EFECTUL PREGĂTIRII SUPRAFEȚEI DE OȚEL ASUPRA CARACTERISTICILOR ACOPERIRILOR DE Ni-P ȘI Ni-P-Al₂O₃ DEPUSE CHIMIC
EFFECT OF LOW CARBON STEEL SURFACE PREPARATION ON Ni-P AND Ni-P-Al₂O₃ ELECTROLESS COATINGS CHARACTERISTICS

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Electroless nickel is applied to many types of substrates to take advantage of the coating's properties. The final electroless nickel-based deposit quality is only as good as the quality of the base substrate metal since the coating's ability to level or hide imperfections in the base material is poor. In fact, any defect in the substrate will be more visible after the part is plated with electroless nickel. A variety of contaminants include machining oils, drawing lubricants, buffing compounds, sulfurized oils, chlorinated oils, waxes, etc. Experimental work was carried out in order to establish the effectiveness of the method for degreasing thin low carbon steel strips before chemical coating. One alkaline (Solution A) and two acidic based on deoxidants (Solution B and Solution C) were tested at a temperature of 75 ⁰C.

Before the chemical deposition of Ni-P și Ni-P-Al₂O₃ coatings, water break test was performed on steel substrate to evaluate the presence of hydrophobic contaminants, which can be detrimental to adhesion of coatings. Nickel sulphate hexahydrate was used as the source of nickel and sodium hypophosphite was used as the reducing agent, which also serves as the source of phosphorus in the coating. Sodium acetate, ammonium sulphate, sodium citrate, sodium dodecyl sulphate and lead acetate were used as additives in the plating bath, to accelerate the rate of deposition of the coating or as stabilizers to prevent the decomposition of the plating bath. During plating (45 minutes), the temperature of the bath was maintained at 80 °C using a constant temperature bath and the pH of the bath was maintained at 5.2.

The waterbreak test has been used to evaluate how clean a surface may be. The test is based on the ability of a properly cleaned surface to retain an unbroken film or sheet of water. Normally, dirty surfaces show a water break.

The samples of thin steel strip before and after deposition electroless Ni-P and Ni-P-nano - Al₂O₃ layers were characterized regarding the chemical composition, layer thickness, macroscopic appearance, uniformity and adhesion.
 The chemical composition of steel substrate and of the layers was determined by X-ray Fluorescence. In order to investigate the morphology and microcomposition of metallic substrate and of deposition layers and thickness coating for the samples were studied by using Scanning Electron Microscope coupled with Energy-Dispersive X-ray Spectroscopy

Nichelul electroless este aplicat pe multe tipuri de substraturi pentru a beneficia de proprietățile acoperirii. Calitatea finală a depunerilor pe bază de nichel electroless este la fel de bună ca și calitatea metalului substratului de bază, deoarece capacitatea acoperirii de a nivela sau ascunde imperfecțiunile din materialul de bază este slabă. De fapt, orice defect al substratului va fi mai vizibil după ce piesa este placată cu nichel electroless. O varietate de contaminanți includ uleiuri de prelucrare, lubrifianți de trefilare, compuși de lustruire, uleiuri sulfurate, uleiuri clorurate, ceară etc. S-au efectuat experimente pentru a stabili eficacitatea metodei de degresare a benzilor subțiri de oțel cu conținut scăzut de carbon înainte de acoperirea chimică. O soluție alcalină (soluția A) și două acide pe bază de deoxidanți (soluția B și soluția C) au fost testate la o temperatură de 75°C.
Înainte de depunerea chimică a straturilor de Ni-P și Ni-P-Al₂O₃, a fost efectuat testul de rupere a apei pe substrat de oțel pentru a evalua prezența contaminanților hidrofobi, care pot fi dăunătoare aderenței acoperirilor. Ca sursă de nichel a fost folosit sulfat de nichel hexahidrat, iar hipofosfitul de sodiu a fost folosit ca agent reducător, servind și ca sursă de fosfor în acoperire. Acetatul de sodiu, sulfatul de amoniu, citratul de sodiu, dodecil sulfat de sodiu și acetat de plumb au fost utilizați ca aditivi în baia de placare, pentru a accelera viteza de depunere a acoperirii sau ca stabilizatori pentru a preveni descompunerea băii de placare. În timpul placării (45 minute), temperatura băii a fost menținută la 80°C folosind o baie cu temperatură constantă și pH-ul băii care a fost menținut la 5,2.
 Testul de rupere a apei a fost folosit pentru a evalua cât de curată poate fi o suprafață. Testul se bazează pe capacitatea unei suprafețe curățate corespunzător de a reține un film neîntrerupt sau o peliculă de apă. În mod normal, suprafețele murdare prezintă o rupere a peliculei.
 Probele de bandă subțire de oțel înainte și după depunerea straturilor de Ni-P și Ni-P-nano - Al₂O₃ neelectrolitice au fost caracterizate în ceea ce privește compoziția chimică, grosimea stratului, aspectul macroscopic, uniformitatea și aderența. Compoziția chimică a substratului de oțel și a straturilor a fost determinată prin fluorescență cu raze X. Pentru a investiga morfologia și microcompoziția substratului metalic și a straturilor de depunere și grosimea straturilor de acoperire pentru probe au fost studiate cu microscopul electronic cu scanare cuplat cu spectroscopie cu raze X cu dispersie energetică.

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1.Introduction

Chemical coating with nickel (Electroless Plating) differs from other methods of metal coating (galvanizing, vacuum metallization, galvanizing) in that the substrate initiates the autocatalytic process of chemical reduction [1, 2]. From the point of view of the prepared surface, the most frequently coated substrates can be grouped into low-alloyed steels, carbon steels and high-alloy steels [3,4]. The significance and importance of surface preparation and its effect on the resulting deposit quality is too often overlooked as a primary cause of problems in the plating line [5-9]. A pretreatment cycle that works well on one substrate with one type of contaminant soil may be completely ineffective on the same substrate with other types. There are also a wide range of literature sources that discuss metal surface cleaning [10-15].

Iron and its alloys are the most frequently plated substrates [16-21]. From a surface preparation standpoint, they can be grouped as low alloy and carbon steels; cast iron; and high alloy steels. The principles of preparing ferrous surfaces are based on successive steps for soil removal, deoxidation, and surface activation. The way these steps are carried out will depend on the type of alloy processed.

Carbon and low-alloyed steels are deoxidized using either acid pickling solutions or alkaline deoxidants [4-5]. The acid pickling solutions used are hydrochloric or sulfuric acid, combinations of these acids or their salts. For c*arbon steels* a solution of 10 - 50% hydrochloric acid or 2 - 10% sulfuric acid is used. In this process it is desirable to avoid the use of pickling inhibitors, as they may interfere with the initiation and activation required for chemical nickel plating (electroless plating).

Alkaline deoxidants containing organic chelating agents and / or sodium cyanide are commonly used for surface preparation because they offer specific advantages over acidic deoxidants [6-8].

Alkaline deoxidants remove oxides without attacking the substrate metal and are less likely to cause hydrogen embrittlement than acidic solutions. Alkaline deoxidants are used electrolytically, either in the anodic mode (parts become anode) or using periodic reverse current (PR) when in the process the parts are sequentially anode or cathode. The use of periodic reverse current with alkaline deoxidants is especially useful in combination with acid pickling of steels, as carbon and other alloying elements can form layers with poor adhesion to the substrate [5-7]. These products must be removed from the surface before coating, in order to obtain a good adhesion of the nickel on the substrate. The procedures required to obtain the initiation and adhesion of the coating on the substrate (substrate activation) will depend mainly on the composition of the substrate. In the case of carbon steels, good

cleaning and deoxidation are sufficient for good adhesion, and in the case of high alloy steels, special techniques are required to obtain a good coating and adhesion.

High-alloyed steels require special treatments to activate the surface and obtain an adhesive layer. In general, for the activation of stainless steel, hydrochloric acid is used at relatively high concentrations. When the latter deoxidation method is used for high alloy steels, the last cycle must be performed with the parts on the cathodic side to avoid the formation of passive oxide layers (which occur under anodic conditions) [5].

High carbon steel cycles use similar strategies, with concern that a black film of carbon may form after acid activation. One method used successfully to obtain active surfaces is the so-called Woods strike, electrolytic treatment in a nickel chloride-hydrochloric acid bath. Treatment with nickel sulfamate and nickel glycolate by the strike method is sometimes used for activation. These electrolytic treatments, which act as a chemical deoxidizer, allow the deposition of a thin layer of active nickel and ensure a catalytic surface prepared for a good development of the chemical deposition process of nickel (electroless) [6,7].

High carbon steel cycles use similar strategies, with concern that a black film of carbon may form after acid activation [5-8,17].

Different metals may require different preplate cleaners, cycles and approaches.

Our experimental work was carried out in order to establish the effectiveness of the method for degreasing thin cold rolled steel strips before electroless Ni-P and Ni-P-Al$_2$O$_3$ coatings. Also, we have investigated the influence of low carbon steel surface pretreatment on these depositions' quality. Surfaces that are naturally active can become passive are contaminated with foreign residues or oxide layers. For this reason, the preparation of the surface for chemical nickel coating requires the highest degree of care and control of all metal finishing procedures.

Greases that are generally found on cold rolled steel strips fall into two categories:

a) Fats of animal or vegetable origin are combinations of fatty acids and glycerol or metal soaps (combinations of fatty acids with metals). Fatty acids found in vegetable or animal fats can be saturated, unsaturated and fatty acids that also contain the OH group of alcohols. The importance of these lubricating greases has decreased due to the increasing share of mineral oil production, but they are still widely used (for example palm oil is used to lubricate steel in the cold rolling process of thin strips. Most are saponifiable, ie they are hotly decomposed by alkalis (sodium or potassium), some being decomposed by alkali derivatives (carbonates), which by reaction with fatty acids give alkaline salts soluble in water, releasing glycerin (or

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Composition of solutions used for degreasing the thin low carbon steel strips /
Compoziţia soluţiilor utilizate pentru degresarea benzilor subţiri de oţel cu conţinut scăzut de carbon

Reagent components	Alkaline Solution A	Acid Solution B	Acid Solution C
Sodium hydroxide- NaOH	30g/l	30g/l	30g/l
Sodium carbonate- Na$_2$CO$_3$	10 g/l	10 g/l	10 g/l
Trisodium phosphate -Ca$_3$(PO$_4$)$_2$	10 g/l	10 g/l	10 g/l
Ethylene diamine-tetra-acetic acid (EDTA) - C$_{10}$H$_{16}$N$_2$O$_8$	5 g/l	5 g/l	5 g/l
Sodium gluconate- NaC$_6$H$_{11}$O$_7$	-	10 g/l	-
Sodium citrate- (NH$_4$)$_3$C$_6$H$_5$O$_7$	-	-	10 g/l
pH	12.6	5.5	4.5

glycerol), which is also soluble in. These fats can also be solubilized by organic solvents.

b) Fats of mineral origin are hydrocarbons, and therefore, are not saponifiable. They cannot be dissolved or transformed into water-soluble compounds by the action of alkalis. The only action of alkaline lye added with emulsifiers is to put these fats in suspension in the form of fine particles. These particles contain in addition to mineral fats and other solid materials, which otherwise cannot be removed. These fats are soluble in organic solvents. Given that the physical time of exposure of the strips in the degreasing stage is very short, being of the order of 2-3 seconds. From this point of view, perchlorethylene has an energetic action on the fat film, having a high dissociating power. Instead, due to the very high volatility, the vapors produced above the degreasing bath are emitted into the atmosphere, being very difficult to seize.

2. Experimentals
2.1. Establishing the effectiveness of the method of degreasing of cold rolled steel thin strips

In a first stage, laboratory experiments were carried out degreasing procedure on low carbon steel strips before chemical coating with nickel. For experiments, three kinds of solutions were prepared starting from p.a. purity reagents, namely: one alkaline (Solution A) and two acidic-based on deoxidants (Solution B and Solution C) with compositions given in Table 1. All these solutions were used at a temperature of 75^0 C on medium oiled low carbon steel strip. The experiments aimed to try to replace the surface cleaning method by using a solution with organic solvents.

Water break test was performed for each thin low carbon steel strip. This is pass/fail method used to evaluate surfaces for the presence of hydrophobic contaminants, which can be detrimental to adhesion of coatings. It is a qualitative means of evaluating surface energy, which is directly related to surface cleanliness. In this test, a stream of water is visually evaluated as it flows over a surface. If it spreads out into a continuous, unbroken sheet, it indicates that the surface is substantially free of hydrophobic contaminants. If the surface is contaminated with low surface energy

substances, the flowing water will not sheet uniformly over the surface but rather it will break into rivulets and tend to bead up (termed "water break"), and the result is only a binary 'water break free/not water break free, it is unknown whether it is too sensitive for some applications or not sensitive enough.

Surface preparation of thin low carbon steel strip has a decisive role in obtaining an adherent, uniform and continuous coating, it consisted of chemical degreasing at 75°C, followed by washing in hot water for 2 minutes and cold pickling in 20% concentration hydrochloric acid and washing in warm water, at nickel plating bath temperature.

2.2. Ni-P and Ni-P-Al$_3$O$_3$ coatings deposition on low carbon steel surface

Coatings based on Ni-P alloys were obtained by electroless deposition by using a bath (A) as related in [22]: starting from nickel sulfate, sodium hypophosphite, sodium acetate, ammonium sulphate, sodium citrate, sodium dodecyl sulphate and lead acetate in order to obtain uniform and adherent layers, which were achieved on thin steel strip of 1-2 mm thickness [22]. In the case of Ni-P-Al$_2$O$_3$ composites coatings, in the chemical nickel bath have been added alumina particles of 10 nm respectively in the amount of 2g/l. The electrochemical bath solutions were freshly prepared from analytical grade chemicals and distilled water. The introduction of Al$_2$O$_3$ powder in the electrolyte causes rapid destabilization of nickel-plating bath, this phenomenon was avoided by increasing the amount of stabilizer (lead acetate). Magnetic stirring at 300 rot/minute at laboratory level is needed to remove the hydrogen from the deposition bath and to maintain chemical homogeneity of the electrolyte. The electrochemical bath with a pH of 5.2. was connected by immersing the pretreated steel substrate and activating it in 100 ml of solution for 45 minutes, respectively. The temperature was controlled using a thermostatically controlled bath at 80°C.

2.3. Characterization of steel surface and of electroless coatings

The samples of thin steel strip before and after deposition electroless Ni-P and Ni-P-nano Al$_2$O$_3$ layers were characterized regarding the
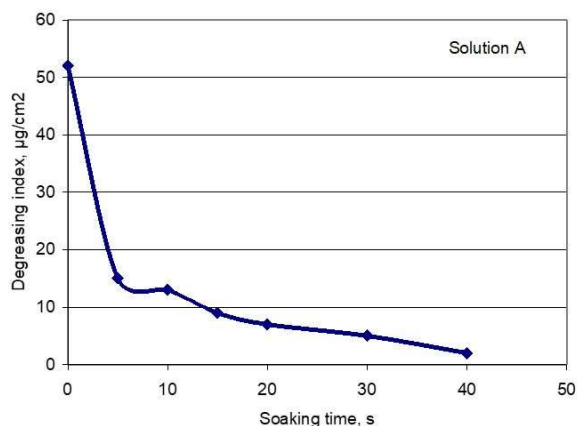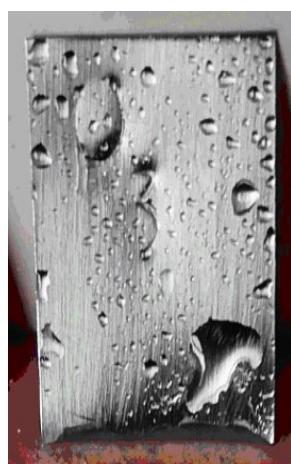
Fig. 1 - Evolution grease (oil) contamination level on low carbon steel surface at different soaking time in the alkaline solution A with pH = 12.6 at temperature of 75°C./ *Evoluția gradului de contaminare cu grăsime (ulei) pe suprafața oțelului cu conținut scăzut de carbon la timpi diferiți de înmuiere în soluția alcalină A cu pH = 12,6 la o temperatură de 75°C.*
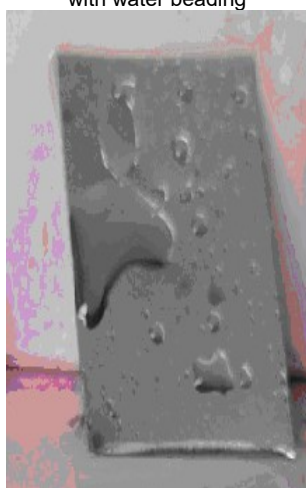

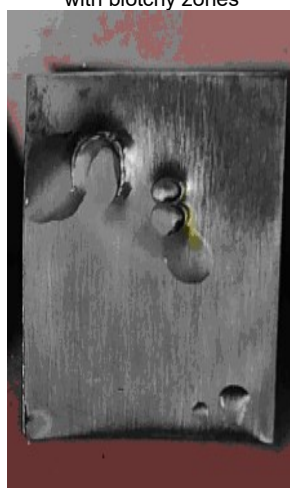(a) 5 seconds
Highly contaminated surface
with water beading

(b) 10 seconds
Highly contaminated surface
with blotchy zones
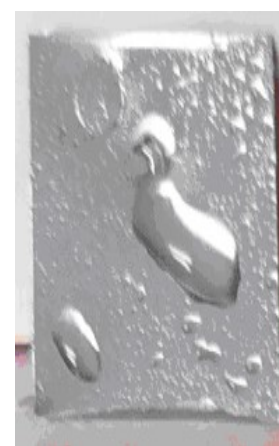
(c) 15 seconds
Unevently contaminated surface
with blotchy zones

(d) 20 seconds
Unevently contaminated surface
with blotchy zones

(e) 30 seconds
Low contaminated surface
with few blotchy zones

(f) 40 seconds
Well defined clean area

Fig.2 - Depiction of water break test results. Low carbon steel surface after different soaking time in the alkaline solution A with pH = 12 at temperature of 75°C. Top portion of the panel displays a non-water break free surface (water beads up). Bottom portion displays a water break free surface (water spreads out). / *Reprezentarea rezultatelor testului de rupere al apei. Suprafață din oțel cu conținut scăzut de carbon după timpi diferiți de înmuiere în soluția alcalină A cu pH = 12 la temperatura de 75°C. Partea superioară a plăcuței prezintă o suprafață care nu se sparge de apă (perle de apă în sus). Partea de jos arată o suprafață fără rupere de apă (apa se răspândește).*
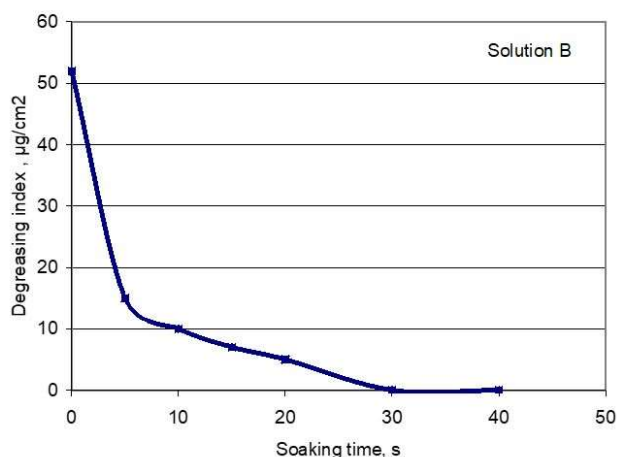
Fig. 3 - Evolution grease (oil) contamination level on low carbon steel surface at different soaking time in the alkaline solution B with pH = 5.5 at temperature of 75°C / *Evoluția gradului de contaminare cu grăsime (ulei) pe suprafața oțelului cu conținut scăzut de carbon la timpi diferiți de înmuiere în soluția alcalină B cu pH = 5,5 la o temperatură de 75°C.*
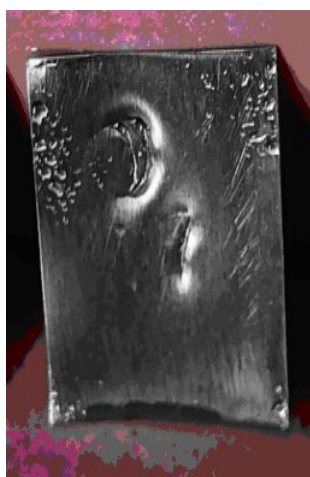

(a) 5 seconds
Highly contaminated surface
with water beading

(b) 10 seconds
Highly contaminated surface
with blotchy zones

(c) 15 seconds
Unevently contaminated surface
with blotchy zones

(d) 20 seconds
Low contaminated surface
with few blotchy zones

(e) 30 seconds
Well defined clean area

Fig.4 - Depiction of water break test results. Low carbon steel surface after different soaking time in the alkaline solution B with pH = 5.5 at temperature of 75°C. Top portion of the panel displays a non-water break free surface (water beads up). Bottom portion displays a water break free surface (water spreads out) / *Reprezentarea rezultatelor testului de rupere al apei. Suprafață din oțel cu conținut scăzut de carbon după timpi diferiți de înmuiere în soluția alcalină B cu pH = 5,5 la temperatura de 75°C. Partea superioară a plăcuței prezintă o suprafață care nu se sparge de apă (perle de apă în sus). Partea de jos arată o suprafață fără rupere de apă (apa se răspândește).*
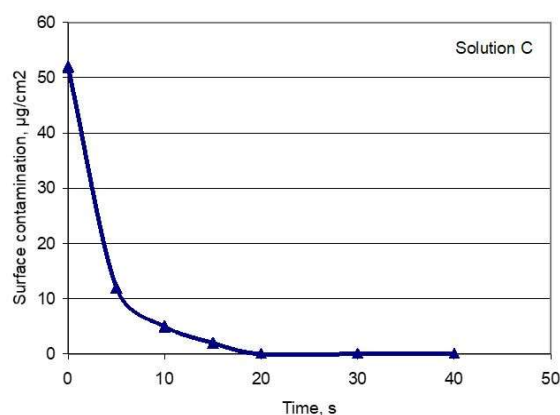
Fig.5. - Evolution grease (oil) contamination level on low carbon steel surface at different soaking time in the alkaline solution C with pH = 4.5 at temperature of 75°C. / *Evoluția gradului de contaminare cu grăsime (ulei) pe suprafața oțelului cu conținut scăzut de carbon la timpi diferiți de înmuiere în soluția alcalină C cu pH = 4,5 la o temperatură de 75°C.*
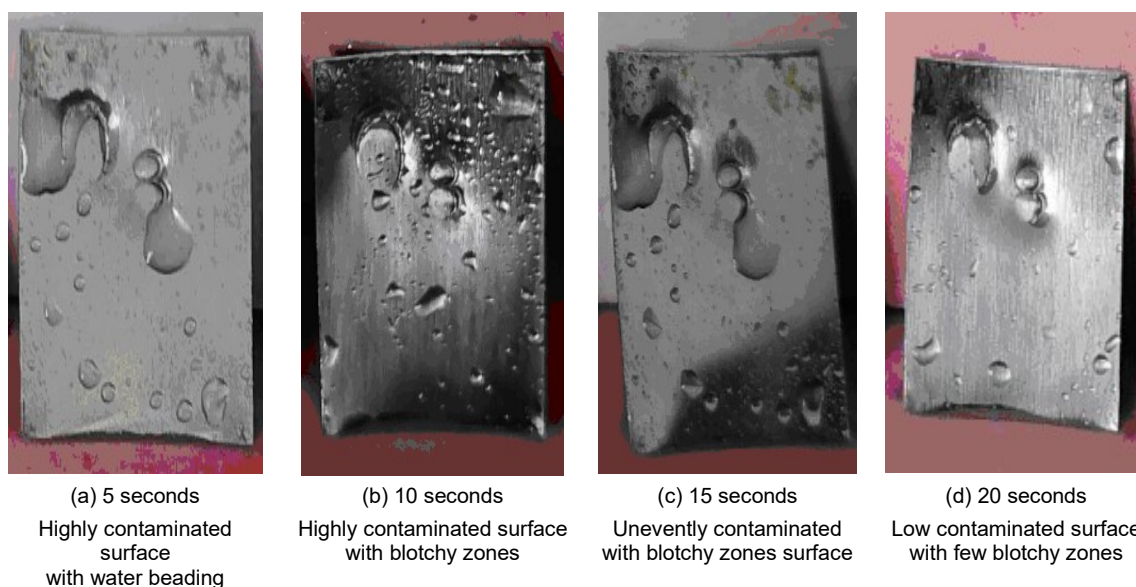

(a) 5 seconds	(b) 10 seconds	(c) 15 seconds	(d) 20 seconds
Highly contaminated surface with water beading	Highly contaminated surface with blotchy zones	Unevently contaminated with blotchy zones surface	Low contaminated surface with few blotchy zones

Fig.6 - Depiction of water break test results. Low carbon steel surface after different soaking time in the alkaline solution C with pH = 5.5 at temperature of 75°C. Top portion of the panel displays a non-water break free surface (water beads up). Bottom portion displays a water break free surface (water spreads out). / *Reprezentarea rezultatelor testului de rupere al apei. Suprafață din oțel cu conținut scăzut de carbon după timpi diferiți de înmuiere în soluția alcalină C cu pH = 5,5 la temperatura de 75°C. Partea superioară a plăcuței afișează o suprafață care nu se sparge de apă (perle de apă în sus). Partea de jos arată o suprafață fără rupere de apă (apa se răspândește).*

chemical composition, layer thickness, macroscopic appearance, uniformity and adhesion. The chemical composition of the layers was determined by X-ray Fluorescence (XRF) Panalytical AXIOS X-ray fluorescence spectrometer operating at 60 KV and current of up to 160 mA with dual multi-channel analyzer (DMCA) and commercial software Super Q, analytical programs (IQ+, WROXI, Ni-Fe-Co, TOXEL, Cu BASE). In order to investigate the morphology and micro composition of metal substrate and of deposition layers, and thickness coating for the samples were studied by using Scanning Electron Microscope: Quanta Inspect F coupled with Energy-Dispersive X-ray Spectroscopy EDXS.

3. Results and discussion
3.1. Method of degreasing low carbon steel thin strips

Degreasing is the process by which water-insoluble contaminants such as fats and oils of mineral or animal origin, petroleum products, resins, etc. are removed from metal surfaces. Degreasing is a process that precedes metal coating (galvanizing, soldering, nickel plating). For example, the removal of contaminants by degreasing allows proper metal coating (the presence of contaminants on the surface before coating does not allow the layer used to adhere properly which leads to its exfoliation). In industrial metal coating processes,degreasing

is most often followed by pickling. Degreasing is an operation of cleaning the surface by a chemical reaction or only by a physical dissolution, depending on the nature of the layer of grease on the surface of the strip and degreasing products. This is one of the most important operations, because improper degreasing is difficult to detect immediately, the effects appearing during subsequent operations. These effects are manifested by inadequate adhesion (uncovered portions, blisters or pitting in the coating).

On Fig.1 is displayed the evolution grease (oil) contamination on low carbon steel surface at different soaking time in the alkaline solution A with pH = 12.6 at temperature of 75°C. On can be noticed that after 5-30 seconds the surface is not degreased properly. The degreasing level increases with the immersion time; after 40 seconds the steel surface being completely degreased.

Depiction of water break test results for low carbon steel surface after different soaking time in the alkaline solution A with pH = 12.6 at temperature of 75°C is given in Fig.2.

On Fig.3 is shown the evolution grease (oil) contamination on low carbon steel surface at different soaking time in the alkaline solution B with pH = 5.5 at temperature of 75°C. On can be noticed that after 5-20 seconds the surface is not degreased properly. The degreasing level increases with the immersion time; after 30 seconds the steel surface being completely degreased.

Depiction of water break test results for low carbon steel surface after different soaking time in the alkaline solution B with pH = 5.5. at temperature of 75 °C is given in Fig.4.

The solution B is more efficient, completely degreasing the board after 30 seconds of immersion was recorded. On Fig.5 is shown the evolution grease (oil) contamination on low carbon steel surface at different soaking time in the alkaline solution C with pH = 4.5 at temperature of 75°C. On can be noticed that after 5 -10 seconds the surface is not degreased properly. The degreasing level increases with the immersion time; after 20 seconds the steel surface being completely degreased.

On Fig.6 is shown the evolution grease (oil) contamination on low carbon steel surface at different soaking time in the alkaline solution C with pH = 4.5 at temperature of 75°C. On can be noticed that after 5 -15 seconds the surface is not degreased properly. The degreasing level increases with the immersion time; after 20 seconds the steel surface being completely degreased.

The solution C had the same composition as the second, to which was added a derivative of a polyacid (sodium citrate) at a concentration of 10 g / l. The solution has a pH of 4.5 and is also used at 75°C.

As can be seen on **Fig.6,** the degreasing time has been halved (20 sec) comparatively with solution alkaline solution A and the adhesion of water droplets to the metal surface no longer takes place, which indicates an advanced degree of surface cleaning.

Given the fast operation potential, a very short exposure time of the steel strip results during the coating process, the optimal degreasing option is based on the solution C. During the processing of some test batches, it proved to be effective. This method can ensure excellent preparation of the strip surface following a treatment that removes any traces of dirt left over from previous processes.

The experienced degreasing method, based on deoxidants, is a clean one in terms of environmental impact, in the sense that it does not emit gaseous effluents and does not require cyclic evacuation of the used solution. It successfully replaces the use of perchlorethylene, with a very harmful impact on environmental factors, due to emissions of highly bioaccumulative volatile organic compounds.

Alkaline deoxidizers containing organic chelating offer specific advantages over acid deoxidizers in surface preparation. Alkaline deoxidant as solution A removes oxides without attacking the substrate metal and are less prone to cause hydrogen embrittlement than acid solutions B and C.

It should be noticed the water break free surfaces were observed for 2, 5, 7 and 15 µg/cm². Above 15 µg/cm² a completely non-water break free surface was observed (Fig. 4-6). Water break and degreasing rate of steel surface show a positive correlation with contamination level, however, are not able to quantify direct to the level of contamination. Cleaning and deoxidation residues can increase the porosity of the chemically deposited nickel, creating passive stains that will not initiate chemical coating. To ensure that the films remaining on the surface interface are adequately removed repeated rinses in distilled water was applied (up to 2 min). Following rinsing, the steel surface was activated by pickling in 20% concentration HCl solution for 30 seconds.

3.2. Ni-P and Ni-P-Al₂O₃ coatings deposition on low carbon steel surface

Electroless nickel deposits are known for reproducing the topography of the substrate. They are not leveling deposits like electrolytic nickel processes. If a streak or mark appears in or on the substrate, expect the electroless nickel deposit to magnify the defect. One should not expect the electroless nickel to hide the substrate problem. In fact, it is common for an electroless nickel deposit to magnify or highlight a defect. Coating performance, such as corrosion resistance, is closely tied to the surface preparation success or
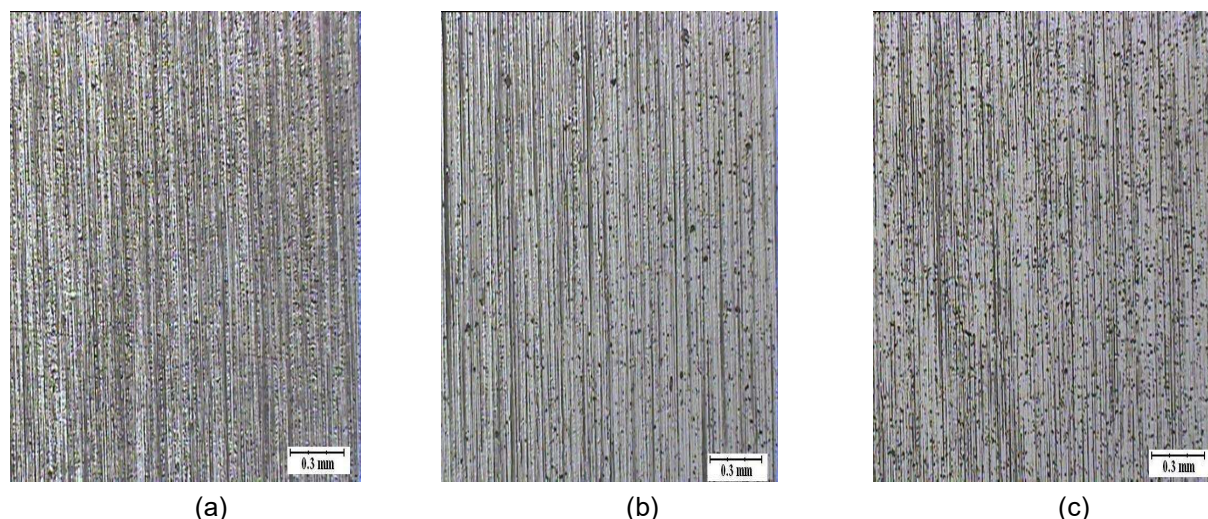
<center>(a)   (b)   (c)</center>

Fig.7 - The appearance of the steel strip surface after deoxidation before electroless deposition; Magnification: x 40 after treatment with alkaline deoxidant A pH=12.6; b) with acid deoxidan B-pH=5.5; c) with acid deoxidan C-pH=4.5 at 75°C and rinsing with hot water
Aspectul suprafeței benzii de oțel după depunerea electroless la 80°C timp de 45 de minute, mărire: x 40 a) cu acoperire Ni-P și b) cu acoperire Ni-P-nanoAl$_2$O$_3$

<center>(a)   (b)</center>

Fig. 8 - The aspect of steel strip surface after electroless deposition at 80°C for 45 minutes, Magnification: x 40 a) with Ni-P coating and b) with Ni-P-nanoAl$_2$O$_3$ coating / *Aspectul suprafeței benzii de oțel după depunerea electroless la 80°C timp de 45 de minute, mărire: x 40 a) cu acoperire Ni-P și b) cu acoperire Ni-P-nanoAl$_2$O$_3$*

failure. Any step in the surface preparation that creates porosity, pits or roughness from smut formation will impact negatively on the corrosion performance. Plating over a film that is not adequately rinsed will likely be the root cause of poor adhesion or increased porosity of the final deposit. The appearance of the steel strip surface after deoxidation and rinsing with hot water before electroless deposition after treatment with alkaline deoxidant A pH=12.6 (Fig.7.a), respectively after acid deoxidation at pH=5.5 (Fig. 7b) and after acid deoxidation pH=4.5 at 75°C (Fig. 7c). There are noticeable stripes finer than 0.01 mm and numerous pits of 0.001-0.01 mm. The appearance of the Ni-P electroless coated surface is shown in Fig.7b, showing the presence of ripples of approx. 0.01-0.015 mm, as well as micropores with dimensions below 0.01 mm. Alkaline deoxidizers containing organic chelating offer specific advantages (Fig.7a) over acid deoxidizers in surface preparation (Fig.7b and Fig.7c). Alkaline deoxidants remove oxides without attacking the substrate metal and are less prone to cause hydrogen embrittlement than acid solutions. One can conclude that the pretreatment of steel surface for electroless deposition of nickel-based coatings requires the highest degree of care and control of all metal finishing procedures. Another reason why a careful selection of the preparation process is needed is that it can significantly affect the porosity of the metal deposit.

The surface appearance electroless deposited Ni-P layer and respectively Ni-P-nano-Al$_2$O$_3$ layer is shown in Fig.8 (a, b). There is a

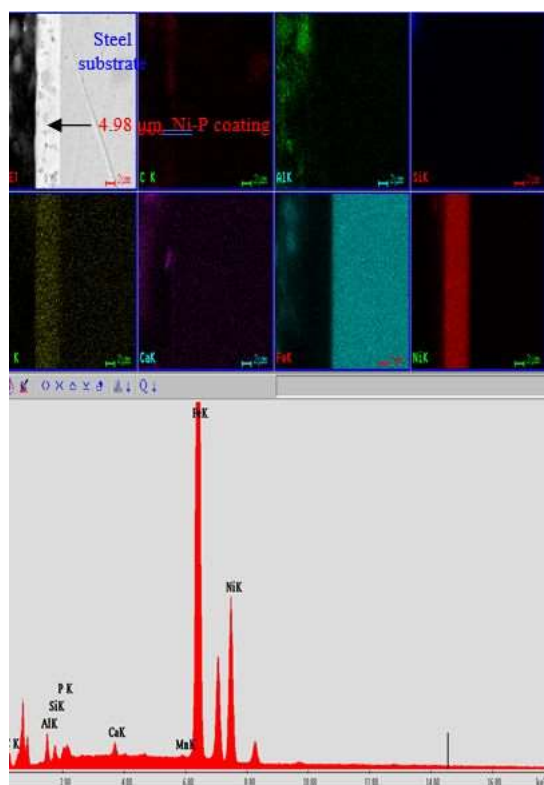**Fig.9 -** General EDS image of the distribution of FeKα, PKα, NiKα elements in electroless Ni-P coating / *Imagine generală EDS a distribuţiei elementelor FeKα, PKα, NiKα în acoperirea Ni-P fără electroless*
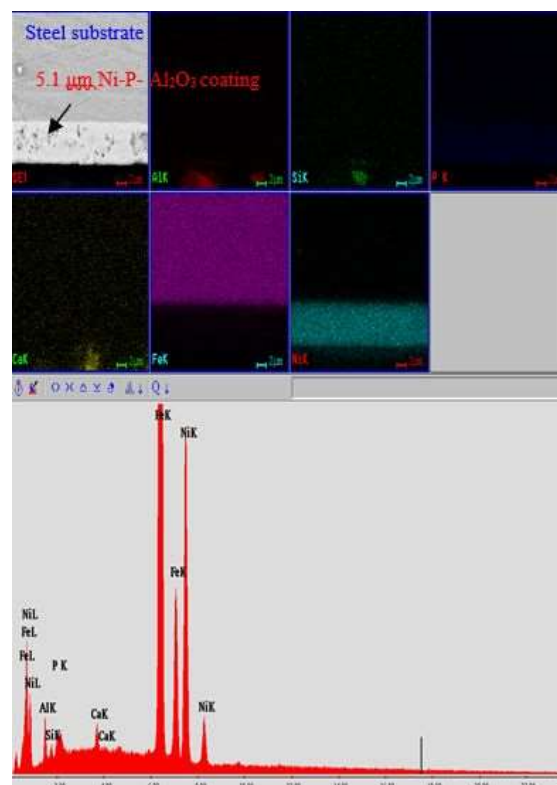

Fig.10 - General EDS image of the distribution of FeKα, PKα, NiKα elements in electroless Ni-P-nano-Al₂O₃ coating *Imagine generală EDS a distribuţiei elementelor FeKα, PKα, NiKα în Ni-P-nano-Al₂O₃ fără electroless*

relatively homogeneous coverage with an appropriate adherence of the deposited layer and the presence of much more attenuated ripples below 0.01 mm, and the presence of "stings" is although much diminished, it can be noticed to be concentrated along the ripples.

In the case of investigated low carbon steels, good cleaning and deoxidation is in most cases sufficient for good bonding of electro less coating.

General EDS image of the main elements' distribution (FeKα, PKα, NiKα) on electroless coatings are given in Fig.9 in Ni-P deposition, respectively in Fig. 10 in Ni-P-nano-Al₂O₃. The thickness of Ni-P coating is about 4.8 - 4.9 μm, respectively about 5.0 -5.2 μm for Ni-P-nano-Al₂O₃ coating.

Chemically deposited thin layers of nickel (less than 5 μm) are more porous than electrochemically deposited nickel layers of comparable thickness. During chemical coating with nickel, the deposition processes are initiated in very small spaces and the substrate will become fully covered by the lateral growth of these spaces. The short coating time does not allow a complete coating of the base material, causing porous chemical deposits.

The final electroless nickel-based deposit quality is only as good as the quality of the base substrate metal since the coating's ability to level or hide imperfections in the base material is poor.

In fact, any defect in the substrate will be more visible after the part is plated with electroless nickel.

In summary, the following cycles for low carbon ferrous surfaces was introduced:

Alkaline soak cleaning → Water rinse →

→ Activation in 20% HCl → Water rinse →

→ Electroless nickel plating
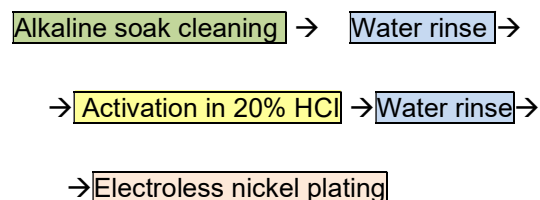
4. Conclusions

In the case of chemical coating with nickel (electroless method) of metal substrates, with different compositions and properties, specific procedures are required for each type of substrate, being impossible to choose a general approach to surface preparation. The principles of preparation of ferrous surfaces are based on successive cleaning cycles, for removing soils, deoxidation and activating the surface of the processed material.

To achieve an efficient and economical cleaning of steel surface to be electroless plated, the choice of the cleaning method depends on the nature of the impurity that contaminates the surface and the nature of the substrate on which the deposit

is made. There are many more types of materials that can be as a contaminant including dirt, smut, oxides, rust machining oils, drawing lubricants, buffing compounds, sulfurized oils, chlorinated oils, waxes and heat scale. Difficult-to-remove oils or compounds can be imbedded into the surface of the part causing dull or nonadherent coatings.

Our trial for low carbon steel surface substrate preparation shows that a combination of alkaline solution of sodium hydroxide, carbonate, phosphates, and organic surfactants is effective at 75oC, under 20- 40 seconds soaking. Alkaline deoxidizers containing organic chelating offer specific advantages over acid deoxidizers in surface preparation. Alkaline deoxidizers remove oxides without attacking the substrate metal and are less prone to cause hydrogen embrittlement than acid solutions.

The waterbreak test has been used to evaluate how clean a surface may be. The test is based on the ability of a properly cleaned surface to retain an unbroken film or sheet of water. Normally, dirty surfaces show a water break. Water break test and degreasing rate of low carbon steel surface show a positive correlation with contamination level.

To obtain initiation and adhesion of the coating to the substrate (substrate activation) depend mainly on the composition of the substrate.

The low carbon steel surface pretreatment efficacity was demonstrated by deposition of electroless Ni-P respectively Ni-P-nano Al₂O₃ layers, which were characterized regarding the chemical composition, layer thickness, macroscopic appearance showing a proper adhesion and uniformity.

One can conclude that the pretreatment of steel surface for electroless deposition of nickel-based coatings requires the highest degree of care and control of all metal finishing procedures. Another reason why a careful selection of the preparation process is needed is that it can significantly affect the porosity of the metal deposit.

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