing at different densities (5.5 - 7.0 g cm⁻³) and sintering at 1120 °C in an N₂ - H₂ atmosphere. The ferroxyl test was used to evaluate the grade of superficial porosity, and the salt spray test helped to obtain the corrosion resistance of the Ni-P deposits on the PM compacts. Porosity of powder metallurgy samples represents disadvantages when a top coat layer is deposited. The present work determined that the amount of maximum porosity of iron powder
should be < 12 % in order to achieve good adherence between the samples and the electroless nickel coating. If samples generate elevated porosity poor coating deposition accompanied with low barrier and mechanical properties are achieved.

3. Conclusion
This work has presented different surface technologies alternatives developed in order to enhance the behavior of electroless nickel coatings. Deposition on PBT, ADI and powder metallurgy pieces show significance improvement in corrosion properties and wear resistance when topcoat layers of different Ni-P alloys are deposited. Hard particulates, ternary coatings alloys, heat treatments in conjunction with other surface technologies (thermal-spray), provide surface engineering systems that open new industrial applications.

4. References
[1] Barba A 2001 Ciencia e Ingeniería de la Superficie de los Materiales Metálicos ed. A J Vázquez and J J de Damborenea (Madrid: Textos Universitarios No. 31/CSIC) pp 261–279
[2] Vargas L, Barba A, Sánchez F and Bolarín A Age Hardening of Ni-P-Mo electroless deposit 2006 Surf. Eng. 22 58
[3] Sánchez F, Bolarín A, Barba A, Torres and Hernández L Obtención y Caracterización de Recubrimientos Compuestos Ni-P-X (X = SiC y WC) via química 2012 Superficies y Vacío 25 128
[4] Trujillo M 2011 Sobre el Niquelado Químico de Polímeros (México: Ph D Thesis/UNAM)
[5] Nofal A and Jekova L Novel processing techniques and applications of austempered ductile iron (Review) 2009 J. Univ. Chem. Tech. and Metallurgy 44 213
[6] Torres R 2007 Obtención y Caracterización de fundiciones nodulares austemperizadas recubiertas por niquelado químico (México: Sc. Master. Thesis/UNAM)
[7] Barba A, Hernández M, Sánchez F, Bolarín A and Valdez R 2011 Obtención de Recubrimientos Duplex Níquel Químico – Proyección Térmica sobre Acero de Bajo Carbono. Efecto en su Comportamiento a la Corrosión en Medio Salino: Memorias del XVII Congreso de la SOMIM (San Luis Potosi, México, 21-23 September 2011) p 719
[8] Bolarin A, Sanchez F, Barba A, Coreño O and Coreño J Electroless Nickel Plating of Atomised and Sponge Iron Compacts 2003 Surf. Eng. 19 364
[9] Ploof L Electroless Nickel. Composite Coatings 2008 Adv. Mat. Proc. 36
[10] Nováka M, Vojtêcha D and Zelinková M Heat Treatment of Ni-P-Al2O3 Electroless Coatings 2009 Metal 19 19

Acknowledgments
Authors (ABP, MAHG, MTB and RVN) acknowledge the support by DGAPA UNAM PAPIIT Research Project IT102612 “Desarrollo de Tecnologías de Modificación Superficial para la Optimización del Rendimiento de Materiales”.