REVIEW ON THE VARIOUS CHEMICAL COMPOSITION OF AUTO-CATALYTIC NICKEL PLATING

NUR ASYKIN BINTI ZAINUDDIN, MD AMIN HASHIM, SUHAIZA HANIM HANIPAH

Faculty of Chemical Engineering, Universiti Teknologi Mara, 40450 Shah Alam, Selangor, Malaysia

Abstract— **Autocatalytic nickel plating, also known as electroless nickel plating is a chemical technique used to deposit a layer of nickel on an object or workpiece without the use of electric current or an external electrodes to prevent corrosion. It involves the presence of a chemical reducing agent that will reduce the nickel ions, Ni^{2+}, to nickel metal, Ni. This study is conducted to determine the various chemical composition that exist in the industries for the electroless nickel bath solution. The recorded components of a nickel plating solution are a source of nickel ions, reducing agent, complexing agent, accelerators or buffer, stabilizers or inhibitor. The other parameter of the bath such as pH and temperature are also considered. In order to achieve the objectives, this study is done by collecting data from various journals, books or any other relevant resources for example, reports, websites, patents and manufacturing companies related to autocatalytic nickel plating process. It is hope to collect a resources from year 2004 until 2016 and any relevant data about the process, the different type of reducing agent, the different type of complexing agent, accelerators used, stabilizers or inhibitors and its quantity in the bath.**

Keywords

Electroless nickel plating, electroless deposition of nickel, autocatalytic deposition of nickel, nickel plating solution

I. INTRODUCTION

Most metal are extracted from its ore, because of this the fundamental tendency of nature is abruptly reversed. For example, iron if unprotected by coating, will corrode in most environments. Corrosion prevention had been an essential factor in the economic utilisation of steel. Choosing the right protective coating technique can benefits designers, specifier, material engineers, consultant and fabricators to protect and improve their steel products (Eade, 1995).

In present days, there are many corrosion prevention techniques had been established such as catalytic and autocatalytic plating, galvanizing, painting, polymer coating, cladding and chemical additives and electrochemical method such as cathodic protection. This research is focus on one type of corrosion prevention technique available and in ever-growing popularity, autocatalytic plating, which is focus on nickel deposition on metal. This research is conducted to prepare a complete review on the various compositions of auto catalytic nickel plating.

The corrosion prevention techniques also call as metal finishing technique as it gives finishing of metal and non-metal in which a metallic coating is formed from an aqueous solution or a molten salt by means of an electrochemical reaction. Nickel as a coating is the most widely chosen due to its high corrosion resistance and the attractive finished appearance of metal. The metallizing of plastic using nickel also gives the material a metallic appearance, a higher reflectivity and a low weight deposition. In electroforming, nickel are used because of it higher hardness, wear and corrosion resistance (Kanani, 2004).

Autocatalytic plating, also known as electroless plating, involves a chemical reducing agent in the bath solution to reduce the metallic ions to the metal state instead of using an electric current so instead of using an anode, the metal is supplied by the metal salt and instead of a cathode to reduce the metal, a substrate is used while the electrons is supplied by the reducing agent (Durkin, 2016). This process only occurs on the catalytic surfaces but if the process is not controlled properly, the reduction process will take place throughout the solution and gives undesirable results (Schlesinger, 2010).

This deposition of metallic coating by a controlled chemical reduction that is catalyzed by a metal or alloys being deposited had many advantages over other techniques. The throwing power of this process is basically perfect with no excessive buildup on edges and projections, the deposit are less porous and have better corrosion resistance (Schlesinger, 2010).

This study is to collect the various compositions of electroless nickel plating bath solution available in the market and the roles of various chemical components that exist in the nickel plating solution. The recorded components of a nickel plating solution are;

a. A source of nickel ions,
b. A reducing agent,
c. Suitable complexing agent,
d. Accelerators,
e. Stabilizers or inhibitor

II. AUTOCATALYTIC NICKEL PLATING

2.1 Corrosion and electroless nickel plating

Corrosion resulted when metal is unprotected and exposed to the environment. Corrosion happened when there is two chemical reactions, anodic and cathodic reaction, occurred at the surface of the metal (Schlesinger, 2010). The coating that is applied to the metal (nickel) is functioned as the sacrificial metal as the corrosion process occurred thus nickel will corrodes, preferentially to the metal. This is known as the cathodic protection (Roos, 2006).

The main constituent in electroless nickel plating is the nickel salt, the complexing agent and the reducing agent (Durkin, 2016). The redox potential of the reducing agent has to be more cathodic than the metal is being reduced, in this case is, nickel. However, too much negativity can result in spontaneous reduction in solution because of the enhanced nucleation rate which results in useless, finely divided suspension of the metal in the electrolyte (Kanani, 2004).

The cathodic half reaction in electroless plating is (O.G.Palanna, 2009)

$$M^{n+} + n\bar{e} \rightarrow M \qquad (1)$$

The anodic half reaction in electroless plating is

$$Reducing\ agent \rightarrow oxidised\ product + n\bar{e} \qquad (2)$$

2.2 Pretreatment for substrate before plating process

Autocatalytic nickel plating, also known as electroless nickel plating (G. O. Mallory, 1990), is a process that produces a layer of nickel alloy on a substrate, usually plastic or a metal, which works to strengthen and buff the material (Durkin, 2016). The technique is a purely chemical alternative to electroplating. It is known that electroless nickel plating is effective coating measure if the pretreatment process is adequately chosen. In order to achieve even, efficient and wieldy layer of nickel coating, greases, oils, imperfections and other contaminants need to be removed prior to the plating process. By removing the unwanted contaminants that may hinder the bonding process and results in low quality or unusable results, the process can be time consuming that required several step as the substrate need to be cleaned with a series of base or acid chemicals. In between each chemical treatment, the substrate needs to be rinse by water to remove residual chemical adhesion. ("Pretreatment of Parts for Electroless Nickle Plating", 2016)

Electroless nickel plating can be applied to a metallic and nonmetallic substrate with a different compositions and properties (Zhang, 2016). Due to this reason, there are many general approaches to the surface preparation of substrate. Specific procedures are required to a specific type of substrate ("Pretreatment of Parts for Electroless Nickle Plating", 2016). An important characteristic of plating metals is the strength of the bond that can develop between the base metal and the coating (Jothi Sudagar, 2013). Metal-to-metal bonds with high adhesion values require thorough surface preparation (Hajdu, 1990). The removal of foreign contaminants is generally accomplished by using commercial alkaline cleaners. The selection is based on the nature of the contaminants and the type of substrate. The removal of surface oxidation and unwanted metal is accomplished by chemical attack (Hajdu, 1990). Acid pickling solutions and alkaline deoxidizing materials, similar to those used in electroplating, are also effective for electroless nickel plating. In some cases, mechanical surface treatments, such as shot peening or sandblasting, are used in surface finishing prior to chemical treatment, especially with large, expensive parts that allow the use of manual processing. (Hajdu, 1990)

Another reason for the need of a very careful selection of the preparation process is that it can significantly affect the porosity of the metal deposit. Residues from cleaners and deoxidizers can increase the porosity of electroless nickel, creating passive spots that will not initiate electroless plating. (Saubestre & Haydu, 1968)

The preparation of substrates demand very careful control, autocatalytic nickel deposit is very sensitive to the physical and chemical conditions of underlying metal (V. Vitry, 2015). Substantial variation in properties such as corrosion resistance can occur if the cleaning process is done with incompatible system (Engineers, 2003) (Durney, 1996). It is impossible to produce a physically and chemically clean surface, what is really required is that all detrimental contaminant is detached and replaced with chemically compatible surfaces. Water break test (Engineers, 2003) can indicated the physical cleanliness but it do not gives any guide to the chemical activity of the metal that will form the bond at the deposit interface. The use of any form of inhibitor in acid activators may be detrimental to the corrosion performance of articles and that the last electroclean stage before plating should be free of surfactants or cyanides (Maqsood Ahmad Malik, 2011) (Ayman M. Atta, 2015). These measures are intended to limit the level of adsorbed materials on the bonding surface and to leave the substrate as active as possible. (Durney, 1996)

Table 1: Process differences on different substrate metals. (Durney, 1996)

Type of Substrate	Pretreatment Cycle
Low-alloy mild steels (L.W. Pinder, 2017) (Rockel, 2008)	1. Vapor degrease or emulsion soak cleaner. 2. Alkaline soak cleaner. 3. Anodic electrolytic cleaner. 4. Rinse, cold water. 5. Acid activate10-15% sulfuric acid. 6. Rinse, cold water. 7. Electroless nickel plate.
Aluminium and aluminium alloys (Prof. Dr. F. Beck, 2004) (Fettis, 2008) (Kissell, 2004)	1. Solvent clean, if required. 2. No-etch soak clean. 3. Cold water rinse. 4. Deoxidize surface to remove any heavy oxide films, using 50% v/v nitric acid or proprietary deoxidizer. 5. Cold water rinse. 6. Alkaline etch if required by the condition of the substrate or if requested by customer. 7. Cold water rinse. 8. Acid pickle (the formulation of the acid pickle is determined by the alloy to be plated). 9. Cold water rinse. 10. Zincate following supplier's recommendations. 11. Cold water rinse. 12. Strip zincate in 50% v/v nitric acid. 13. Cold water rinse. 14. Zincate. 15. Cold water rinse. 16. Cold water rinse. 17. Electroless nickel plate to required thickness.
Copper, Brass and Beryllium Copper alloys (Durney, 2000)(K. J. Dai, 2013)	1. Solvent degrease if required. 2. Soak clean. 3. Cold water rinse. 4. Cathodic electroclean. 5. Cold water rinse. 6. Acid dip in proprietary dry acid salt. 7. Cold water clean. 8. Optional-strike in electrolytic nickel bath 9. Cold water bath. 10. Electroless nickel plate.

2.3 Electroless nickel plating process

The electroless nickel plating bath basically consists of a metal salt and a reducing agent for converting metal ions to a metal (Mallory, 1990). A solution containing only these two ingredients is highly unstable and a chemical reaction proceeds spontaneously (P. Sahoo, 2017).

A complexing agent, a pH buffer/stabilizer and other chemical reagent need to be added to suppress the chemical reaction and stabilize the solution (P. Sahoo, 2017).

The plating process start with immersion of a substrate material into the solution and the metal reduction process will occur on the substrate surface which acts as a catalyst. Reduced metal atoms will chemically bond on the surface and produces a metal film. After the metal film covers the whole substrate surface, it will act as an autocatalyst and increased the thickness. The crystal size changes with the amount of the alloying elements, as the alloying element increase the film becomes fine-grained and at some concentration, turns amorphous. (Watanabe, 2004)

In electroless plating process, metal ions migrate toward the substrate surface via diffusion through the metal ion gradient or drift with the aid of solution agitation. The reducing agent will be oxidized on the catalytic substrate surface and generate electrons. This electron will combine with incoming metal ions and form neutral metal atoms. The neutral metal atoms become adatoms after undergoing a physical or chemical adsorption process followed by the formation of an electroless film. (Watanabe, 2004). This process is shown on Figure 1.

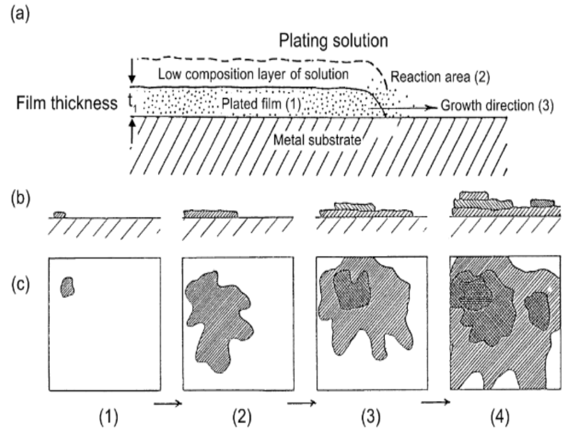

Figure 1: A schematic diagram showing a mechanism of electroless film formation. The film formation processes are illustrated: (a) at the edge of the metal island, (b) in the cross sectional view, and (c) from the top view. (Watanabe, 2004)

Figure 1 (a) show a surface reaction phenomenon on the substrate. For initiating metal deposition, the substrate has to possess catalytic activity. The immersion of this substrate into electroless solution results in spontaneous metal deposition. However, there are such metal depositions that may not occur readily due to the adsorption of chemical species such as H, OH or O which made the substrate surface catalytically inactive. In this case, the process of deposition can be initiated by passing a current (contact plating) to the substrate by touching the substrate with a less noble metal. This initiation treatment will serve as an autocatalyst for subsequent metal deposition that may not occur due to the reduction in catalytic activity caused by adsorbed chemical species. (Watanabe, 2004)

As seen in Figure 1 (b) and (c), the metal layer first forms on a catalytic substrate surface in the shape of a flat island. This first layer's edge region is highly activated due to heat evolution and violent solution movement caused by the reaction therefore the edge of the metal island will grow and expand laterally in a two-dimentional manner over the substrate surface. When the first layer island height reached a certain critical thickness, t_1, a layer of low metal ions concentration is generated at the solution island interface. The film cannot grow beyond the critical thickness until the layer of low metal ion concentration is destroyed by solution agitation and replaced with a fresh solution of high metal ion concentration from the bulk electrolyte. When the fresh solution come into contact with the first layer, the formation of the second layer become possible. In the same process as the first layer, the second layer will grow up to the critical thickness on top of the first layer and the process will repeat for the next layer. A layer having a critical thickness, t_1, is the basic building for the layered microstructure of electroless films. The critical thickness, t_1, depends on the metal ions concentration and temperature of the solution thus an increased in the concentration and temperature will increased the thickness, t_1. (Watanabe, 2004)

The growth rate of electroless films is controlled by the thickness, agitation speed and solution temperature. However, in practice there will be a certain amount of solution convection and thus the film can grow without agitation. Microscopic examination of the cross section of electroless films often reveals the presence of a layer structure that is different from Figure 8. These layer represent a trace of compositional modulation induced by a change in solution pH and temperature. Figure 2 is a plan view TEM micrographs that showed the formation of the 1st, 2nd, and the 3rd layers in the electroless nickel films. In Figure 2 (a) the 1st layer, (1) are seen in the shape of an islands, the region marked with (0) is the substrate which no metal have yet grown. In Figure 2(b), the overlapped 1st (1), 2nd (2) and 3rd (3) layers are visible. Figure 2(c) is the example of the case where the 1st layer is porous and the 2nd layer grown in such a way as to fill the pores in the 1st layer. (Watanabe, 2004)

In electroless plating processes, the film thickness are grown by layer thus the thickness variation is relatively small. Figure 3 showed the cross section TEM micrograph of a 28-nm thick electroless Ni-P film grown on an etched pure copper substrate. The film thickness appeared to be very uniform regardless of any surface irregularity on the substrate. As the thickness increased, nodules may nucleate at the protrusions, where the flow rate of the solution becomes very rapid (T. Tashiro, 1996). The protrusions described are already present on the substrate surface and not generated during electroless plating. (Watanabe, 2004)

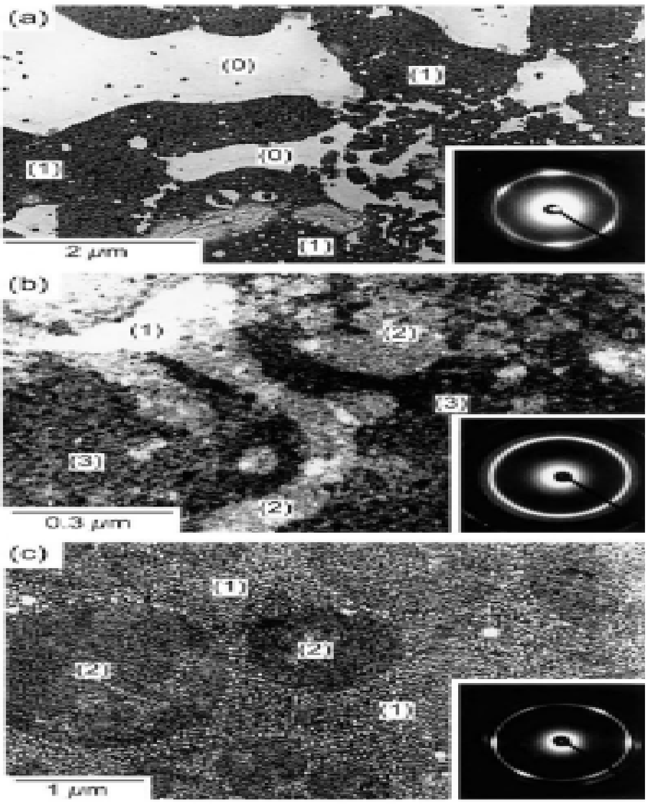

Figure 2: TEM micrographs showing the initial film formation stages of electroless Ni-B alloy films. Symbols denoted by (0), (1), (2), and (3) in the micrographs indicate the number of overlapped layers. Growth of (a) the 1st layer, (b) the triple (1st, 2nd, and *3rd) layer, and (c) the 2nd layer on top of the 1st layer.* (Watanabe, 2004)

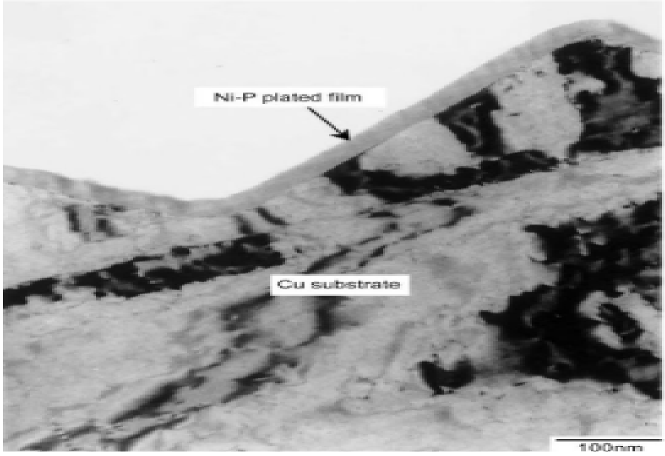

Figure 3: A cross section TEM micrograph showing an electroless Ni-P alloy film grown on an etched copper substrate. (Watanabe, 2004)

III. COMPOSITIONS OF AUTOCATALYTIC NICKEL PLATING BATH

Electroless nickel plating is famous due to its unique properties of the nickel deposits. The chemical and physical properties of an electroless nickel coating depend on its composition which depends on the formulation and operating condition of the bath (G. O. Mallory, 1990). Electroless nickel plating bath are blends of different chemicals with each had its own important roles. The component of a nickel plating solution is:

a) A sources of nickel ions,
b) A reducing agent,
c) Suitable complexing agent,
d) Accelerators and
e) Stabilizers or inhibitor.

3.1 Sources of nickel

The most important constituent of the bath is the sources of nickel ions. The ideal sources of nickel ions is the nickel salt from Hypophosphorus Acid, $Ni(H_2PO_2)_2$ (Durkin, 2016). This can eliminate the addition of sulfate anions and keep the buildup of alkali metal ions to a minimum while replenishing the reactants consumed during the deposition. The sources for nickel cations usually from nickel sulfate, nickel chloride or nickel acetate (P. Sahoo, 2017). But the application of nickel chloride and nickel acetate are very limited, the chloride anion can be harmful for aluminium or ferrous alloys plating because it can act deleteriously when the bath is used and the use of nickel acetate does not yield any significant improvement in the bath performance or deposits quality when compared to nickel sulfate but nickel sulfate are lower in cost (Mallory, 1990).

3.2 Reducing agent

There are four type of reducing agent that usually used in the bath, which is Sodium Hypophosphite, $NaH_2PO_2.H_2O$, Sodium Borohydride, $NaBH_4$, Dimethylamine Borane (DMAB), $(CH_3)_2NHBH_3$, and Hydrazine, $N_2H_4.H_2O$ (Schlesinger, 2010) (Takeshi Bessho, 2012) (Boris A. Janssen, 2013) (Robert Janik, 2015) (Chul Min Lee, 2010). The function of reducing agent in bath solution is to supply electrons for the reduction of nickel.

3.2.1 Sodium Hypophosphite

Sodium hypophosphite baths – more than 70% electroless nickel is deposited from solutions reduced by this reducing agent. The advantages of this bath over other reduced baths are greater ease of process control and lower costs (R. C. Agarwala, 2015). Most wide accepted mechanisms are illustrated by the following equation (Gutzeit, 1960).

I. Electrochemical mechanism - catalytic oxidation of the hypophosphite yield electrons at the catalytic surface and reduced nickel and hydrogen ions.

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^- \quad (1)$$

$$Ni^{2+} + 2e^- \rightarrow Ni \quad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \quad (4)$$

II. Atomic hydrogen mechanism – atomic hydrogen is released as the result of the catalytic dehydrogenation of hypophosphite molecule adsorbed at the surface.

$$H_2PO_2^- + H_2O \rightarrow HPO_3^{2-} + H^+2H_{ads} \quad (5)$$

$$2H_{ads} + Ni^{2+} \rightarrow Ni + 2H^+ \quad (6)$$

Simultaneously, some of the absorbed hydrogen reduces a small amount of the hypophosphite at the catalytic surface to water, hydroxyl ion and phosphorus

$$H_2PO_2 + H_{ads} \rightarrow H_2O + OH^- + P \quad (7)$$

III. The adsorbed active hydrogen (6) then reduces nickel at the surface of the catalyst.

$$(H_2PO_2)^{2-} + H_2O \rightarrow H^+ + (HPO_3)^{2-} + H_2 \quad (8)$$

Most of the hypophosphite present is catalytic, which is oxidized to orthophosphate and gaseous hydrogen, causing low efficiency of electroless nickel solution for alloy coating while the deposition of nickel and phosphorus continues.

3.2.2 Sodium Borohydride

Sodium borohydride baths – the reduction efficiency of sodium borohydride is higher than DMAB and sodium hypophosphite. Borohydride-reduced baths are preferred to DMAB-reduced baths because of the cost effectiveness of operation. However, control of pH is crucial in order to avoid the spontaneous decomposition of the bath solution. The borohydride-reduced baths usually used as alkaline baths M. Palaniappa, 2013).

The borohydride anion hydrolyzes almost spontaneously in neutral or acidic aqueous solutions. The reaction is illustrated below (Mallory, 1990):

Neutral:

$$BH_4 + 4H_2O \rightarrow B(OH)_4 + 4H_2 \quad (1)$$

Acidic:

$$BH_4 + H^+ \rightarrow BH_3 + H_2 \quad (2)$$

When nickel ions are present in the solution, the homogeneous reaction occurs, precipitating nickel boride:

$$8BH_4 + 4Ni^{2+} + 18H_2O \rightarrow 2Ni_2B + 6H_3BO_3 + 25H_2 \quad (3)$$

3.2.3 Dimethylamine Borane

Amineborane baths – the amineborane are effective reducing agent over a wide range of pH up to which the plating process can be carried out (Mallory, 1990). Nickel deposited increased as the pH of the bath increased, the amineborane baths in the range pH of 6 to 9 and the operating temperature range from 50-80°C but it can be used at temperature as low as 30°C (R. C. Agarwala, 2015). DMAB hydrolysis reaction is illustrated below (Mallory, 1990):

Acidic:

$$(CH_3)_2NHBH_3 + 3H_2O \vec{H} \ (CH_3)_2NH_2 + B(OH)_3 + 3H_2 \qquad (1)$$

Neutral:

$$(CH_3)_2NHBH_3 + 3H_2O \rightarrow (CH_3)_2NH_2 + B(OH)_3 + 3H_2 \qquad (2)$$

3.2.4 Hydrazine

Hydrazine baths – hydrazine-reduced baths operate in the temperature range of 363-368 K and pH range of 10-11. Their rate of deposition is approximately 12μm/h. The hydrazine-reduced bath is unstable at high temperature and difficult to control. The deposited also are brittle and highly stressed for practical applications (M. Palaniappa, 2013). The mechanisms are illustrated by the following equation by (Katsuhiko Tashiro, 2000)

$$N_2H_4 + 2OH^- \rightarrow N_2 + 2H_2O + H_2 + 2e^- \qquad (1)$$

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \qquad (2)$$

3.3 Complexing agent

It is difficult to maintain the bath composition as the plating proceeds. Continuously lowering the rate of reduction of coating element may occur as the baths cannot be replenished due to the formation of some unwanted compounds. Because of this, the additives known as complexing agent are added (M. Palaniappa, 2013). Complexing agent are organic acids or their salts that are added to avoid spontaneous decompositions of electroless nickel solutions and to control the reaction so that it occurs only on the catalytic surface, it control the amount of free nickel available for reaction and stabilize the bath. It also retard the precipitation of nickel phosphite (Davis, 2000(Robert Janik, 2015). Useful carboxylic acids include mono-, di-, tri- and tetra-carboxylic acids are selected as complexing agents. The carboxylic acids may be substituted with various substituent moieties such as hydroxy or amino groups and the acids may be introduced into the plating solutions as their sodium, potassium or ammonium salts (Boris A. Janssen, 2013).

3.4 Accelerators

Due to complexing agent action which reduces the speed of deposition, it can cause the plating rate to become uneconomically slow (Davis, 2000). The electroless nickel plating solution composition may further include at least one of organic acid and alkali metal salt. The organic acid and the alkali metal salt are used to prevent the reduction of a plating speed due to phosphorous acid and pH of the electroless nickel plating solution composition. Thus organics additives called accelerators or exultant are added to the bath in small amounts (Chul Min Lee, 2010). The accelerator may be a compound having at least one or more carboxyl. For example, acetic acid, sodium acetate, propionic acid, sodium propionate, formic acid, sodium formate, potassium formate, adipic acid, sodium adipate, succinic acid and sodium succinate (Chul Min Lee, 2010).

3.5 Inhibitor and stabilizer

An electroless nickel plating bath that is operated under normal operating condition over extended period of time can decompose spontaneously at any time, to avoid this an inhibitor or stabilizer are added (G. O. Mallory, 1990) (Davis, 2000). It is added to prevent the homogeneous reaction that triggers the subsequent random decomposition of the bath (Davis, 2000). If a problem arise in the bath can be solved by adding a stabilizer, the compatibility of it with the process being used must be deduce to avoid any adverse loss in catalytic activity due to the synergistic action with any other additive present in the bath (Manoj B. Gawande, 2016). When two or more stabilizers are used, the action of one must not inhibit or lessen the effectiveness of the other stabilizers (Mallory, 1990). Due to this, stabilizers are selected on the basis that they only affect the plating process in a manner that the resultant deposit will be able to meet any required performance criteria (Mallory, 1990) (J. K. Dennis, 2013). Stabilizing agents include organic and/or inorganic stabilizing agents such as lead ions, cadmium ions, tin ions, bismuth ions, antimony ions and zinc ions, which can be introduced in the form of bath soluble and compatible salts such as the acetates. Suitable bismuth compounds for example, bismuth oxide, bismuth sulfate, bismuth sulfite, bismuth nitrate, bismuth chloride, bismuth acetate and the like. Organic stabilizers include sulfur containing compounds such as thiourea, mercaptans, sulfonates and thiocyanates) (Robert Janik, 2015).

IV. POSSIBLE COMPOSITIONS OF THE BATH CLASSIFIED BY THE TYPE OF REDUCING AGENT

Based on reducing agent, there are four famous reducing agent that are usually used by the industrial company. The famous four are sodium hyphophosphite, sodium borohydride, dimethylamine borane and hysrazine. Based on the information obtained, the widely used reducing agent is sodium hypophosphite. More than 70% of electroless nickel is deposited from solutions reduced by this reducing agent. The advantages of this bath over other reduced baths are the greater ease of process control and lower costs (R. C. Agarwala, 2015).

Due to the famous usage of hypophosphite as reducing agent, there are several type of bath composition that are listed. The bath composition are different for acidic and alkaline, the quantity for each component used are also tabulated as below. (Pearlstein, 1974)

Table 2: Bath composition for electroless nickel deposition using Sodium hypophosphate, $NaH_2PO_3.H_2O$ reducing agent. (Pearlstein, 1974)

Bath Constituent (gL^{-1})	Acidic			
	Bath 1	Bath 2	Bath 3	Bath 4
Nickel chloride, $NiCl_2.H_2O$	30	30	-	21
Nickel sulfate, $NiSO_4.6H_2O$	-	-	25	-
Sodium hypophosphate, $NaH_2PO_3.H_2O$	10	10	23	24
Hydroxyacetic acid, $HOCH_2COOH$	35	-	-	-
Sodium citrate, $Na_3C_6H_5O_7.H_2O$	-	12.6	-	-
Sodium acetate, $NaC_2H_3O_2$	-	5	9	-
Succinic acid, $C_4H_6O_4$	-	-	-	7
Sodium fluoride, NaF	-	-	-	5

Lactic acid, $C_3H_6O_3$	-	-	-	-
Propionic acid, $C_3H_6O_2$	-	-	-	-
Ammonium chloride, NH_4Cl	-	-	-	-
Sodium pyrophosphate, $Na_4P_2O_7$	-	-	-	-
Lead ions, Pd^{2+}	-	-	0.001	-
pH	4-6	4-6	4-8	4-6
Temperature (°C)	100	100	85	100

Bath Constituent (gL^{-1})	Alkaline			
	Bath 5	Bath 6	Bath 7	Bath 8
Nickel chloride, $NiCl_2.H_2O$	26	30	20	-
Nickel sulfate, $NiSO_4.6H_2O$	-	-	-	25
Sodium hypophosphate, $NaH_2PO_3.H_2O$	24	10	20	25
Hydroxyacetic acid, $HOCH_2COOH$	-	-	-	-
Sodium citrate, $Na_3C_6H_5O_7.H_2O$	-	84	10	-
Sodium acetate, $NaC_2H_3O_2$	-	-	-	-
Succinic acid, $C_4H_6O_4$	-	-	-	-
Sodium fluoride, NaF	-	-	-	-
Lactic acid, $C_3H_6O_3$	27	-	-	-
Propionic acid, $C_3H_6O_2$	2.2	-	-	-
Ammonium chloride, NH_4Cl	-	50	35	-
Sodium pyrophosphate, $Na_4P_2O_7$	-	-	-	50
Lead ions, Pd^{2+}	0.002	-	-	-
pH	6	8-10	9-10	10-11
Temperature (°C)	100	95	85	70

These tables showed possible bath formulations for the electroless nickel deposition by using sodium hypophosphite in different value as the reducing agent. For bath 1 to bath 4, the bath compositions are acidic and for bath 5 to bath 8 is alkaline bath composition. There are wide ranges in pH value that are suitable for the bath from 4 to 11. Parkinson, 1997 stated that when sodium hypophosphite is used as the reducing agent, the deposited is 92% nickel and 7% phosphorus. From the deposited film, by using a low pH (acidic), the film will have phosphorus content up to 25% and at an alkaline range, the phosphorus content in the film is as low as 1% (Schlesinger, 2010).

The industry normally identifies electroless nickel coating according to their phosphorus content and choosing their bath composition based on the phosphorus content because the composition, structure and properties of the nickel plating deposited mostly depend on the phosphorus content.

The electroless nickel deposited has an amorphous structure or one consisting of ultrafine crystallites which different from the crystalline structure of electrodeposited nickel (Bayes, 1995). The structure eliminated the chances of intergranular corrosion that can occur with crystalline structure (Parkinson, 1997). At higher phosphorus content, the amorphous structure of the deposited nickel becomes more dominant.

The density of electroless nickel is not constant and decreased with increasing phosphorus content. The resistivity of high purity nickel is 7.8x10-6 ohmcm but for electroless nickel the value can be greater as ten times due to the disruption of the regular lattice structure of high purity nickel by the codeposition of phosphorus (Parkinson, 1997). The ferromagnetism associated with high purity nickel decreases with increasing phosphorus content and deposits with over 11% phosphorus are described essentially as non-magnetic (T-6A-53, 1997). The phosphorus content and structure of electroless nickel coatings also have a strong effect on wear resistance, under abrasive wear conditions, the wear of medium and high phosphorus coatings is higher than low phosphorus content (T-6A-53, 1997).

Because of the positive outcome on the deposited film characteristic by using hypophosphite reduced bath, it become the most famous and frequently used reducing agent.

The other reducing agent is sodium hydroxide. Sodium borohydride's reduction efficiency is higher than DMAB and sodium hypophosphite. However, control of pH is crucial for this type of reduced bath in order to avoid the spontaneous decomposition of the bath solution. The borohydride-reduced baths usually used as alkaline baths (M. Palaniappa, 2013). The possible bath composition for sodium borohydride is as follow.

Table 3: Bath composition for electroless nickel deposition using sodium borohydride, $NaBH_4$ reducing agent. (G. O. Mallory, 1990)

Component	Concentration, g/L					
	Bath 1	Bath 2	Bath 3	Bath 4	Bath 5	Bath 6
Ni^{2+}	7.4	7.4	2.5	7.6	5.0	6.0
Ethylenediamine (98%)	45	40	-	-	-	-
EDTA disodium salt	-	-	35	-	-	-
Triethylene tetramine	-	-	-	87	-	-
Sodium potassium tartrate	-	-	-	-	65	-
Ammonium hydroxide (28%)	-	-	-	-	-	120mL/L
Sodium hydroxide	40	40	40	40	40	-
Sodium borohydride	1.5	1.2	0.5	1.0	0.75	0.4
$TINO_2$, mg/L	100	-	50	50	-	-
$Pb(NO_3)_2$, mg/L	-	40	-	-	10	-
2-MBT, mg/L	-	5	-	-	-	20
Temperature, °C	95	95	95	97	92	60
pH	14	13	14	14	13	12

By using sodium borohydride as the reducing agent, the deposited film containing nickel and boron. This bath need to maintain the pH above 12 to suppress the nickel boride precipitation thus this reducing agent only used as an alkaline bath (Schlesinger, 2010). Due to its only possible bath are in alkaline at pH 12 and above, only substrate that can withstand the high alkalinity can be plated using these solution.

Ethylenediamine tetraacetic acid (EDTA) and ethylenediamine are used to prevent the precipitation of basic nickel salts or nickel hydroxide due to its effectiveness in sequestering nickel ions within the pH range (Mallory,1990).

In this type of bath, the important factors are temperature and the concentration of borohydride. The rate of the plating reaction increased exponentially with the temperature as in Figure 4, thus to increase the plating rate in order to plate faster, the temperature of 95°C is suitable than 85°C.

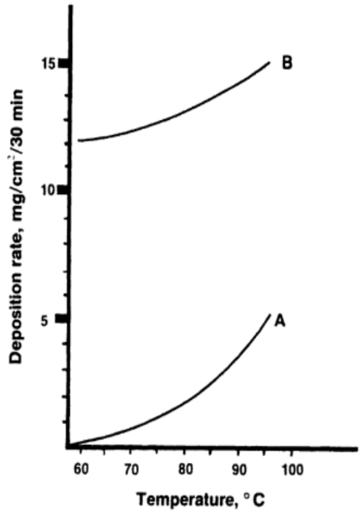

Figure 4: Effect of temperature on plating rate. Curve A has no stabilizer added to the bath. Curve B contain 100 ppm TINO2. (K. Gorbunova, 1973)

The concentration of borohydride is a crucial value to be control because at high concentration, the stability of the bath decreased. It is recommended that small quantities of the sodium borohydride be added at very close intervals with the additions of sodium or potassium hydroxide to maintain the concentration, pH, plating rate and activity of the borohydride ion (Mallory, 1990). From Figure 5, it is shown that as the concentration of BH4- increased, the stability of the plating bath decreased.

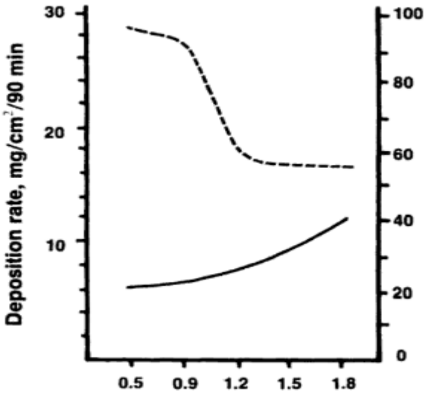

Figure 5: Effect of $NaBH_4$ concentration on plating rate (solid line) and solution stability (dash line). No stabilizer present. (K. Gorbunova, 1973)

Based on Figure 6, the effects of $NaBH_4$ concentration on plating rate and bath stability gave an improvement in the presence of stabilizer, $TINO_2$. The presence of $TINO_2$ allow the deposition process to take place at a lower temperature with a relatively high deposition rate. However, the uses of $TINO_2$ will result in thallium codeposits in to the alloy in significant quantities. Some nickel-boron alloys contain 6% thallium. The comparison between Figure 5 & Figure 6 concludes that a stabilizer can influence the process. (Mallory, 1990)

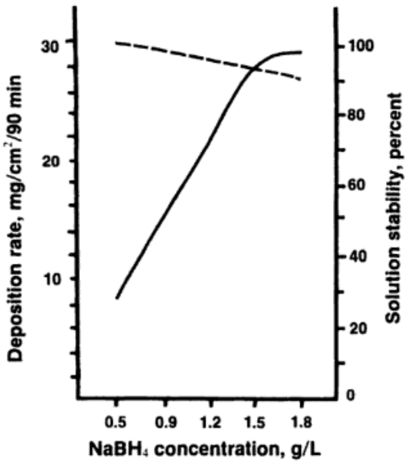

Figure 6: The effect of $NaBH_4$ concentration on plating rate (solid line) and solution stability (dash line). Bath contains 100 ppm $TINO_2$. (K. Gorbunova, 1973)

Borohydride-reduced baths are preferred to DMAB-reduced baths because of the cost effectiveness of operation (M. Palaniappa, 2013). However, the amineborane are effective reducing agent over a wide range of pH up to which the plating process can be carried out (Mallory, 1990).

Table 4: Bath composition for electroless nickel deposition using Dimethylamine borane, DMAB, $(CH_3)_2NHBH_3$ reducing agent. (G. O. Mallory, 1990)

Component	Concentration, g/L			
	Bath 1	Bath 2	Bath 3	Bath 4
Ni^{2+}	6.0	11.0	7.5	7.5
Lactic acid (88%)	30.0	25.0	-	-
Citric acid	-	25.0	-	-
Sodium succinate	-	-	20	-
Sodium acetate	15.0	-	-	-
Sodium glycolate	-	-	40	-
Sodium pyrophosphate	-	-	-	60
DMAB	2.5	2.5	2.5	2.5
Thiourea, mg	1	-	2	-
$Pb(NO_3)_2$, mg	-	2	-	-
Thiodiglycolic acid, mg	-	70	-	50
pH (with NH_4OH)	6.1	6.3	7.0	9.0
Temperature (°C)	60	50	65	40

The compositions of Ni-B alloys produced with DMAB as reducing agent are 95 to 99.8% by weight nickel, the remainder is boron. If these deposit is formed by bath solution that does not contain stress reducer, their internal stress is high and tensile in nature thus thiourea and thiodiglycolic acid are added. The pH of a DMAB-reduced electroless plating bath should be in the acidic range above pH 5.0 to minimize DMAB hydrolysis (Mallory, 1990) (Schlesinger, 2010). At pH below 5.0, the DMAB hydrolysis is very temperature dependent and at above pH 5.0, the DMAB hydrolysis does not become a major consideration unless the temperature exceeds 70°C (Schlesinger, 2010). Figure 7 showed the effect of pH value on deposition rate at temperature 71°C and concentration 0.06M DMAB.

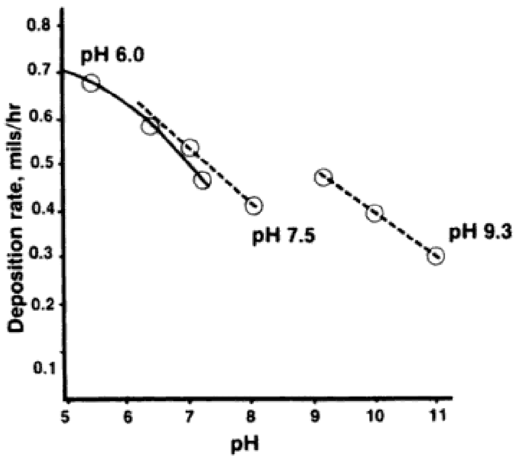

Figure 7: The effect of pH value on deposition rate at temperature 71°C and concentration (0.06M) DMAB. (Mallory, 1990)

In the presence of reducible ions, such as Ni^{2+}, the DMAB hydrolysis become temperature dependent regardless the pH value. The rate of deposition increases when the pH of the bath is decreased. (Mallory, 1990).

The most uncommon reducing agent are hydrazine. The hydrazine-reduced bath is unstable at high temperature and difficult to control. The deposited also are brittle and highly stressed for practical applications (Mallory, 1990) (M. Palaniappa, 2013) thus this type of reducing agent is the least famous for usage. However, an electroless nickel plating bath with a hydrazine reducing agent has been investigated and a bath with a deposition rate of about 3µm/hr and superior bath stability as compared to previously reported bath has been developed (Katsuhiko Tashiro, 2000) (M. Palaniappa, 2013).

Table 5: Bath composition for electroless nickel deposition using hydrazine, $N_2H_4.H_2O$ reducing agent. (Katsuhiko Tashiro, 2000)

Components	Concentration, mol/dm^3
	Bath
$NiCl_2.6H_2O$	0.05
$N_2H_4.H_2O$	0.40
Glycine	0.30
Boric acid	0.50
pH	12
Temperature (°C)	85-90
Deposition rate	About 3µm/h

An electroless nickel plating bath with a hydrazine reducing agent has been investigated and a bath with a deposition rate of about 3µm/hr and superior bath stability as compared to previously reported bath has been developed. The new bath is simple system consisting of glycine and boric acid in addition to nickel and hydrazine. The optimum plating conditions for the bath are in the range of 85-90°C at a pH of 12. The deposits obtained from the developed bath are black with a surface morphology that has a dendrite structure and the deposited specific resistance and solderability were superior to those of conventional nickel-phosphorus deposits. Results confirmed that nickel was directly deposited on a copper substrate from an electroless nickel plating bath with hydrazine reducing bath without an activation step in pretreatment. (Katsuhiko Tashiro, 2000)

V. POSSIBLE COMPOSITIONS OF THE BATH CLASSIFIED BY THE COUNTRY OF ORIGIN

Another data collected in this literature review is research based on the patents from Germany, Japan, Korea and United State of America revised from year 2003 to 2017, those countries published at most three patents of electroless nickel plating in a year and Germany had been the most frequent country in publishing the patents. The patents available in the online Google Patent are collected and their data is summarized according to the compositions of the nickel plating bath. Table 6 shows the list of patents found in this literature review. From those patents, the data for four countries are tabulated.

Table 6: Country of origin versus no. of patents registered.

Country	No. of patents registered
	Auto-catalytic nickel
Japan	1. WO 2012052832 A2 (2012) 2. WO2012052832A3 (2012) 3. WO2012052832A8 (2012)
Germany	1. WO 2008135179 A1 (2008) 2. EP1988192 A1 (2008) 3. US20100119713 A1 (2010) 4. CN101675186 A (2010) 5. CN101675186 B (2012) 6. US8152914 B2 (2012) 7. EP1988192 B1 (2012) 8. WO2013013941 A1 (2013) 9. CN103946420 A (2014) 10. EP2737107 A1 (2014) 11. US20140150689 A1 (2014) 12. CN103946420 B (2015) 13. EP2737107 B1 (2015)
United State of America	1. US 20030232148 A1 (2003) 2. US6797312B2 (2004) 3. US 8858693 B2 (2014) 4. US20150044374 A1 (2015) 5. WO 2015020772 A1 (2015) 6. CN 105452528 A (2016) 7. EP 3030688 A1 (2016)
South Korea	1. US20100155108 A1 (2010) 2. CN101760731A (2010)

5.1 Japan

From Figure 8, Japan published in 2012 and they published three patents on electroless nickel plating that year. Based on the patents, data for the bath composition are extracted in Table 7.

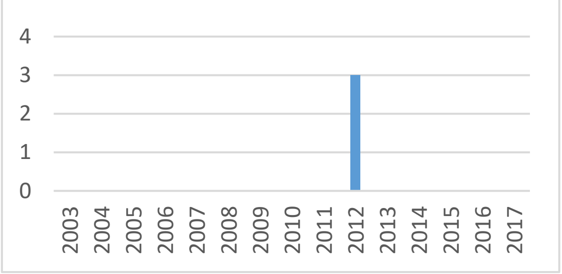

Figure 8: Graph of number of patents against years in Japan

Table 7: Possible compositions of autocatalytic nickel plating in Japan

Components	Bath constituents	Value (g/L)
Sources of nickel	Nickel sulfate, nickel chloride, nickel carbonate, nickel acetate, nickel hypophosphite, nickel sulfamate or nickel citrate.	0.05 to 0.20 mol/L

Reducing agent	Hypophosphorous acid, sodium hypophosphite, DMAB (dimethyl amino borane) or hydrazine	0.10 to 0.25 mol/L
Complexing agent	Succinic acid or one of malic acid and lactic acid	0.10 to 0.25 mol/L
Inhibitor or stabilizer	Metal antimony, antimony chloride, antimony acetate, antimony oxide or antimonyl potassium tartrate	0.0002 to 0.02
Buffering agent	Ammonium chloride, ammonium sulfate or boric acid	2-10
pH		4.6
Temperature (°C)		80-85

5.2 Germany

In Figure 9, it can be seen that this country published patent for electroless nickel plating in the industries in year 2008, from that year, the country had been actively contributed in publishing several patents from two to three patents in years 2010 to 2015.

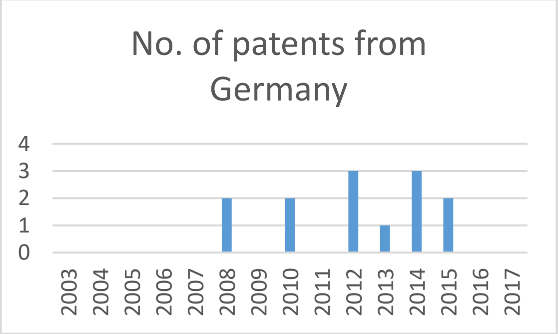

Figure 9: Graph of number of patents against years in Germany

Table 8: Possible compositions of autocatalytic nickel plating in Germany

Components	Bath constituents	Value (g/L)
Sources of nickel	Nickel sulfate	3-9
Reducing agent	Sodium hypophosphite, potassium hypophosphite or ammonium hypophosphite	20-45
Complexing agent	Carboxylic acids, polyamines or sulfonic acids	15-75
Inhibitor or stabilizer	The group consisting of hydrogen, sodium and potassium.	3 to 30 ppm
Buffering agent	Acetic acid, propionic acid or boric acid	2-10
pH		4-6
Temperature (°C)		80-90

5.3 United State of America

From Figure 10, United State of America published one patent of electroless nickel plating on 2003 and 2004 took a long time before they published several patents more on years 2014 to 2016. They published two patents per year in 2015 and 2016.

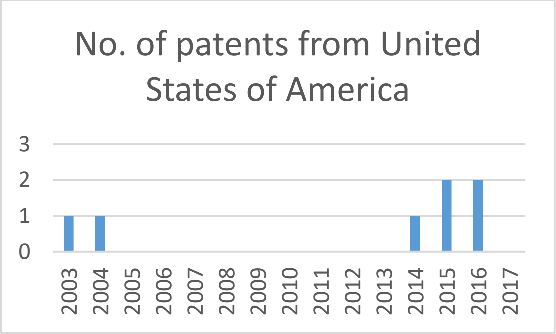

Figure 10: Graph of number of patents against years in United State of America

Table 9: Possible compositions of autocatalytic nickel plating in United State of America

Components	Bath constituents	Value (g/L)
Sources of nickel	Nickel bromide, nickel fluoroborate, nickel sulfonate, nickel sulfamate, nickel alkyl sulfonate, nickel sulfate, nickel chloride, nickel acetate or nickel hypophosphite	4-9
Reducing agent	Sodium hypophosphite, sodium borohydride, dimethylamine borane and trimethylamine borane such as diethylamine borane and isopropylamine borane and hydrazine.	20-50
Complexing agent	Acetic acid, glycolic acid, glycine, alanine, lactic acid; dicarboxylic acids such as succinic acid, aspartic acid, malic acid, malonic acid, tartaric acid; tricarboxylic acids such as citric acid; and tetracarboxylic acids such as ethylene diamine tetra acetic acid (EDTA),	20-40
Inhibitor or stabilizer	Lead ions, cadmium ions, tin ions, bismuth ions, antimony ions or zinc ions	0.0005-0.003
Buffering agent	Acetic acid, propionic acid or boric acid	2-10
pH		8-9
Temperature (°F)		190-210
Brightener agent	2-amino ethane sulfonic acid, toluene sulfonamide, 1-octane sulfonic acid, 2-chloro-2-hydroxy-propane sulfonic acid, saccharin, sodium diamyl sulfosuccinate, sodium 1,4 bis (1,3-dimethylbutyl) sulfosuccinate, sulfosuccinic acid, or sodium alkyl sulfonate	0.0005-0.002

5.4 South Korea

South Korea published the patent earlier then Japan since they already published two patents on 2010.

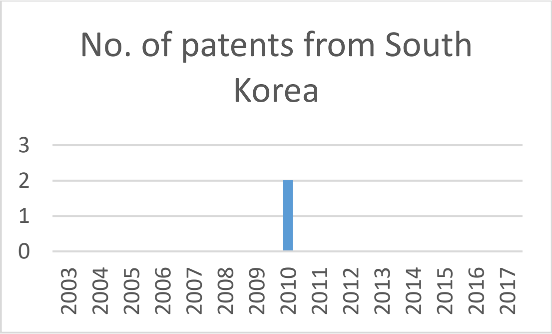

Figure 11: Graph of number of patents against years in South Korea

Table 10: Bath composition based on patents from South Korea

Components	Bath constituents	Value
Sources of nickel	Nickel sulfate and nickel chloride	1.0 to 10.0 wt % based on the total weight of the electroless nickel plating solution composition
Reducing agent	A group consisting of hypophosphorous acid, potassium hypophosphite, hydrazine or sodium hypophosphite.	1.0 to 10 wt % based on the total weight of the electroless nickel plating solution composition.
Complexing agent	Lactic acid, glycolic acid or malic acid	2.0 to 5.0 wt% based on the total weight of the electroless nickel plating solution composition
Inhibitor or stabilizer	Thiourea, alkyl thiourea, a mercapto compound, a tyazole compound, sodium thiosulfate, sodium thiocyanate, potassium thiocyanate, thio glycolic acid or thio- diglycolic acid	0.0001 to 0.1 wt% based on the total weight of the electroless nickel plating solution composition.
Accelerator	Acetic acid, sodium acetate, propionic acid, sodium propionate, formic acid, sodium formate, potassium formate, adipic acid, sodium adipate, succinic acid or sodium succinate	1.0 to 10 wt % based on the total weight of the electroless nickel plating solution composition.
pH		4-6
Temperature (°C)		80-85

After collecting patents available in 2003 until 2017, the data were analyze to investigate at what year does autocatalytic nickel plating are at its peak in popularity in between year 2003 until 2017.

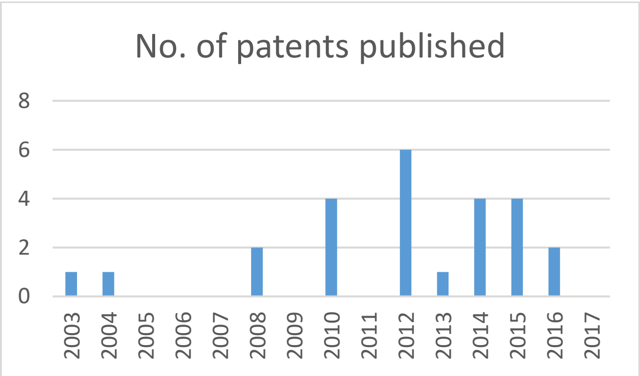

Figure 12: Graph of number of patents against years for four country

Based Figure 12, it can be concluded that in year 2012, the publishing of patents on autocatalytic nickel plating reach it highest where at that particular year, there are six (6) patents for autocatalytic nickel plating had been published. Meaning on this particular year, the industry of autocatalytic nickel plating had reached its peak popularity in usage.

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