

# Effect of Polishing Grits, Temperatures and Selected Activators on Electroless-nickel Deposition on Cast Aluminium Substrates

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## ABSTRACT

The state of the surface of a material controls how stable and lasting such material will be under the service condition. Wear and corrosion take place on the contacting surfaces. For an efficient engineering design, the surface has to be protected by different method of surface deposition technique such as electroless-nickel (EN) plating. The firmness and the dependability is built strongly on the morphology of the metallic film. This paper aimed to study the effect of grinding grits, types of activator and plating operation temperatures on the quantity (EN deposition per unit area) and quality (appearance, lustre, adhesion) of the nickel plating on Al substrate. A number of experiments were performed from which the best of results were used to model the trend of each individual effect on plating process. Different grades of polishing grits were applied and their effects on the adhesion, appearance and quantity of EN deposits per unit area on cast aluminium substrates were studied.

**Keywords:** Cast Aluminium Alloy, Electroless-Nickel Deposition, Selected Activators, Substrate, Surface Polishing, Plating Temperature

## 1.0 INTRODUCTION

Many types of aluminium alloys are employed for engineering purposes where both or either of light weight and/or corrosion resistance is required [1] such as automotive engines. Among these vast classes are aluminium-magnesium alloys, being found useful in automotive engine cylinder, brake and clutch master cylinder, yet are subject to wear and corrosion. There is certain number of environment under which aluminium gets widely corroded and this occurs mostly in strongly acidic or strongly alkaline solutions though there are specific exceptions [2,3,4,5,6]. Since 2010, Ajibola and Jimoh, and Ajibola *et al.*, had been involved in understudying the properties, application and problems of wear and corrosion of cast aluminium alloys used in brake master cylinders with hydraulic fluids (Figure 1 a,b). The reports of such findings are progressively presented both at local conferences [7,8] and international conferences [9]. The studies by Ajibola *et al.*, [10,11] were performed to assess the metallurgical properties and wear rates of brake master cylinder pistons with the view to improving on the wear and corrosion resistance of the Al alloy substrates in brake fluid. Also, report of studies by Ajibola *et al.*, [10,11] had recommended the application of surface treatment and deposition of resilient metallic film as solution to alleviating wear and corrosion problems of this useful machine part immersed in brake oil.

There is variety of techniques of metal coating. These include processes like hot dipping, electroplating, anodising, electroless and autocatalytic deposition [12–13], cladding, parkerizing and galvanising [14, 15, 16]. Plating has been practiced for many years, but it is also very significant for modern technological practices. Metallic coating is utilized for decoration, corrosion inhibition, to improve solderability, to enhance hardness, to

increase wear resistance, to lessen friction, to improve paint adhesion, to alter conductivity, for radiation shielding, and for other purposes. Metal plating usually fail only in small sections, and if the plating is more noble than the substrate (for example, chromium on steel), a galvanic couple will cause any exposed area to corrode much more rapidly than an uncoated surface would.

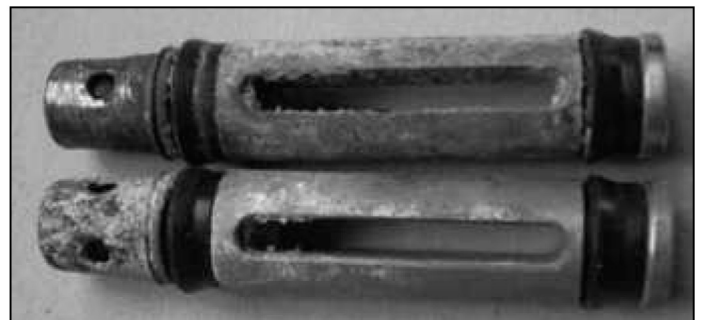
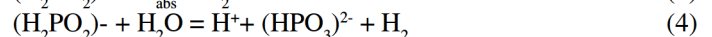
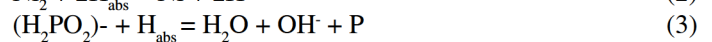
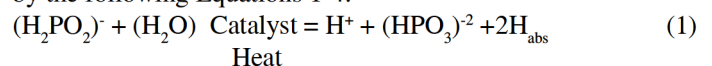


Figure 1: Surface of corroded hydraulic brake pistons samples after long immersion in brake oil.

Electroless-nickel (EN) deposition is a chemical autocatalytic reduction procedure which is principled on the reduction of nickel ions in an aqueous solution (containing a chemical reducing agent) and the subsequent deposition of nickel metal without the application of electricity. Agarwala and Agarwala, [17] presented the most widely accepted mechanism by the following Equations 1-4:



In the presence of a catalytic surface and sufficient energy, hypophosphite ions are oxidized to orthophosphite. Acid solutions were found to have several advantages over alkaline solutions: higher plating rate, better stability, greater ease of control, and improved deposit corrosion resistance. Using a proper surface pre-treatment order and precise process control, high-quality adhesion and outstanding service performance, very homogeneous thickness is produced all over the part, even for asymmetrical shapes, holes, recesses, internal surfaces and valves.

High-quality adhesion of EN deposits on Al alloy emanates from excellent cleaning and lowest amount etching operations. There is now a better understanding of the features influencing adhesion properties. Good adhesion is reliant on having a dirt-free surface free from soils, oxides, particulate matter and embedded materials. For instance, gentle etch alkaline cleaners work well for many surface contaminating soils.

There are different surfactants such as applicable in cleaning, surface modification, sensitization, catalyzing, activation (acceleration) and as stabilizers. Surfactants are also used as wetting agents that lower the surface tension of a liquid, allowing easier distribution, and lower the interfacial tension between two liquids or a liquid and solid surface. In an EN bath, existences of surfactants encourage the deposition reaction between the bath solution and the immersed substrate surface [18]. The deposition of Electroless-Ni on cast aluminium was investigated for its wear and corrosion properties through experimental methods and is reported in this paper.

## 2.0 MATERIALS AND METHOD

The commercial aluminium alloy sample was sourced from the hydraulic brake master cylinder floating pistons (callipers). The piston (designated as 'As-received Al alloy' or 'AR') was procured from automobile spare part market in Ado Ekiti, Nigeria from which cast rod (designated as 'Cast Al alloy' or 'AC') was produced. Aqueous solutions of different chemicals such as Emulsifier, Sodium hydroxide, Hydrochloric acid, Sodium phosphate, Zinc oxide, Potassium sodium tartrate, Sodium nitrate, and Ferric chloride used in pre-treating the aluminium samples, and EN plating chemical including Palladium chloride, Nickel Chloride, Sodium Hypophosphite, Sodium citrate, Ammonium chloride, anti-tarnish chemical (potassium-dichromate solution) were procured from scientific chemical stores in Ado Ekiti, Nigeria. The equipments used for the experiment include: Electronic digital weight meter (model DT-502A, 0.0001g), lathe machine, drilling machine, electrical cutting saw, electroless Nickel plating line (Figure 3), and thermometer.

### 2.1 Chemical analyses of Aluminium alloy substrates

The chemical compositions and hardness of aluminium alloy substrates (as-received Al and cast Al) were determined using Atomic Absorption Spectrometer (AAS) Thermo series 2000

Model, and Brinell hardness tester respectively. The results are presented in Table 1.

### 2.2 Preparation of cast samples used for EN plating

2000g of as-received aluminium alloy sourced from purchased piston (calliper) was weighed into a melting pot and melted at temperature range of 750°C to 800°C in electric furnace under a controlled atmosphere. The molten metal was sand cast into rods of 300mm long by 30mm diameter from which the two set of tests specimen (pistons and coins) were cut and machined out. They were sliced to obtain 15mm thick by 25mm diameter coin size used for plating tests (Figure 2). The surfaces of the aluminium alloy substrates were grinded and polished with different types of polishing grits on the grinding and polishing machines (Metaserv 2000 model). The microstructure and surfaces of the samples were examined under the metallurgical microscope of X800 maximum magnification (Nikon Eclipse ME600 model).



Figure 2: Pieces of Al alloy specimens for EN plating test.

#### 2.2.1 Cleaning of samples, surface activation and EN plating

Table 2 shows the EN pre-treatment and plating chemicals, media concentrations, operating temperatures and the immersion periods. The polished samples are cleaned in a series of chemicals such as bases and acids to prepare the surface for good adhesion. Each of the chemical pre-treatment is followed by water rinsing to remove the chemical that adheres to the surface. Degreasing removes soil and oil, while acid cleaning removes scaling. The surface activation is done in six different types of solutions: sodium-di-chromate, palladium chloride solution at 85°C, zincate, water, HCl and NaOH solution before they are finally plated with electroless nickel. The surface activation is done in six different types of solutions before they are finally plated with electroless nickel.

Pre-cleaned and surface activated samples are immersed into the electroless-nickel baths operated at varying temperatures comprising of nickel chloride (source of nickel), sodium hypophosphite (reducing agent) and sodium citrate (stabilizer). The pH of the EN bath was fixed by adding required quantity of ammonium solution or sodium hydroxide solution. After the coating process, coated material is immersed in anti-tarnish chemical to prevent unwanted stains. The EN coated samples are washed in distilled water after, and dried in the oven after which the quantity of deposition per unit area is determined.

Table 1: Chemical composition and hardness of aluminium alloy substrates.

Samples	Al	Si	Mg	Fe	Mn	Cu	Zn	Cr	Ti	BHN
As-received Al.	98.87	0.38	0.40	0.23	0.001	0.01	0.001	0.001	0.001	43.6
Cast Aluminium alloy coins	98.44	0.32	0.29	0.16	0.001	0.01	0.001	0.001	0.001	63.8

**Table 2: Plating chemicals and the mixing ratio**

Bath	Media	Concentration (g/l or ml/l)	Temperature (°C)	Time (mins)
Emulsifying	Emulsifier: Kerosene with Detergent solution	15 ml/l	60±5	1-5
		15 g/l		
Alkaline cleaning	Sodium hydroxide	0.4 g/l	60±5	1-5
Acid cleaning	Hydrochloric acid	5 ml/l	60±5	1-5
Surfactant	PCl <sub>2</sub>	0.0 ~ 0.12 g/l	85	0.5-2
Plating	Nickel Chloride	30 g/l	85±5	2 - 10
	Sodium Hypophosphite	40 g/l		
	Sodium citrate	25 g/l		
	Ammonium chloride	50 g/l		
	PCl <sub>2</sub>	0.02/l		

The effect of surface finishing on the EN plating was studied using different emery paper polishing grits (60µm, 120µm, 220µm, 320µm, 400µm, 600µm, 800µm and 1200µm). In another case, the effects of six selected chemical media used as surfactants (sodium-di-chromate, palladium chloride, zincate, water, HCl and NaOH) were also studied. The influence of plating bath temperatures varied from 80°C, 85°C and 90°C temperatures were also examined on the EN plating characteristics.

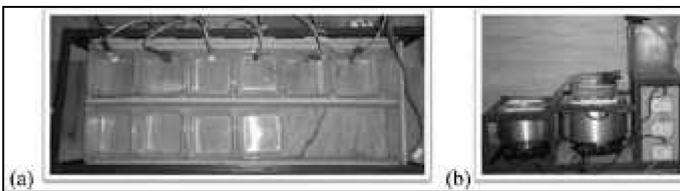
The amount of EN deposit (g) is determined from the difference between the initial weight ( $M_i$ ) and final weight ( $M_f$ ), measured before and after EN plating using electronic digital weight meter, from which the amount deposited per unit area ( $g/mm^2$ ) and EN plating rate ( $g/mm^2/min$ ) are calculated;

$$\Delta W = M_f - M_i \quad (5)$$

$$\text{Amount EN deposited per unit area} = \Delta W / (A_T) \quad (6)$$

$$\text{EN deposition rate } R_{EN} = \Delta W / (A_T \times t) \quad (7)$$

where  $W_i$  = weight of the sample before EN-plating,  $W_f$  = weight of the sample after EN-plating and  $\Delta W$  = EN film weight deposited,  $A_T$  = Total surface area of substrate,  $t$  = plating time.



**Figure 3: Pictorial views of complete assembly of the cleaning line (a) and EN plating bath (b).**

### 3.0 RESULTS AND DISCUSSIONS

#### 3.1 Characteristics of the aluminium substrates

The aluminium alloy substrates, (as-received Al or AR and cast Al or AC samples) were characterised by atomic absorption spectrometry to ascertain the chemical composition of the

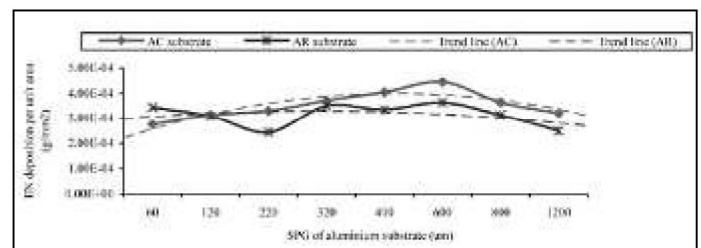
substrates. The micro-structural examination is carried out to reveal the micro structure of the alloy and to compare the similarities and differences. The hardness values are compared as means of predicting their behaviour under friction with respect to their composition and micro-structure. With these, some reasons for their corrosion and wear behaviours of the aluminium alloy substrates could be understood. Table 1 shows the results of chemical compositions and hardness of as-received Al alloy (control sample) and cast Al alloy used in the experiment. The chemical analysis shows that 98.87%Al, 0.38%Si, 0.40%Mg, and 0.23%Fe were present in the AR, that 98.44%Al, 0.32%Si, 0.29%Mg, and 0.16%Fe were present in the AC while equal amount of 0.001%Mn, 0.01%Cu, 0.001%Zn, 0.001%Cr and 0.001%Ti were present in both AR and AC alloys.

#### 3.2 EN deposition per unit area on aluminium substrates

The trends and amount of electroless-nickel deposition per unit area on AR and AC alloy substrates at various polishing grits, temperatures and surface activation are illustrated in Figures 4-23.

#### 3.3 Effect of surface polishing grits SFG variation on amount of EN deposition on AR and AC at 85°C using PdCl<sub>2</sub>

Deposition of electroless-nickel on as-received and cast aluminium alloy substrates at various polishing grit is carried out for 10 minutes at 85°C.



**Figure 4: Effect of SFG variation on EN deposition per unit area ( $g/mm^2$ ) on AR and AC samples operated at 85°C plating temperature.**

Figure 4 shows that there is more of EN deposition per unit area on the 60µm and 120µm grits polished as-received alloy than the cast aluminium substrate. There is steady increase in the quantity of EN deposition per unit area on cast aluminium substrate as the grade of surface polishing grits increased from 60µm to 600µm, above which there was reduction in the amount of EN deposition per unit area obtained on the cast aluminium substrate. There is subsequent greater amount of EN deposition per unit area on cast substrate than the as-received substrate with respect to the increase in the grade of surface polishing grits used.

It is observed that there is fall in the quantity of EN deposition per unit area on as-received alloy as grade of surface polishing grits increased from 60µm to 220µm, above which there was increase in the amount of EN deposition per unit area obtained on the as-received aluminium substrate. 600µm surface polishing grits produced the highest quantity of EN deposition per unit area on both the cast and as-received aluminium substrates.

The trend of the amount of EN deposited with respect to increasing polishing grit was studied using the experimental data generated from the experiment. The best fit models for the trend using MS excel application were of polynomial equations to power 2 relating the amount of EN deposited to surface polishing grits (um). The developed models from the study are:

$$M_{n1} = -8E-06x^2 + 8E-05x + 0.0002 \quad (8)$$

$$M_{n2} = -3E-06x^2 + 2E-05x + 0.0003 \quad (9)$$

where  $60 \geq x \geq 1200\mu\text{m}$ ,  $x$  = grade of surface polishing grits,  $M_{n1}$  and  $M_{n2}$  are the amount (g/mm<sup>2</sup>) of EN deposited with respect to surface polishing grits on cast and as-received aluminium alloy respectively in acidic sodium hypophosphite reduced bath. The EN deposition per unit area increased with increasing SFG from 60 $\mu\text{m}$  to 600 $\mu\text{m}$  after which there is reduction in the amount of EN deposition per unit area on AC Al alloy substrate. The case is dissimilar in the AR Al alloy, there is decline in the EN deposition per unit area on 60 $\mu\text{m}$  to 220 $\mu\text{m}$  grits polished samples; there is boost in EN deposition per unit area from 220 $\mu\text{m}$  to 600 $\mu\text{m}$  after which there is decrease in EN deposition per unit area obtained. 0.000446g/mm<sup>2</sup> and 0.000364g/mm<sup>2</sup> maximum EN plating per unit area were obtained on the 600 $\mu\text{m}$  grit polished cast and as-received aluminium samples respectively.

Rough surfaces have more points and crevices than the smooth surfaces, hence rough surface are likely to have larger surface areas. Unlike electro-deposition processes (electroplating, electroforming, etc). Where deposition concentrate more at points and less at crevices, electroless plating give a more uniform plating thickness that electro-deposition process, hence the electroless plating is not solely controlled by the degree of roughness of surface.

### 3.4 Effect of SPG and temperature variation on amount of EN deposition AR and AC at 85°C using PdCl<sub>2</sub>

Figures 5-12 show the variation in the quantity of EN deposit (g) on cast and as-received aluminium alloy substrates in acidic sodium hypophosphite reduced bath at varying plating bath temperatures and surface polishing grits. The temperature is varied from 80, 85 and 90°C while the surface polishing grits varied from 60 to 1200 $\mu\text{m}$ .

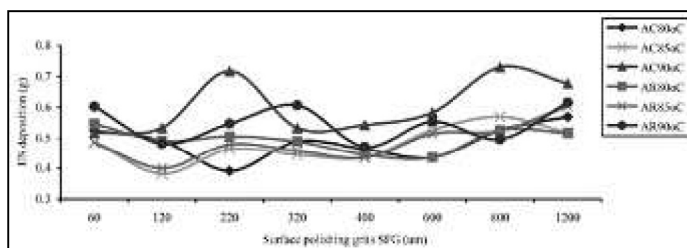


Figure 5: Effect of SFG variation on amount (g) of EN deposition per unit area on AC and AR samples operated at different plating temperatures (°C).

In Figure 5, 60 $\mu\text{m}$  polishing of cast aluminium produced highest EN deposition per unit area at 80°C followed by 85°C and 90°C while on other polished surfaces grits from 120 $\mu\text{m}$  to 1200 $\mu\text{m}$ , highest values of EN deposition per unit area are obtained at 90°C. The result obtained at 85°C shows that there is decline in quantity of EN deposit on 60 $\mu\text{m}$  to 220 $\mu\text{m}$  polished Al substrate. The 60 $\mu\text{m}$  polishing on as-received aluminium

produced least quantity of EN deposition per unit area at 80°C followed by 85°C and 90°C. The 90°C plating temperature produced highest values of EN deposition per unit area on 220, 320, 400, 600 and 1200 $\mu\text{m}$  grit polished surfaces. Similar trends in quantity of EN deposition per unit area are obtained on 400 to 1200 $\mu\text{m}$  grit polished surfaces for 85°C and 90°C plating temperature operated baths. In principle, electroless deposition is energy driven. It is a chemical reaction process that is highly controlled by temperature and time. The kinetics of the reaction is more favoured and result oriented at higher temperature. In case of EN deposition, working at temperatures above 80°C had been encouraged.

The amount of EN deposition per unit area (g/mm<sup>2</sup>) in Figures 6-11 are derived from Figure 5. The effect of SFG and Temperature variations on amount of EN deposition per unit area (g/mm<sup>2</sup>) on AC and AR samples with the errors bars are illustrated in Figure 6-11. All the plots in Figures 6-11 show the amount of EN deposition per unit area (g/mm<sup>2</sup>) on cast Al alloy and as-received Al alloy substrates measured from 8 different SFG values. The error bars for each plot give the upper and lower limit (maximum and minimum amount) of EN deposition per unit area obtained from each of SPG values. For the cast and as-received substrate samples, the 48 points are within the 5% the error bars for EN deposition per unit area of the SPG points. The polynomial trendlines equations (10) to (15) are also derived from the plots.

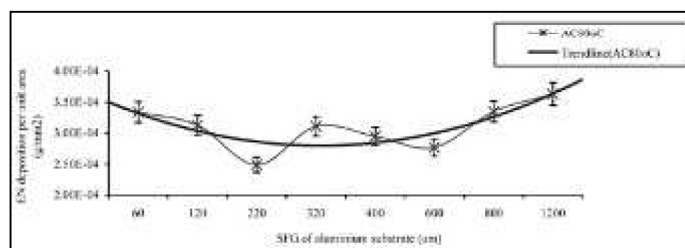


Figure 6: Trend of EN deposition per unit area on AC samples on operated at 80°C plating temperatures with SFG variation with the errors bars.

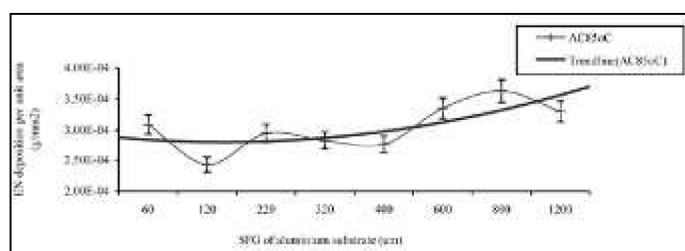


Figure 7: Trend of EN deposition per unit area on AC samples on operated at 85°C plating temperatures with SFG variation with the errors bars.

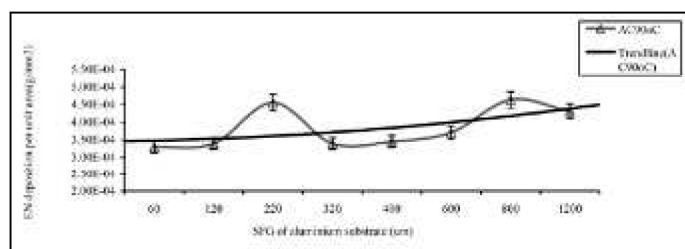


Figure 8: Trend of EN deposition per unit area on AC samples on operated at 90°C plating temperatures with SFG variation with the errors bars.

Figures 6-8 are derived from Figure 5. Comparisons of results of EN deposition on cast samples at different temperatures in Figures 5, 6, 7 and 8; show that EN deposition per unit area on AR and AC are of close trend and values in each of the plating temperatures (80°C and 85°C). Hence, the deposition is more dependent on the degree of polished surface grits rather than the aluminium material type; while further observation shows that for 90°C plating temperature, the deposition is dependent on both polished surface grits and the aluminium material types. The trend of the amount of EN deposited per unit area with respect to increasing plating bath temperature was studied using the experimental data generated from the experiment. The polynomial fit equations for the trend using MS excel application relates the amount of EN deposited to plating bath temperature (°C) and surface polishing grits operated at 80°C, 85°C and 90°C respectively as:

$$M_{n3} = 5E-06x^2 - 4E-05x + 0.0004 \quad (10)$$

$$M_{n4} = 2E-06x^2 - 1E-05x + 0.0003 \quad (11)$$

$$M_{n5} = 1E-06x^2 + 1E-06x + 0.0003 \quad (12)$$

Where  $60 \geq x \geq 1200\mu\text{m}$ ,  $x$  = surface polishing grits,  $M_{n3}$ ,  $M_{n4}$  and  $M_{n5}$  are the amount of EN deposited per unit area ( $\text{g}/\text{mm}^2$ ) with respect to plating bath temperatures operated at 80°C, 85°C and 90°C, respectively on cast aluminium alloy in acidic sodium hypophosphite reduced bath.

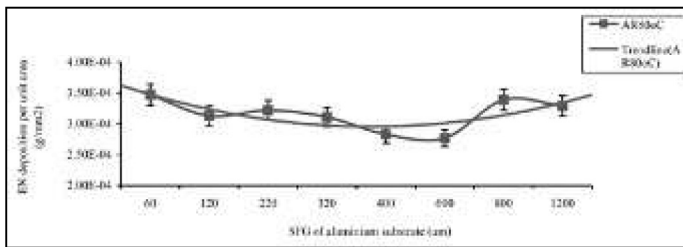


Figure 9: Trend of EN deposition per unit area on AR samples on operated at 80 oC plating temperatures with SFG variation with the errors bars.

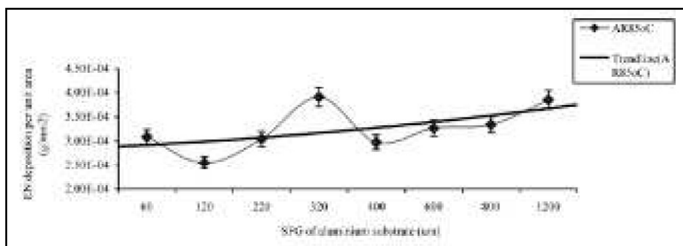


Figure 10: Trend of EN deposition per unit area on AR samples on operated at 85°C plating temperatures with SFG variation with the errors bars.

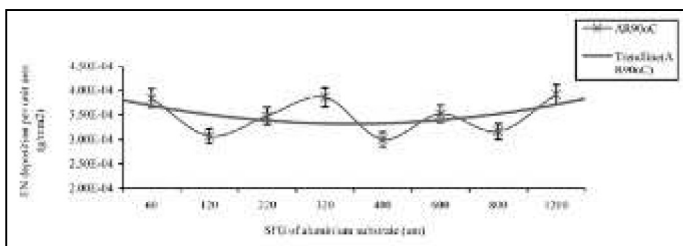


Figure 11: Trend of EN deposition per unit area on AR samples on operated at 90 oC plating temperatures with SFG variation with the errors bars.

Figures 9-11 are also derived from Figure 5. The trend of the amount of EN deposited per unit area with respect to increasing plating bath temperature was studied using the experimental data generated from the experiment. The polynomial fit equations for the trend using MS excel application relates the amount of EN deposited on as-received Al alloy (AR) substrates to plating bath temperature (°C) and surface polishing grits operated at 80°C, 85°C and 90°C respectively as:

$$M_{n6} = 4E-06x^2 - 3E-05x + 0.0004 \quad (13)$$

$$M_{n7} = 6E-07x^2 + 5E-06x + 0.0003 \quad (14)$$

$$M_{n8} = 3E-06x^2 - 3E-05x + 0.0004 \quad (15)$$

Where  $60 \geq x \geq 1200\mu\text{m}$ ,  $x$  = surface polishing grits ( $\mu\text{m}$ ),  $M_{n6}$ ,  $M_{n7}$  and  $M_{n8}$  are the amount of EN deposited per unit area ( $\text{g}/\text{mm}^2$ ) with respect to plating bath temperatures operated at 80°C, 85°C and 90°C, respectively on as-received aluminium alloy in acidic sodium hypophosphite reduced bath.

From Figures 5-11, EN deposition on AR and AC is not solely dependent on the increase in level of the polishing grit. The least trend of deposition per unit area is obtained at 85°C, producing best of the adhesion and appearance at SFG of 600µm and above. The trend of EN deposition per unit area at all plating temperatures is observed to be controlled by the increasing plating temperature especially for 400 to 1200µm polished surfaces grits. Figure 12 show the appearance of EN plating on cast aluminium substrate at (a) 80°C, (b) 85°C and (c) 90°C using 1200µm polishing grit.

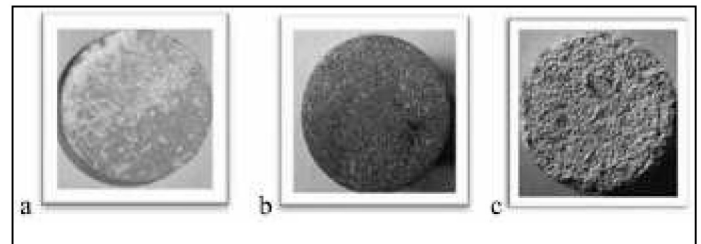


Figure 12: Micrograph of EN plating on cast aluminium substrate at (a) 80°C, (b) 85°C and (c) 90°C using 1200µm polishing grit.

### 3.5. Effect of surface activation on amount of EN deposition per unit area of Al substrate.

Deposition requires one or more of the following steps such as (i) cleaning, (ii) surface modification, (iii) sensitization, (iv) catalyzing or catalyzing, and activation (acceleration)[19]. Rinsing is required between the steps. The steps (iii) and (iv) as sensitization and catalyzing. In this work, the selected surface activators used include HCl, NaOH, water, sodium-di-chromate, zincate, and palladium chloride solution, before the cast substrates are immersed into the EN plating baths. Figures 13-16 show the variation in the quantity of EN deposit on cast aluminium alloy substrates in acidic sodium hypophosphite reduced bath using six different reagents as the surface activators.

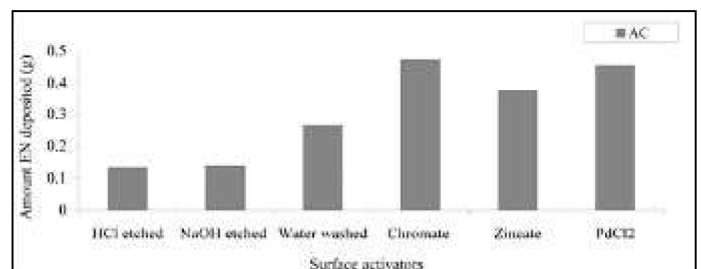


Figure 13: Effect of activators on EN deposition (g) on 1200µm polished AC samples operated at 85°C temperatures (°C).

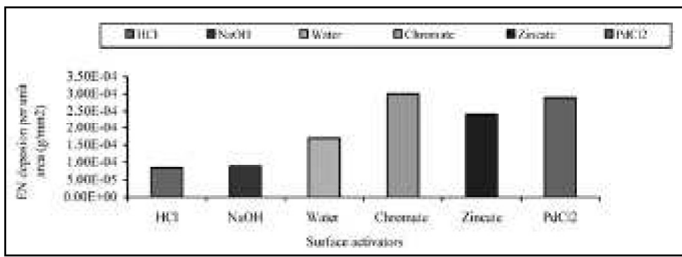


Figure 14: Effect of activators on EN deposition per unit area (g/mm<sup>2</sup>) on 1200µm polished AC samples operated at 85°C temperatures (°C).

The Figure 14 is derived from Figure 13. Figures 13 and 14 illustrate the effects of 6 activators and SFG variations on EN deposition (g) and EN deposition per unit area (g/mm<sup>2</sup>) on 1200µm polished AC samples operated at 85°C temperatures (°C). The effects of 2 activators (zincate and chloride) and SFG variations on EN deposition per unit area (g/mm<sup>2</sup>) on 6 different grits polished AC samples operated at 85°C temperature (°C) are presented in Figure 15 and 16. The quantities of EN deposit with respect to activators decline in order of the chromate, palladium chloride, zincate, water, NaOH and HCl.

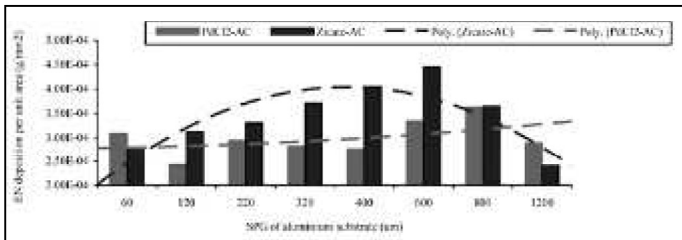


Figure 15: Trends of EN deposition per unit area (g/mm<sup>2</sup>) on zincate and PdCl<sub>2</sub> activated AC samples operated at 85°C temperatures (°C) with SFG variations.

Comparing the two activators in Figure 15, the patterns of trend lines generated from the plots are not similar; zincate is parabolic while PdCl<sub>2</sub> is linear (because the integer of x<sup>2</sup> is zero); though the amount of EN deposited per unit area (g/mm<sup>2</sup>) on cast aluminium sample increased with SFG using the zincate as well as the chloride.

The trends of the amount of EN deposited per unit area with respect to decreasing SFG were studied using the experimental data generated from the experiment. The polynomial fit equations for the trend using MS excel application relates the amount of EN deposited per unit area to types of activators (PdCl<sub>2</sub>, zincate) used and the surface polishing grits for baths operated at 85°C as:

$$M_{n9} = 7E-06x + 0.0003 \quad (16)$$

$$M_{n10} = -1E-05x^2 + 0.0001x + 0.0002 \quad (17)$$

where  $60 \geq x \geq 1200\mu\text{m}$ ,  $x$  = surface polishing grits,  $M_{n9}$  and  $M_{n10}$  are the amount of EN deposited per unit area (g/mm<sup>2</sup>) on cast aluminium alloy using PdCl<sub>2</sub> and zincate as activators respectively, in acidic sodium hypophosphite reduced bath operated at 85°C.

In Figure 16, the use PdCl<sub>2</sub> have much significant difference on the amount of EN deposition per unit area on the 600µm and 800µm grits polished surfaces as the SFG increased from 60 to 1200 µm. The application of zincate gave EN deposition increased with the increasing SFG values from 60 to 600 µm after which there is reduction in the EN deposition as SFG increased from 600 to 1200 µm.

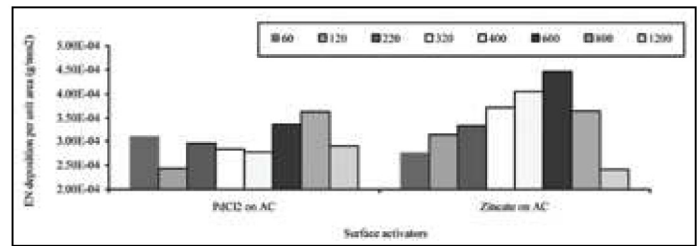


Figure 16: Effect of activators and SFG variations on EN deposition per unit area (g/mm<sup>2</sup>) on AC samples operated at 85°C temperatures (°C).

The zincate produced relative higher values of EN depositions than the Chlorides on six of the eight grits tested. Among the six activators presented in Figures 13-16, only the zincate and chloride yielded quality EN deposition that could possibly be of practical benefit.

Deposition of electroless-nickel on AC and AR alloy substrates at various polishing grits is carried out for 10 minutes in EN baths operated at 85°C. Figure 17 shows the appearances of EN deposition on (a) 60µm (b) 320µm (c) 600µm (d) 800µm (e) 1200µm polished cast substrates (AC) in acidic sodium hypophosphite reduced bath without use of activators.

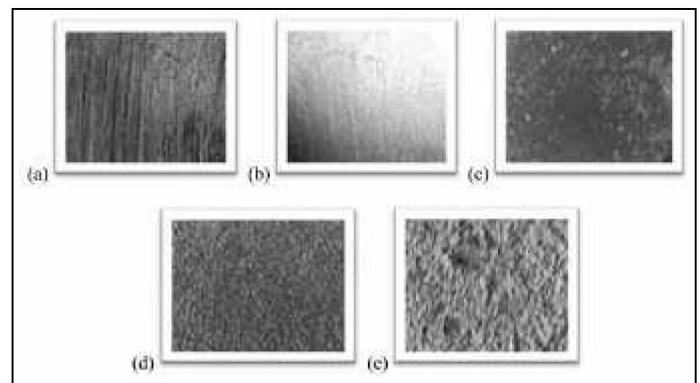


Figure 17: Micrograph of appearances (x50 mag) of (a) 60µm, (b) 320µm, (c) 600µm, (d) 800µm, and (e) 1200µm polished EN coated cast substrates.

Figures 18-20 show the variation in the quality (appearances, texture, brightness) of EN deposit on cast aluminium alloy substrates in acidic sodium hypophosphite reduced bath using different surface activators.

### 3.5.1 Effects of H<sub>2</sub>O, NaOH etched and HCl etched activation on EN deposition

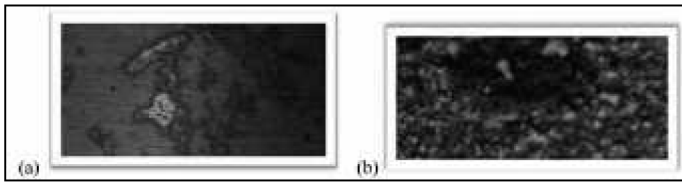
By water rinsing immediately after the catalytic process (prior to immersion in the metallizing bath), the amount of oxide material (Al<sub>2</sub>O<sub>3</sub>) present on the surface makes it difficult to obtain reliable EN deposition. In addition, at that stage the ultra thin supporting substrate and the deposit are virtually non-conductors.

Etching in HCl acid media stages are oxidation and hydrogen evolution controlled, while in the case of etching in NaOH alkaline media the following Metal deposition and Hydrogen evolution stages are prevailing, thus the deposition reaction can be considered to be the combined result of two independent electrode reaction as cathodic partial reactions and anodic partial reaction.

The activation (acceleration) step involves the removal of the layer formed by the stabilizing agent with chemicals such as HCl or NaOH. Thus more EN deposits were obtained from HCl

or NaOH etched Al substrates than in water rinsed surfaces. In some cases the activation (acceleration) step can be omitted, but then the plating solution may get contaminated [25].

It was observed that HCl, NaOH and water activated cast



(a) Metallic, bright EN deposition (x50 mag). (b) mixed, bright and dull EN deposition (x80 mag)

Figure 18: Micrograph of EN plating on (a) NaOH etched as-cast Al and (b) HCl etched 1200µm polished cast Al substrates at 10 minutes plating time.

aluminium alloy substrates did not yield much substantive quantity and quality EN deposit as compared with sodium-di-chromate, zincate, and palladium chloride activated cast aluminium alloy substrates immersed into acidic sodium hypophosphite reduced EN bath.

### 3.5.2 Effect of PdCl<sub>2</sub> activation and temperatures on EN deposition

A number of compounds, referred to as stabilizers, exist which can render an electroless deposition bath stable or at the least retard precipitation e.g PdCl<sub>2</sub>. In the present work, the used of PdCl<sub>2</sub> as surfactant, serves as both a catalyst (in the pre-treatment line) and as a stabiliser in the EN plating bath. Hence, a more balance trend of EN deposition was obtained from the used of PdCl<sub>2</sub> than what was obtainable in the zincate (Figure 15) when compared.

Heavy metal cations such as Pb, alter the activity of the catalytic substrate – hence their marked influence at even low concentrations [25]. In principle, an oversimplified model assumes that the sensitizing ion can reduce the active metal from the catalyst solution of a more noble metal (Au, Pt, Rh, Os, and Ag solutions) and such as PdCl<sub>2</sub> in the EN process for example (18),

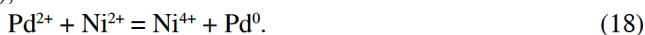
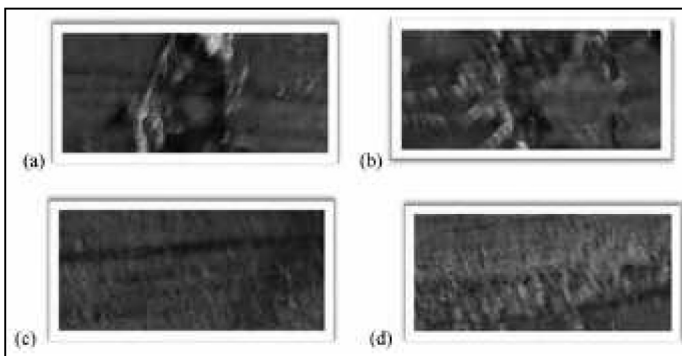


Figure 19 shows the Micrograph of EN plating on (a-d) 60µm cast Aluminium substrate at different temperatures. Observations show that EN plated cast aluminium alloy substrates (polished



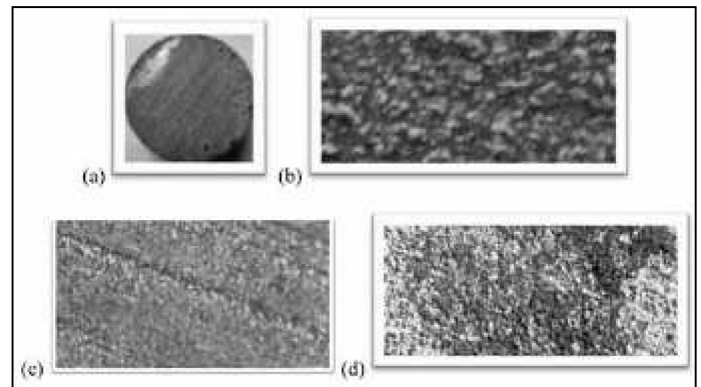
(a) PdCl<sub>2</sub> activated EN chips at 85°C (x100 mag), (b) PdCl<sub>2</sub> activated dull EN flakes at 90°C (x100 mag), (c) Dull EN deposition at 85°C (x50 mag), (d) Bright EN deposition at 90°C (x50 mag),

Figure 19: Micrograph of EN plating on (a-d) PdCl<sub>2</sub> activated 60µm grit polished cast aluminium substrate at different temperatures.

below 400µm) under microscopic examination are more prone to high porosity than the EN coated as-received substrates. It is observed that the quantity of EN deposition per area is dependent on the type and roughness of the surface of the aluminium alloy substrates, whereas the adhesion and brightness are not solely controlled by the surface polishing grits. There are instances where low polishing grit produced better and more tenacious coating than the higher polishing grit.

### 3.5.3 Effect of zincate activation on EN deposition

Zincating is more or less a metalised type of surface activation or catalysing process for Al alloy, using a basic solution which consisted of sodium hydroxide and zinc oxide, and at times contains iron, a zincate film formed by single zincate treatment. Most of the Ni-P baths are acidic, Ni is more electro-positive than Al on the electromotive scale, immersion deposits of nickel and chemical attack of the aluminium substrate will occur, interfering with the good adhesion of the electroless nickel coating. In protecting the Al substrate during EN plating process, zinc immersion deposits are used. The zinc deposit protects aluminium surface against re-oxidation from atmosphere and re-dissolves in the EN solution, hence forming adherent EN coatings on an exposed oxide free aluminium substrate.



(a) Uniform deposition, (b) Lumpy, bright and dull deposition at 90°C (x80 mag), (c) Sparingly coated (x50 mag). (d) Fine, bright and dull deposition at 85°C (x50 mag),

Figure 20: Micrographs of EN plating on (a) 60µm zincated surface (b) 120µm zincated substrate, (c) 120µm polished cast substrate and (d) 1200µm cast substrate.

Figure 21 shows the appearances of the PdCl<sub>2</sub> (Figure 21b) and zincate (Figure 21c) activated EN plated cast aluminium pistons obtained from 600µm polishing grit. The depositions were uniform, continuous, of very bright metallic lustre with good adhesion.

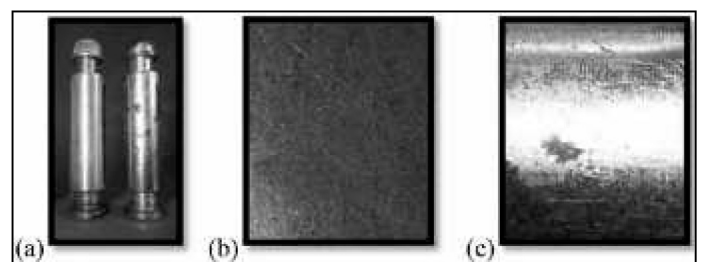


Figure 21: (a-c) surfaces showing (b) PdCl<sub>2</sub> and (c) zincate activated EN plated cast aluminium samples

Calculating the plating rates based on data generated from Figures 14 using equation (7); lower plating rates of 0.00849 mg/mm<sup>2</sup>/min, 0.00886 mg/mm<sup>2</sup>/min and 0.0169 mg/mm<sup>2</sup>/min were obtained from using HCl, NaOH and water as cleaning reagents. Pure and aluminium alloy form layer of oxide when exposed to air and water. This oxide reduces the adhesion of EN on the surface. The oxide is reactive to both acid and alkaline; hence they disallow the continuity of autocatalytic reaction at the immediate interface of the EN solution and the substrate.

Higher plating rates of 0.0301 mg/mm<sup>2</sup>/min, 0.0241 mg/mm<sup>2</sup>/min and 0.0290 mg/mm<sup>2</sup>/min were obtained from cleaning with chromate, zincate and chloride. The highest plating rate is obtained from chromate cleaned substrate but of worst adhesion quality among the three. Zincate and chloride cleaned aluminium substrates yielded better quality than chromate cleaned cast aluminium substrate. The application of zincates as primer on cast aluminium substrate before EN-deposition has been widely accepted, reported to be result oriented and encouraged for better adhesion. [20, 21, 22, 23, 24].

Adhesion problem is one of the major experienced challenges of EN plating especially when the substrate is aluminium alloy. The cast aluminium alloy has greater challenges of EN plating than other wrought aluminium materials hence cast Al surfaces are specially prepared by cleaning in diverse reagents and followed by surface activation. 17-20 show the variation in the quality of EN deposit on cast aluminium alloy substrates in acidic sodium hypophosphite reduced bath using six different reagents as the surface activators. The best yield in terms of the plating quality (adhesion and appearance) is obtained from the activation in palladium chloride solutions (Figure 19) and in zincate (Figure 20), though gotten in Figure 12 are of lower quality yields as compared with what was obtainable in zincate pre-treated cast aluminium (Figures 20 and 21).

Adhesion problem is one of the major experienced challenges of EN plating especially when the substrate is aluminium alloy. The cast aluminium alloy has greater challenges of EN plating than the wrought aluminium materials. Cast surfaces are specially prepared by cleaning in diverse reagents and followed by surface activation. It has been identified that the single zincate treatment by using the basic zincate solution resulted in such poor adhesive strength of the electroless nickel-phosphorus plated film as to peel off the substrate due to its residual stress as compared with the double zincate treatment [23, 24]. In light of overcoming abnormalities such as poor adhesion, porosity, film discontinuity resulting from EN deposition, it has been suggested that some procedure has to be applied [25]. Using a variety of sensitizing solutions and the catalytic solution, a metal (nickel) is deposited electrolessly on the sensitized catalyzed surface by immersion in the metallizing bath for fixed amounts of time.

#### 4.0 CONCLUSION

EN has been deposited on the cast aluminium substrate in sodium hypophosphite bath. With the variation in the surface finishing, temperature and different types of surfactants, the results show that that the amount of EN deposition per unit area is dependent on both the Al Alloy type and roughness of the surface of the Aluminium alloy substrates used, temperature and the types of pre-treatment surfactant. On the other hand, such properties as the adhesion, porosity, colour and brightness are not solely controlled by the surface polishing grits. In some instances,

rough polishing grit produced improved and more firm, tenacious coatings than the smooth polishing grits. Of the six surfactants tested, zincate and palladium chloride solutions produced the best of the results in terms of the plating quality porosity, colour, adhesion and appearance. The zincate produced relative higher amount of EN depositions than the chloride on six (120-800µm) of the eight grits tested. Zincating on cast aluminium substrate prior to EN-plating as it has been reported to be result oriented and hence, encouraged for better adhesion. The SFG variation seems to have similar trend of EN deposition on AR and AC samples operated at 85°C plating temperature. The 90°C plating temperature produced highest values of EN deposition per unit area on a range of 220-1200µm grits polished Al alloy surfaces. EN deposition on AR and AC is not solely dependent on the increase in level of the polishing grit.

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