# ORGANIC AND INORGANIC PASSIVATION PERFORMANCE ON ELECTROLESS NICKEL (LP)

### SHARQIYAH BINTI ABDUL MALICK

A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Engineering (Mechanical)

Faculty of Mechanical Engineering Universiti Teknologi Malaysia

DECEMBER 2007

To my beloved Abah and Mak..

#### ACKNOWLEDGEMENTS

Alhamdulillah, I was very thankful to Allah S.W.T. for His blessing and guidance through all difficulties that I met and giving me the strength to live in this challenging world. I have managed to finished this project within only six months and this would not have been possible without the helps of many people.

I would like to express my appreciation to my supervisors, Mr. Noor Hisham Ab. Hamid and Associate Prof. Dr. Ali Ourdjini for giving me this opportunities and shared their knowledge throughout the course. I would like to acknowledge the Pengkalan Jitu Sdn. Bhd. (PJSB) for sponsoring all the equipments, raw materials, and samples to this project as well as to dedicate En. Yazid (Plant Manager) and his team. Not to forget, a special thank you to Material Science Laboratory technicians; Mr. Zainal, Mr. Ayub, Mr. Jefri, Mr. Azri, Mr. Adnan, and Mr. Zam, and Metrology Laboratory technician, En. Khalid, for their technical assistance during this project.

A big thank you to my beloved parents, brothers and sisters for encourage me to do the best in my life and also for your endless loves, cares, and supports towards me. To my friends who always there for me; Lia, Fatihah, Jamie, AZ, Ieyja, and the rest, thank you for your cares and helps.

#### ABSTRACT

Passivation is a very important process after Electroless Nickel (EN-P) plating where it serves to protect the nickel surface against further dissolution or corrosion. Passivation will reduce the reactivity of chemically active metal surface by immersion in a passivation solution. The objectives of this study were to investigate and analyse the organic and inorganic passivation on EN low phosphorous (LP) of the characteristics and corrosion performance on the aluminium alloy component. There are two types of passivation solution that had been used which were chromic acid based solution (inorganic type) and silicate based solution (organic type) and it was found that their optimum passivation time were 210 sec and 90 sec respectively. FESEM (EDX) was used to characterize the surface of EN-P layers with both passivation types. XRD was also used to characterize the compound bonding nature of elements on the EN-P surface. FESEM (EDX) and XRD results showed that the EN-P surface with organic and inorganic passivation were oxidized and composed of nickel oxide, nickel hydroxide, and nickel phosphate, but for organic passivation its exhibits the presence of silicon. It was also shown that the passivation layer thickness was in the range of between 200 to 300 nm. Salt spray test was used to study their corrosion performance for 24, 48, and 72 hours. Most of the specimens were corrode as EN (LP) did not performed corrosion protection to the substrate as EN (HP). However, specimens with organic passivation exhibited more corrosion resistance as indicated from the corrosion rate analysis.

#### ABSTRAK

Passivation adalah suatu proses yang amat penting selepas proses Electroless Nickel (EN-P) dimana ia akan melindungi permukaan logam daripada tindakbalas selanjutnya atau kakisan. Passivation akan mengurangkan tindakbalas kimia terhadap permukaan logam yang aktif dengan pengutuban elektrokimia atau rendaman di dalam larutan *passivation*. Objektif bagi kajian ini adalah untuk mengkaji sifat-sifat dan perlaksanaan kakisan mengenai *passivation* secara organik atau tidak organik terhadap *electroless nickel* rendah fosforus EN (LP) pada komponen aloi aluminium. Terdapat dua jenis larutan passivation yang digunakan iaitu larutan asas asid kromik (jenis tidak organik) dan larutan asas silikat (jenis organik) dan didapati bahawa masa optimum bagi passivation adalah 210 saat dan 90 saat bagi masing-masing. FESEM (EDX) telah digunakan untuk menggambarkan sifat bagi permukaan lapisan EN-P dengan kedua-dua jenis passivation. XRD juga digunakan untuk mengkaji ikatan semulajadi bagi gabungan elemen-elemen pada permukaan EN-P. Keputusan bagi FESEM (EDX) dan XRD menunjukkan bahawa permukaan EN-P dengan passivation secara organik atau tidak organik akan teroksida dan mengandungi nikel oksida, nikel hidroksida, dan nikel fosfat tetapi passivation secara organik juga membentuk silikon pada permukaan EN-P. Ia juga menunjukkan bahawa lapisan passivation mempunyai ketebalan antara 200 hingga 300 nm. Ujian semburan garam pula digunakan untuk mengkaji perlaksanaan kakisan selama 24, 48, dan 72 jam. Hampir semua spesimen terkakis kerana EN (LP) tidak memberi perlindungan kakisan terhadap logam asas. Walaubagaimanapun, spesimen dengan passivation secara organik memberi lebih rintangan terhadap kakisan sebagaimana yang terdapat pada analisis kadar kakisan.

### TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENTS	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	Х
	LIST OF FIGURES	xii
	LIST OF ABBREVIATIONS	XV
	LIST OF APPENDICES	xvi

1	INTE	RODUCTION		
	1.1	Title	1	
	1.2	Background Study	1	
	1.3	Objectives of the Study	2	
	1.4	Scope of the Study	2	

LITE	ERATURE REVIEW	3
2.1	Electroless Nickel Plating	3
	2.1.1 Introduction	3
	2.1.2 Types of EN	6
	2.1.3 The application of EN	8
	2.1.4 The properties of EN	10
2.2	The Substrate of EN	19
	2.2.1 Aluminium alloy	19
2.3	The Mechanism of EN	22
	2.3.1 Control of EN baths	25
2.4	Processes of EN	27
	2.4.1 Pre-treatment	27
	2.4.2 Plating	30
	2.4.1 Post-treatment	30
2.5	Passivation	31
	2.5.1 Thickness	35
	2.5.2 Passivation Solution	36
МЕТ	THODOLOGY	38
3.1	Methodology	38
3.2.	EN Process	39
3.3.	Sample Quantity	40
3.4	Surface Roughness Test	41
3.5	FESEM/EDX	43
	3.5.1 Specimens preparations	43
3.6	X-ray Diffraction (XRD)	45
3.7	Salt Spray Test	46
	3.7.1 Apparatus	48
	3.7.2 Test specimens preparation	48
	3.7.3 Salt solution	49
	3.7.4 Position of specimens during test	49
	3.7.5 Condition of the salt spray test	50
	3.5.5 Procedure of tested specimens	51

2

3

4	RESU	ESULTS AND DISCUSSION		
	4.1.	Result	5	52
		4.1.1.	Surface roughness	53
		4.1.2.	Chemical compositions of the specimens	55
		4.1.3.	Specimens of Ni-P layer without passivation	55
		4.1.4.	Specimens with passivation	56
		4.1.5.	Thickness	60
		4.1.6.	Salt-spray tests	69
	4.2.	Discus	sions	77
		4.2.1.	Characterization	77
		4.2.2.	Thickness	80
		4.2.3.	Corrosion protection	81
5	CON	CLUSI	DN	82
6	RECO	OMME	NDATION	83

REFERENCES	84
APPENDICES	88

# LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Electroless nickel plating compared with hard chromium	
	plating	5
2.2	The industrial application of EN and their thickness	
	requirement	9
2.3	Chemical Properties of Al 7075	20
2.4	Physical Properties of Al 7075	21
3.1	Solution, process flow and parameter	39
3.2	Samples for passivation solutions	40
3.3	The requirements for NSS tests	47
3.4	Label of EN-P specimens with chromic acid and silicate	
	passivation for salt spray test	49
4.1	Label of EN-P specimens with chromic acid and silicate	
	passivation	52
4.2	Chemical composition of the specimens	55
4.3	Chemical composition of EN-P layer at point A and B	55
4.4	Chemical composition of passivation layer for sample 4	57
4.5	Chemical composition of passivation layer for sample 7	58
4.6	Thickness of EN-P layer with chromic acid and silicate	
	passivation	63
4.7	Thickness of passivation layer for chromic acid and silicate	
	passivation	68
4.8	EN with chromic acid passivation (scratched)	70
4.9	EN with chromic acid passivation (non-scratch)	71

4.10	EN with silicate acid passivation (scratched)	72
4.11	EN with silicate acid passivation (non-scratch)	73
4.12	Comparison results of element and compound between FESEM	
	(EDX) and XRD	78

# LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Primary uses for EN coating	8
2.2	Products of EN plating	9
2.3	EN deposit density increases as phosphorus content	
	decreases	11
2.4	The relationship between tensile strength and phosphorus	
	content	13
2.5	Cyclic voltammogram of EN-P coated sample 1 in 0.5M	
	NaOH at different scan rates; (a) 10 mV/s, (b) 0.050 V/s,	
	(c) 0.100 V/s, (d) 0.200 V/s, (e) 0.300 V/s, (f) 0.400 V/s,	
	(g) 0.500 V/s	16
2.6	Corrosion resistance of EN increases with phosphorus	
	content. Test was ASTM B 117 / DIN 50021 (salt spray)	18
2.7	Effect of variables on the rate of deposition from EN solution	26
2.8	Surface roughness for zincating process step: a) single,	
	b) double, c) triple and image of surface morphology:	
	d) single, e) double, f) triple	29
2.9	Principle structure of EN plating	30
2.10	Schematic of the proposed dual layer structure of a NiP surface	e 32
2.11	Surface roughness of EN-P	34
2.12	Optical micrograph of 20 µm thick phosphorus coating	35
2.13	Schematic structures of H <sub>2</sub> CrO <sub>4</sub> and H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	36
3.1	Methodology chart	38

3.2	Image analyser	41
3.3	Surface roughness test machine	42
3.4	FESEM/EDX machine	43
3.5	Gold sputtering machine	44
3.6	XRD machine	45
3.7	Specimens on the racks and supports in the chamber	50
4.1	The surface roughness of specimens (a) without passivation,	
	(b) specimen with chromic acid passivation, and (c) specimen	
	with silicate passivation (Maginification: 200X)	54
4.2	EN-P layer without passivation (Maginification: 3,000 X) and	
	small picture was the surface of point A	
	(Maginification: 20,000 X)	56
4.3	EN-P layer of sample 4 (Maginification: 20,000 X)	57
4.4	Graph of spectrum of passivation layer for sample 4	57
4.5	EN-P layer of sample 7 (Maginification: 20,000 X)	58
4.6	Graph of spectrum of passivation layer for sample 7	58
4.7	EN-P layer with chromic acid and silicate passivation	
	(Magnification: 5,000 X)	60,61
4.8	Passivation layer of EN-P with chromic acid and silicate	
	passivation (Magnification: 20,000 X)	62,63
4.9	EN-P layer of specimen 1 shows the line scan by FESEM	
	(Magnification: 20,000 X)	64
4.10	Graph of oxygen of sample 1	64
4.11	Line scan profile of specimen 1 by FESEM	65
4.12	EN-P layer of specimen 7 shows the line scan by FESEM	
	(Magnification: 20,000 X)	66
4.13	Line scan profile of specimen 7 by FESEM	67
4.14	Graph of oxygen of sample 7	68
4.15	Depth of scratches (Magnification: 200 X)	69
4.16	Specimens of salt-spray test (a) before test, (b) after test,	
	and (c) after ultrasonic cleaning	70
4.17	Graph of weight loss vs passivation time of EN-P with	
	chromic acid passivation (scratched)	74
4.18	Graph of weight loss vs passivation time of EN-P with	

	chromic acid passivation (non-scratch)	74
4.19	Graph of weight loss vs passivation time of EN-P with	
	silicate passivation (scratched)	75
4.20	Graph of weight loss vs passivation time of EN-P with	
	silicate passivation (non-scratch)	76

# LIST OF ABBREVIATIONS

ASTM	-	American Society for Testing and Materials
EN	-	Electroless nickel
EN-P	-	Electroless nickel-phosphorous
EN (HP)	-	Electroless nickel high phosphorous
EN (LP)	-	Electroless nickel low phosphorous
EDX	-	Energy dispersive spectrum
FESEM	-	Field emission scanning electron microscope
Ni-P	-	Nickel phosphorous
Ra	-	Surface roughness
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray diffraction

# LIST OF APPENDICES

APPENDIX	TITLE	PAGE
А	Equipments of EN Process	89
В	Spot Analysis by FESEM (EDX)	91
С	Line Scan Profile by FESEM (EDX)	101
D	Results of XRD	109
E	Results of Surface Roughness Test	116

#### **CHAPTER I**

### INTRODUCTION

#### 4.1 Title

Organic and Inorganic Passivation Performance on Electroless Nickel (LP).

#### 4.2 Background Study

Over more than two decade, electroless plating or known as EN does have widely commercial applications in many fields as a coating technique that used on a solid part like a metal and its alloy, and also plastic because of its excellent properties.. It is still a growing industry in Malaysia as there was not much manufacturer that using this plating technique. The applications of this plating technique can be found in virtually every industry such as aerospace, automotive, chemical processing industry, food processing industry, electronics, and others. The range of nickel-phosphorous alloy as the coating material can be varied with the percentage of phosphorus that is from low phosphorous to medium phosphorous and high phosphorous. There are several processes applied for this method starting with pre-treatment process, plating, and post-treatment process. Each process will give an effect on the plated component whether it is good or not. Passivation is one of the post-treatment processes which is very important for the final touch to the component. After the substrate was coated by Ni-P layer, the passivation is needed to deactivate the Ni-P layer which is in an active form. Generally, there are two types of passivation layer; organic and inorganic. These types of passivation layer have different composition, characteristics, and performances but still give the same function on the EN plating process.

### 4.3 Objectives of the Study

To study organic and inorganic passivation of EN (LP) on characteristics and corrosion performance on the aluminium alloy component.

#### 4.4 Scope of the Study

- 1. Electroless Nickel (HP)
  - a. Surface morphology
  - b. Thickness
  - c. Characterization.
- 2. Passivation (organic and inorganic base)
  - a. Thickness
  - b. Salt spray test
  - c. Surface morphology
  - d. Characterization.