ENVIRONMENTALLY FRIENDLY COPPER ELECTROPLATING PROCESS
DEVELOPMENT

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ABSTRACT

ENVIRONMENTALLY FRIENDLY COPPER ELECTROPLATING PROCESS DEVELOPMENT

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Electroplating is the deposition of a metal by applying electrical current in the presence of an electrolyte. Electroplating industry creates wastes that are heavy metal containing, highly conductive, strongly acidic/alkaline in composition. Many industries are now enforced to prevent their wastes from being formed via pollution prevention guidelines. It is both economically and environmentally more advantageous to consider pollution prevention before establishment of a process. In this study, waste minimization in copper strike plating over aluminium metal using copper cyanide bath was targetted in a laboratory scale production process. In this framework, preliminary setups were conducted to compare several strike baths for copper deposition including copper cyanide and copper pyrophosphate baths. Visual inspection, roughness measurements, SEM imaging and reflectivity measurements were conducted on the products after deposition. Percent deviation in integrating sphere reflectivity measurements ranged between 1-2% and 7-29% for copper pyrophosphate bath and copper cyanide baths, respectively. Similarly, SEM and roughness indicators were more favorable for copper pyrophosphate bath products. Secondary setups were performed in order to compare life time of baths by tracking changes in critical parameters in long run plating processes for two selected baths. The concentrations of copper and cyanide increased by 17.5 % and 11.5%, respectively, after four hours of plating whereas copper and pyrophosphate concentrations fluctuated over time during plating without a significant change. The results have shown that for the field of application of the product, cyanide bath can be replaced by a non-cyanide alternative that is a pyrophosphate strike.

Keywords: cleaner production, waste minimization, copper electroplating process

ÖZ

ÇEVRE DOSTU YAKLAŞIMLARLA BAKIR ELEKTROKAPLAMA SÜRECİNİN GELİŞTİRİLMESİ

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Elektrokaplama bir elektrolit varlığında elektrik akımı uygulanarak metal kaplama işlemidir. Bir endüstri olarak elektrokaplama süreçleri ağır metal içerikli, yüksek iletkenlikli ve hayli asidik/alkali atıklar oluşturur. Kirlilik önleme talimatlarıyla birçok endüstriye atıkları konusunda daha oluşmadan önleme yaptırımı uygulamaktadır. Kirlilik önleme konularının süreç daha oluşturulmadan önce göz önüne alınması hem ekonomik hem de çevresel açıdan avantaj sağlamaktadır. Bu çalışmada, henüz daha laboratuvar aşamasında olan bakır siyanür banyosu kullanılarak aluminyum üzerine ince tabaka (strike) bakır kaplanması prosesinde atık minimizasyonu hedef alınmıştır. Bu çerçevede, ilk deneysel düzenekler siyanür veya pirofosfat temelli çeşitli strike banyolarının bakır kaplama performanlarını değerlendirmek açısından oluşturulmuştur. Kaplamalar yapıldıktan sonra ürünler üzerinde görsel inceleme, pürüzlülük ölçümleri, SEM görüntüleme ve yansıma ölçümleri yapılmıştır. Küre yansıma ölçümleri kullanılarak hesaplanan sapma değerleri pirofosfat banyoları numuneleri için % 1-2 aralığında, siyanür ürünleri için ise % 7-29 aralığında olarak kaydedilmiştir. Benzer şekilde SEM görüntüleri ve pürüzlülük ölçümleri de bakır pirofosfat banyosu ürünlerini daha cazip kılmıştır. İkinci deneysel düzenekler için bir pirofosfat ve bir siyanür banyosu seçilmiş ve bu banyolarda uzun süreli kaplama yapılarak banyo parametresi takibi yapılmıştır. Bakır siyanür banyosundaki dört saatlik kaplama sırasında bakır ve siyanür konsantrasyonlarında sırasıyla %17.5 ve %11.5 artış kaydedilmişken, bakır pirofosfat banyosunda bakır ve pirofosfat konsantrasyonları önemli bir değişim olmaksızın dalgalanmalar göstermiştir. Elde edilmiş olan sonuçlar, ürünün kullanım alanı düşünüldüğünde, bakır siyanür banyosunun siyanürsüz bir alternatif olan bakır pirofosfat banyosuyla değiştirilebileceğini göstermiştir.

Anahtar Kelimeler: temiz üretim, atık minimizasyonu, bakır elektrokaplama süreci

To My Country,

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

Electroplating is an electrochemical process in which a thin layer of metal is deposited onto a substrate by applying electrical current in the presence of an electrolyte. Automobile, ship, aerospace, machinery, electronics, jewelry, defence and medical industries are among the industries which commonly employ electroplating processes (Badr et. al., 2007; Lou et.al., 2006). There are mainly four intentions to apply electroplating, these are; (i) to end up with a decorative finish, (ii) to form a protective layer, (iii) to get benefit from surface properties of the plated layer, (iv) to use engineering or mechanical properties of the deposited metal (URL1). Electroforming is an another application which is based on electroplating principles. The difference between electroplating and electroforming is that, in electroforming, a convenient mandrel is deposited with metal layer(s) by electroplating and the mandrel is then separated from plated metal layer(s). This process results in a free standing object of deposited layer(s) (Durney, 1984).

Despite the very wide range application fields, wastes generated in these processes are still a major concern. This is mainly due to their acidic, basic, heavy metal containing and highly conductive nature. The waste originating from electroplating facilities are a sub-group of metal finishing wastes. These wastes are subject to regulations under the Resource Conservation and Recovery Act (RCRA), the Hazardous and Solid Waste Amendments (HSWA) and Clean Water Act (CWA) in USA (Wang et al., 2009). Turkish legislations categorize the majority of electroplating wastes as hazardous, depending on materials found in their composition, under the Regulation on the Control of Hazardous Wastes (Official Gazette No: 25755 Date: 14 March 2005).

Rather than end-of-pipe treatment of wastes that is treatment of wastes after they are produced, recent decade moves toward a more proactive approach; that is cleaner production/pollution prevention (these two terms are used interchangeably throughout this study). Cleaner production approaches have started to be supported in Turkey as in all over the world. By definition of United Nations Environment Programme (UNEP) cleaner production means: "The continuous application of an integrated environmental strategy to processes, products and services to increase efficiency and reduce risks to humans and the environment"(URL2). In electroplating industries, material substitution, bath-life extension, drag-out reduction or recovery and rinse water reduction are general titles for the most desirable pollution prevention applications which are dedicated as priority one strategies because their application results in minimizing the waste before it is formed. Priority two concerns for electroplating shops are commonly the applications aiming at recycling and reuse. These applications can be reuse of spent baths and rinse water as well as recycling them and waste segregation.

Even if obligations made by legislations are not effective enough for some facilities, motivations held by cleaner production strategies such as decreasing operating, waste treatment or waste disposal costs or reduction of water or raw material consumption which are consumed at significant amounts make the manufacturers take a step towards cleaner production. For those who adopted a specific production process, feasible cleaner production strategies can be limited in respect to the newly developed processes. Modifications proposed may be very costly or may need a complete alteration of the process. However, development of a new process by cleaner production strategies is much more advantageous in terms of allowing a wider variety of options to be applied.

The first step of a specific electroforming application, copper strike (very thin layer of copper) electroplating on polished aluminium, is the subject in this study. Aluminium is being used in electroforming to get use of its material properties as a metal mandrel. In electroforming, aluminium mandrel is being deposited with other metals and then it is dissolved from the inside of the plated metal using a sodium hydroxide solution. As a result a free standing object and recoverable aluminium-caustic solution are gained (URL3).

Aluminium can not be directly plated by copper because of adherence problem. Therefore, a strike application is first needed to cover the surface of the aluminium with a thin layer of copper (about 1-3 µm thick). Strike (very thin) copper depositions can be obtained by using alkaline type of baths which are copper cyanide strike and copper pyrophosphate strike baths. After the initial strike layer is formed, further metallic layers which are much thicker (more than 50 µm) are deposited over the initial strike layer. Striking deposit is just an initial step in electroforming. However, it is a very crucial step in a plating process which affects the complete performance in the product formation. The mishaps faced in the striking will also show up on the completed product (Davis, 2001).

This study aims to develop an environmentally friendly electroplating process for copper strike plating over aluminium by applying a waste minimization strategy that focusses on:

- decreasing environmental risk associated with wastes generated,
- providing more healthy and safe production process,
- improvement in the quality of the product,
- reduction of waste generation,
- decreasing the costs related with laboratory works,
- standardization of the product,
- decreasing raw material, energy and water consumption.

Main goal is waste minimization via material replacement, that is chemical substitution assessment and process monitoring which are included among the priority one pollution prevention strategies. In order to decrease the environmental risks associated with the use of cyanide electroplating baths in the process, several copper strike baths are compared in terms of the quality of the product. These studies are also aimed to provide a more healthy and safety production process with the trials for limiting or eliminating cyanide use by comparing these products. If copper cyanide baths can be substituted with copper pyrophosphate baths, energy will also be conserved because of the difference in operating temperatures of each bath. The comparision of the products obtained in several baths will also yield the better product quality after plating.

The amount of waste generated can be reduced by extending the life time of the electroplating bath which can be enabled by monitoring parameters of the bath. Only the chemicals consumed are added to the solution by regular monitoring, therefore, lower amount of raw materials are used. This fact, in return, will decrease the costs related to the laboratory works. If the contents of a bath can be kept at the same level by monitoring, more consistent products in terms of quality are expected to be obtained from baths.

CHAPTER 2

LITERATURE REVIEW

2.1 Copper Electroplating

Electroplating is mainly depositing a thin layer of metal onto a substrate by applying electrical current in the presence of an electrolyte. Electrolytes are mainly aqueous solutions of salts, acids or bases. The metal to be plated is placed as cathode and the metal which is plated over the cathode is placed as anode (Figure 2.1). Both anode and cathode are submerged into the electrolyte and when an electrical current is applied cathode forms negatively charged electrode and anode forms the positively charged electrode. Metal at anode which is in solid form dissolves in electrolyte by an oxidation reaction as follows (URL1):

$$M(s) \rightarrow M^{z+}(aq) + ze^-$$
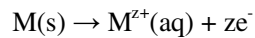
Positively charged metal ions in the electrolyte are reduced at the cathode and depositied in metallic form.

$$M^{z+}(aq) + ze^- \rightarrow M(s)$$
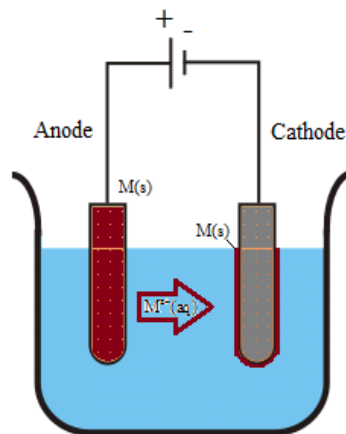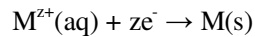
Figure 2.1 Schematic diagram of electroplating.

There are commonly four types of copper electroplating baths which are either acidic or alkaline in composition. Copper cyanide and copper pyrophosphate baths are alkaline whereas copper sulfate and copper fluoborate are acidic in composition. Strike (very thin) copper depositions can be obtained by using alkaline baths. Copper pyrophosphate baths are rarely utilized in processes since they have a narrow band for operating parameters and they are considered to be hard to control (ASM, 1994). Further information about copper cyanide and pyrophosphate electroplating baths is given in Sections 2.1.1 and 2.1.2, respectively.

2.1.1 Copper Cyanide Electroplating Bath

Copper cyanide solutions have anode efficiency of 50-100% and the cathode efficiency offered is in between 10-100%. These solutions are advantegeous in terms of supplying wider operating range for pH. pH variance between 10.3 and 12.8 does not have a large impact on limiting current density. The cleaning ability of the workpiece during depostion is another advantage of copper cyanide baths (Schlesinger and Paunovic, 2010). The purposes in applying copper cyanide solutions are (Schlesinger and Paunovic, 2010):

- to form a protective layer over the metal to be plated from the further operations,
- to enable better adhesion between the metal to be plated and the actual layer desired to be deposited over it,
- to improve the surface characteristics,
- to add a decorative final touch,
- to act as an intermediate layer between steel and nickel and chromium plating,
- to cease case hardening in desired applications,
- to deposit copper over coins,
- to conduct electricity by plating on steel wires.

When aluminium needs to be plated, zincating should be first applied in order to protect aluminium from the corrosive nature of the solution (Schlesinger and Paunovic, 2010).

2.1.1.1 Major Components of Copper Cyanide Baths and Their Uses

Copper cyanide: Copper cyanide has little or no solubility in water (URL4). However, if water contains alkaline metal cyanides (that are; NaCN or KCN), copper cyanide forms complexes that are soluble in water (Kanani, 2004) (Schlesinger and Paunovic, 2010). The complexation reactions are as follows (Kanani, 2004):

$$CuCN + 2\,NaCN \rightarrow Na_2[Cu(CN)_3]$$
$$CuCN + 2KCN \rightarrow K_2[Cu(CN)_3]$$
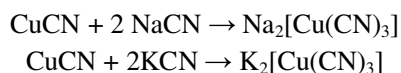
The salt formed (sodium or potassium salt of tricyanocuprate(I)) dissociates as (Kanani, 2004):

$$Na_2[Cu(CN)_3] \rightarrow 2Na^+ + [Cu(CN)_3]^- \rightarrow 2Na^+ + Cu^+ + (CN)^-$$
$$K_2[Cu(CN)_3] \rightarrow 2K^+ + [Cu(CN)_3]^{2-} \rightarrow 2K^+ + Cu^+ + 3(CN)^-$$
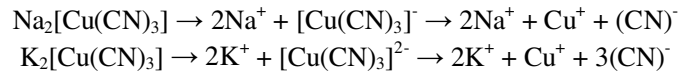
Free cyanide: Cyanide in plating baths is originating from copper cyanide and potassium cyanide (KCN) or sodium cyanide (NaCN) added to the solution. Free cyanide is an excess of KCN or NaCN added to the solution (Kanani, 2004).

The larger the ratio of free cyanide to metal concentration (Schlesinger and Paunovic, 2010):

- the more the corrosion of the anodes are,
- the more adherent deposits can be obtained,
- the more conductive the electrolytes are in strike and Rochelle copper cyanide solutions.

Carbonate: Sodium or potassium salt of carbonate is added as a buffer in copper cyanide electroplating solutions (Johnson and Harach, 2004). Cyanide decomposition and carbondioxide dissolved in the solution are the main reasons for accumulation of carbonate in the plating baths. This accumulation causes problems concerning the efficiency of the anode and the roughness of the deposited product and needs to be under control (Johnson and Harach, 2004; Schlesinger and Paunovic, 2010).

Rochelle salts (K/Na Tartarate): Rochelle salts are being used as complexing agents. Complexing agents bind to copper ions and prevents them to precipitate (Barauskas, 2011). There are still investigations on the effects of the complexing agents in electroplating baths. While studying the effects of a complexing agent in Ni-P plating over aluminium, Chang et al. (2011) pointed out that a complexing agent had effects over the rate of deposition and deposition quality. These effects are claimed to be due to complexed salts formed around the cathode (Schlesinger and Paunovic, 2010).

Sodium or potassium hydroxide: Sodium or potassium hydroxide is generally included in high-efficiency copper cyanide solutions in order to increase the conductivity and to enable the electrolyte to deposit copper more uniformly. It also helps the anode to corrode better. In copper cyanide strike and Rochelle electrolytes, sodium hydroxide is added at small quantities in case of pH adjustment (Schlesinger and Paunovic, 2010).

Additives: The additives are being used to improve the plating quality and efficiency in electroplating processes. There are numerous chemicals that are being used commercially. A general classification can be made as follows (URL5):

i. Carriers: Carriers are mostly composed of polyethers and polyoxyethers. They are being used for improving throwing power that is the ability to deposit metal uniformly on an irregularly shaped cathode.

ii. Levellers: Levellers are generally organic nitrogen compounds, amines, amides and surfactants. They are being used to achieve regular thickness throughout the shape of the cathode.

iii. Brighteners: Brighteners are sulfur containing compounds that function as controller for brightness and hardness.

iv. Wetting agents: Wetters are surfactants enabling reduction in surface tension.

The commercial formulations of these additives are not well-known and being kept as a trade secret. Holt (1946) had studied to derive leveller-brighteners from trimethyl benzyl ammonium hydroxide and trimethyl-C-decyl alpha betaine at different ratios and eventually patented his products at the end.

2.1.1.2 Types of Copper Cyanide Electroplating Baths

It's possible to classify copper cyanide electroplating baths as: strike, Rochelle and high efficiency. This classification is derived from the relative thicknesses obtained by plating as such: relatively thin deposits are obtained by copper cyanide strike solutions, mid-range thickness is achievable by Rochelle baths (Schlesinger and Paunovic, 2010). Typical formulations for cyanide solutions are given in Table 2.1.

Table 2.1 Copper cyanide solution formulations (Schlesinger and Paunovic, 2010).

Constituent	Strike Typical	Strike Limits	Rochelle Typical	Rochelle Limits	High Efficiency Typical	High Efficiency Limits
Copper cyanide (CuCN) (g/L)	22	15-30	26	19-45	75	49-127
Sodium cyanide (NaCN) or	33	23-48	35	26-68	102	62-154
Potassium cyanide (KCN) (g/L)	43	31-64	-		136	76-178
Sodium carbonate (Na_2CO_3) (g/L)	15	0-15	30	15-16		
Sodium hydroxide (NaOH) or	-	-	-		15	22-37
Potassium hydroxide (KOH) (g/L)	-	-	-		15	31-52
Rochelle Salt ($KNaC_4H_4O_6.4H_2O$) (g/L)	15	15	45	30-60	-	-
Operating parameters by analysis						
Copper (g/L)	16	11-21	18	13-32	55	34-89
Free Cyanide (g/L)	9	6-11	6	4-9	19	10-20
Operating conditions for typical copper cyanide solutions						
Temperature (°C)	40-60		55-75		60-80	
Cathode current density (A dm^{-2})	0.5-4		1.5-6.5		1-11	
Ratio of the anode to cathode area	3:1		2:1		3:2	
Agitation - cathode rod	Optional		Preferred		Either or both	
pH						

A case specific formulization of a copper cyanide strike bath is obtained from a commercial chemical supplier via personal e-mail communication and given in Table 2.2. This formulation is prepared excluding the additives.

Table 2.2 Copper cyanide strike solution formulation given by a commercial supplier.

Constituent	Concentration
Copper cyanide (CuCN) (g/L)	53
Potassium cyanide (KCN) (g/L)	103
Rochelle Salt ($KNaC_4H_4O_6.4H_2O$) (g/L)	15
Additive - carrier (mL/L)	4
Additive - brigthener (mL/L)	4

The brightness or dullness of plated copper using copper cyanide plating baths differs even in the same process. In many copper cyanide plating processes, brightness or dullness of the plated copper is not of very much importance (Schlesinger and Paunovic, 2010).

Copper cyanide strike solution is generally used to coat from 0.5 to 1 µm thick copper layer. It is also possible to plate up to 2.5 µm thickness. However, it is important to take into the consideration the fact that; if the process is followed by an acidic plating bath, more plating must be achieved. As an example, the plating on zinc die castings must be 3 or 5 times heavier than the strike solutions which is followed by an acid copper plating process (Schlesinger and Paunovic, 2010).

Copper deposition using a strike bath on a metal is applied as:

• a protective shield over the underlying metal from the other corrosive or damaging plating operations (MRI, 1996),
• a binding agent in order to overcome adherence problem between two metals (Gadag, 2009),
• an agent to enable complete coverage of the plating metal (Davis, 2001).

Striking a deposit is a very crucial step in a plating process which affects the complete performance in the product formation. The mishaps faced in the striking will also show up on the completed product (Davis, 2001).

Copper cyanide strike solutions are also advantageous in terms of its cleaning property (Utaka et al., 2007). Schlesinger et al. (2010) states that the difference between the cathode and anode efficiencies in these baths enables hydrogen gas formation in the bath and the hydrogen bubbles formed cleans the surface of the cathode while plating continues.

Copper cyanide Rochelle solutions with low metal concentrations are being used for striking purposes whereas higher concentrated ones are being used in plating processes up to 7.6 µm thickness (Joseph and Kundig, 1999).

Copper cyanide high efficiency solutions are much more concentrated than strike and Rochelle solutions. These baths have higher operating temperatures than the other two. The deposition rates are 3 to 5 times faster. By using high-efficiency copper cyanide baths, from 7.6 µm to 51 µm thickness of copper can be achieved. However, anti-pitting type of additives may need to be used in order to overcome pitting problem (formation of tiny, little pores) in the deposited metal. It is also advised that a copper cyanide strike solution of 1.3 µm thickness to be applied before high efficiency copper cyanide plating (Joseph and Kundig, 1999).

High efficiency copper cyanide baths do not offer any cleaning ability of the base metal to be plated. Therefore, more care should be taken in the pretreatment of the base metal compared to strike and Rochelle baths (Joseph and Kundig, 1999).

2.1.2   Copper Pyrophosphate Electroplating Bath

The efficiency offerred by copper pyrophosphate solutions is about 100% in terms of anode and cathode. The operating pHs are between 8.0 and 8.7; meaning that being very close to neutral pH. Neutral or near neutral pH ranges are not corrosive. Therefore, the material to be plated does not dissolve in the solution (Davis, 2001). These baths are more susceptible to contamination than cyanide baths. The operating of pyrophosphate baths cost more because of longer times required for plating. However, cyanide involving wastes originating from laboratories cost 1.50 $/L to dispose and non-cyanide ones have 75 ¢/L disposal costs (Dini and Steffani, 1996; USEPA/742/B-97/005, 1997).

Copper pyrophosphate baths have found application in (Schlesinger and Paunovic, 2010):

- electroforming in production of waveguides, paint spray masks, helical antenna, heat exchangers, molds for toy production,
- obtaining platings that are hard, high-strength and wear resistant in characteristics,
- depositing over steel and aluminium,
- replacing copper cyanide,
- forming an intermediate layer before plating bright nickel and chromium over zinc die castings,
- stopping case hardening for specific applications,
- plating the holes on printed wiring boards,
- deposition of copper on plastics.

2.1.2.1 Major Components of Copper Pyrophosphate Baths and Their Uses

Copper and Pyrophosphate: Potassium pyrophosphate salt is generally being preferred to increase the solubility of copper pyrophosphate in solution and to add in conductivity to the solution due to ion mobility of potassium (Davis, 2001; Schlesinger and Paunovic, 2010). Surplus pyrophosphate not only increases the conductivity of the solution but also aid in corrosion of the anodes (Davis, 2001)

Nitrate: Sodium or potassium salts of nitrate and nitrite and also nitric acid are being used as agents to increase applicable current density range (Wells, 1964).

Ammonia: Ammonia added to the copper pyrophosphate baths increase the brightness of the deposited metal and helps to control the pH of the solution. It also supports the corrosion of the anode. The stepwise addition of ammonia is usually preferable owing to the loss by vaporization. However, the amount added to the solution is important in terms of cuprous oxide (Cu_2O) formation which prevents adhesion between the base metal and the metal to be plated (Davis, 2001; Schlesinger and Paunovic, 2010).

Ortophosphate: Ortophosphate is not directly added to the solution, but is derived from pyrophosphate hydrolysis. Ortophosphate formation is increasing by increasing temperature, decreasing pH (less than 7) and increasing pyrophosphate concentration. It is an important agent to control in copper pyrophosphate plating baths from two different aspects: (1) it aids in corrosion of the anodes and buffers the solution up to and above 90 g/L, (2) it adversely affects the deposition quality and solution efficiency (Davis, 2001; Schlesinger and Paunovic, 2010).

Additives: The general classification of the additives in copper pyrophosphate baths is the same as for copper cyanide baths. To illustrate, Tech and Ogden (1978) used 2,5-dimercapto-1,3,4-thiadiazole as a levelling agent and a formulated brightener in their experiments with copper pyrophosphate electroplating baths. Dibasic organic acids such as lactic, tartaric, malic oxalic acids may be used as additives for supplying brightness to the plated copper (Bandes, 1945).

2.1.2.2 Types of Copper Pyrophosphate Electroplating Baths

Copper pyrophosphate electroplating baths are mainly strike and typical plating applications for general use. A special formulation for printed circuit board manufacturing is also given by Barauskas (2011) and shown in Table 2.3.

Table 2.3 Copper pyrophosphate solution formulations (Barauskas, 2011).

Constituent	Strike	Plating	Printed Circuits
Copper pyrophosphate ($Cu_2P_2O_7.3H_2O$) (g/L)	25-30	52.5-84.0	57.8-73.3
Potassium pyrophosphate ($K_4P_2O_7$) (g/L)	95.7-176.0	201.1-349.1	231.0-316.5
Potassium nitrate (KNO_3) (g/L)	1.5-3.0	3-6	8.2-15.8
Concentrated ammonium hydroxide (mL/L)	0.5-1.0	3.75-11.0	2.7-7.5
Operating parameters by analysis			
Copper metal (g/L)	9.0-10.7	18.8-30.0	20.7-26.2
Pyrophosphate (g/L)	63-107	131.6-225.0	150.0-204.4
P_2O_7/ Cu ratio	7:1 to 10:1	7.0:1 to 7.5:1	7.2:1-7.8:1
Operating conditions for typical copper pyrophosphate solutions			
Temperature (^oC)	22-30	43-60	49-54
Cathode current density (A dm^{-2})	0.6-1.5	1.0-8.0	2.5-6.0
Ratio of the anode to cathode area	2:1	2:1	2:1
Agitation	Mechanical or air	Mechanical or air	Mechanical or air
pH	8.0-8.5	8.0-8.7	8.0-8.4

Copper pyrophosphate baths do not have any cleaning properties as copper cyanide baths; therefore, the cleaning of the base metal is a very crucial step in electroplating processes. If pretreatment of the base metal is underestimated, the plating would result in unsuccessful plating in terms of adherence (Dennis and Such, 1993).

Copper pyrophosphate strike solutions are diluted pyrophosphate baths actually. To provide adhesion between the metal to be plated and deposited metal, a strike layer of copper pyrophosphate can be applied in spite of a cyanide one (Barauskas, 2011).

Copper pyrophosphate plating solutions are used to obtain much thicker copper deposits from pyrophosphate baths, a more concentrated solution is being used (Barauskas, 2011).

2.1.3 Toxicity Comparison Between Copper Cyanide and Copper Pyrophosphate Baths

Copper is a micronutrient which is important for several metabolic activities in humans. Toxicity of copper is not clearly identified, however, 2-3 mg/L uptake of copper with water in early ages causes damages in livers. Also, 0.07 mg/kg copper is related to gastrointestinal troubles (Georgopoulos et al., 2001).

Acute toxicity data (LD50 - lethal dose which causes the death of half of test animals) for copper cyanide is 50 mg/kg (intraperitoneal) for rats. In the same source copper pyrophosphate is mentioned to be a mineral added to the foods of animals and there are no dedication to its toxicity (Georgopoulos et al., 2001).

Potassium cyanide which is soluble in water has a LD50 value of 4 mg/kg for rats (intraperitoneal), which corresponds to 10 mg/kg oral intake. LD50 for humans is also given as 2.86 mg/kg for humans (oral) (Patnaik, 2007). Tetrapotassium pyrophosphate are also being used as a fertilizer when its composition is adjusted (Ciopec et al., 2006). In a study examining the toxicity of tetrapotassium pyrophosphate, 0, 250, 500 and 1000 mg/kg doses were applied to rats orally and no deaths were observed (Seo et al., 2011).

2.1.4   Waste Profile in Electroplating Industry

Even though surface treatment industry has been improved a lot in terms of waste management, an important number of industrial water pollution incidents is attributed to this sector. For ten years period, starting from 1992, France had 1.2% severe water pollution incidences originating from the industry in concern. It also needs to be emphasized that the waste generated has a destructive property in biologically mediated sewage treatment and aquatic environments. Moreover, these wastes are potential threats for drinking water resources (IPPC, 2006). Table 2.4 gives input materials and the corresponding potential waste composition in terms of air emissions, process wastewater and solid wastes. As a whole, air emissions from the process are usually a result of volatilization of materials used in the processes and mists of the chemicals. Wastewaters formed in the rinsing stages are the main component of the wastewater streams in electroplating baths, however, they can also be combined with other process wastewaters such as the ones from plating operations. Solid wastes are potentially a greater environmental concern, and they are generally formed when the solution and chemical become useless. For example, treatment of electroplating baths result in treatment sludges.

Table 2.4 Process material inputs and outputs (USEPA/310-R-95-007, 1995).

Process	Material Input	Air Emission	Process Wastewater	Solid Waste
Surface Preparation Solvent Degreasing and Emulsion, Alkaline, and Acid Cleaning	Solvents, emulsifying agents, alkalis, and acids	Solvents (associated with solvent degreasing and emulsion cleaning only)	Solvent, alkaline, and acid wastes	Ignitable wastes, solvent wastes, and still bottoms
Electroplating	Acid/alkaline solutions, heavy metal bearing solutions, and cyanide bearing solutions	Metal-ion-bearing mists and acid mists	Acid/alkaline, cyanide, and metal wastes	Metal and reactive wastes
Plating	Metals (e.g., salts), complexing agents, and alkalis	Metal-ion-bearing mists	Cyanide and metal wastes	Cyanide and metal wastes

As summarized in IPPC, Integrated Pollution Prevention and Control, (2006), from an environmental point of view electroplating, being a sub-category of surface treatment, has major concerns about water, energy and raw material consumption, solid and liquid waste generation, emissions of the facility (Table 2.5).

Table 2.5 Principle substances in concern in the surface finishing industry and medium affected (IPPC, 2006).

Process dependent - Principle substances of concern	Medium affected		
	Water	Soil	Air
Metals			
Zinc	√	√	
Copper	√	√	
Nickel	√	√	
Chromium	√	√	√
Lead	√	√	√
Cadmium	√	√	√
Non-metals			
Cyanides	√	√	√
Hypochlorite	√		√
AOX (absorbable organic halogens)	√	√	
Peroxides			
Surfactants			
Dispersing agents, emulsifiers, detergents, wetting agents (including nonyl and other alkyl phenyl ethoxylates (NP/NPEs), brightening agents, PFOS	√		
Complexing agents			
EDTA	√		
Tartarate, EDDS, NTA, gluconate, Quadrole	√		
Sodium dithionite	√		
Acids and alkalis			
Hydrochloric, nitric, phosphoric, sulphuric, hydrofluoric, acetic	√	√	√
Sodium and potassium hydroxides, lime	√	√	√
Other ions	√	√	
Solvents			
Trichloroethylene (TRI)	√	√	√
Tetrachloroethylene (PER)	√	√	√
Trichlorotrifluoroethane (CFC-113)	√	√	√
Methylene chloride	√	√	√
Gasses			
Chlorine			√
Dusts		√	√
Wastes	√	√	√

According to Toxic Release Inventory Database (TRI) created by the USEPA, discharges of copper, copper compounds and cyanide compounds from various metal fabricating and finishing facilities are given in Table 2.6 (USEPA/310-R-95-007, 1995). All emissions are given in pounds/year.

Table 2.6 Emissions in lbs/yr from related industries according to TRI (USEPA/310-R-95-007, 1995).

Chemical name	Number of facilities reporting the chemical	Air Fugitive	Air Point source	Water discharge	Land disposal
Copper	267	19,231	20,632	2,795	763
Copper compounds	93	4,912	6,028	1,398	256
Cyanide compounds	103	7,686	8,960	298	283

TRI also recorded the transfered amount of wastes from these facilities to a different facility (Table 2.7). These facilities may include a tranfer through pipes or sewers to a municipal wastewater treatment plant (MWTP). The other facilities may be a disposal, recycling, treatment or energy recovery facility.

Table 2.7 The amount of transfers from these facilities (USEPA/310-R-95-007, 1995)

Chemical name	Number of facilities reporting the chemical	MWTP discharges	Disposal	Recycling	Treatment	Energy Recovery
Copper	267	8,784	653,024	53,401,212	60,924	667
Copper compounds	93	13,826	341,003	11,781,033	205,196	7
Cyanide compounds	103	19,581	17,461	12,188	140,767	0

USEPA has introduced a tool called The Metal Finishing Facility Risk Screening (MFFRST) in order to estimate the air emissions from metal finishing facilities. Emissions calculated from copper cyanide strike and plating baths are given in Table 2.8 (USEPA/600/R-01/057, 2001)

Table 2.8 Calculated emissions for copper cyanide baths (USEPA/310-R-95-007, 1995)

Plating Operation	Chemical of concern	Emissions
Copper cyanide strike bath	Copper	2.3×10^{-02} mg/m^3
	Cyanide (CN)	3.3×10^{-02} mg/m^3
Copper cyanide plating bath	Copper	2.0×10^{-02} mg/m^3
	Cyanide (CN)	3.0×10^{-02} mg/m^3

Dash et al. (2009), also reported cyanide emissions from various industrial effluents which are given in Table 2.9.

Table 2.9 Cyanide emissions from various industrial effluents (Dash et al.,2009).

Effluent category	Cyanide (mg CN⁻/L)
Electroplating plants	0.03-0.27
Electroplating plants	0.01-14.24
Electroplating plants / PCB plants	3.0-59.0
Electroplating plants	3.6-6.6
Plating rinse	0.3-4
Plating rinse	32.5
Plating rinse	25
Plating rinse	60-80
Plating rinse	30-50
Plating rinse	1.4-256
Plating industries (rinsing waste)	1.4-256
Plating industries (plating bath)	4,000-100,000
Plating bath	30,000
Plating bath	45,000-100,000
Plating bath	
Brass	16,000-48,000
Bronze	40,000-50,000
Cadmium	20,000-67,000
Copper	15,000-67,000
Silver	12,000-60,000
Tin-zinc	40,000-50,000
Zinc	4,000-64,000

2.2 Pollution Prevention

Legal steps are being taken about pollution prevention issues by laws, regulations etc. in all over the world. However, more systematical approaches are presented by pollution prevention guidelines. These guidelines offer many strategies for reducing the waste generated to many industries. These guidelines are not a must, but, they are expected to be as such, because each and every day governments adopt new policies to encourage the pollution prevention issues.

U.S. EPA and European Commission Institute for Prospective Technological Studies (IPTS) are the leading institutions leading the pollution prevention studies. European Commission has published the Best Available Techniques (BAT) reference documents; BREFs and some reference documents (IPPC, 2006). These references are specific to the industries. Some of these documents have already adopted under both IPPC Directive (2008/1/EC) and the Industrial Emissions Directive (IED). Turkey is in the process of adopting pollution prevention as a national policy in conjuction with the studies held by the European Commission.

For many years the pollution control strategies have been developed essentially on end-of-pipe basis. In terms of end-of-pipe techniques, many treatment strategies and disposal options have been practiced so far. Rather than these strategies recent decade moves towards a more proactive approach, that is, pollution prevention strategies. This study is based on cleaner production strategies presented by pollution prevention guidelines (EPA/742/B-97/005, 1997 and IPPC, 2006) and implementation of the selected strategies on a laboratory scale production process.

2.2.1 Definition of Pollution Prevention

In 1990, Environmental Protection Agency (USEPA) announced pollution prevention as a national policy by the Pollution Prevention Act. The Act defined pollution prevention as any practice to reduce or eliminate pollutants entering the waste stream by (USEPA , 1990):

- improving efficiencies of raw material use, energy use, water use or any other resource use,
- conservation of natural resources.

The Act directly relate pollution prevention to source reduction. As a general approach; "source reduction" refers to the actions taken against the production of wastes in order to minimize wastes from entering into a waste stream. By definition; the activities that can be considered as pollution prevention (source reduction) strategies include (USEPA , 1990):

- modifications on equipments, technology, process or procedure,
- changes on products by renewal of formulation or design,
- material substitution,
- good housekeeping practices,
- regular maintenance,
- personnel training,
- inventory management.

USEPA does not term the actions taken after the waste is generated as pollution prevention measures (USEPA/600/R-92/088, 1992). Some examples of such actions that cannot be counted as pollution prevention measures are (USEPA/600/R-92/088, 1992):

- recycling off-site,
- treatment of waste,
- concentrating the waste or toxic/hazardous content to reduce volume,
- diluting to reduce toxicity or hazard,
- transfering to a different medium (e.g. removal of sulfur compunds in off-gas of a combustion process by scrubbers).

To sustain a more environmentally friendly aproach in the management of wastes, a hieararcial order is adapted all over the world. According to this hierarchy,

- wastes generated should be reduced or reused at source if feasible,
- if source reduction or reusing can not be applied, the wastes should be recycled or composted,
- if possible, wastes should be used for energy recovery,
- if none of the above can be applied, then the generated wastes should be treated.

Environmentally safe disposal or other waste handling options are the last and least desirable option in a waste management hierarchy (USEPA, 2012).

Pollution prevention issues are mainly related to the first priority of this hierarchial approach. While waste management is a general waste handling scheme, pollution prevention mainly focuses on reduction of waste source and reusing/recycling concepts.

2.2.2   Pollution Prevention Strategies For Electroplating Applications

Pollution prevention strategies are very much dependent on the process of the electroplating applications. As a fundamental approach, to decide on the right strategy to minimize the waste originating from the process, pollution prevention hierarchy is a perfect guide to set a starting point. Figure 2.2 is modified from shows Green and Nelson to show pollution prevention strategies in a hierarchial order (2007). Same source lists improved waste water treatment can be counted as a priority three concern. However, treatment of wastewater is not a pollution prevention application as defined in USEPA. Therefore, priority three concern is excluded from the Figure 2.2.

Priority One: Source Reduction
Material substitution
Bath-life extension
Drag-out reduction and recovery
Rinse water reduction

Priority Two: Recycling and Reuse
Reuse of spent baths
Reuse of rinse water
Bath/Rinse water recycling
Waste Segregation
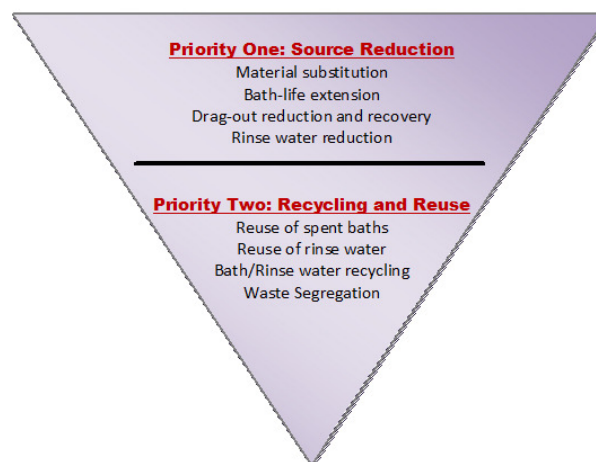
Figure 2.2 Hierarchy of pollution prevention strategies for electroplating industry.

This study focusses on source reduction strategies that are priority one concerns especially because production is in laboratory scale and not yet fully established. Source reduction strategies are eaiser to apply before complete establishment of a process since it would not require a large alteration of a process. The aim is to benefit from cleaner production strategies before large amounts of wastes are produced. In the following section source reduction pollution prevention strategies are explained in detail.

2.2.2.1 Source Reduction Strategies in a Electroplating Production Process

Pollution prevention issues in electroplating applications mainly have applications as:

- Input material changes
- Bath-life extension
- Drag-out reduction
- Drag-out recovery
- Rinse water reduction

Most of these practices are interrelated with each other. The following sections give these practices in detail.

i. Input material changes

The materials or chemicals used in the processes can be subtituted with high purity ones or less environmentally hazardous chemicals. These replacements may range from the complete reformulation of the baths or just substitution of the hazardous constituent in the bath formulation. Replacing tap water with distilled or deionized water, using high purity anodes during electroplating or substituting the hazardous chemicals with more environmentally friendly chemicals are examples of input material changes in electrochemical processing. The use of purer materials improves the efficiency of the process. However, not every substitution results in environmental benefits, so, it's crucial to investigate the environmental aspects of substitutions also (USEPA/742/B-97/005, 1997; USEPA-744-R-01-001, 2001).

Fist of all, water is the main component in the preparation of the electrolytes and the purity of water is a critical parameter to be taken into consideration, since it has effect on both the quality of the electroplating bath and the resultant product quality. Iron in water, for example, results in roughness over the plated surface when the pH of the bath is over 3.5 due to precipitation. Calcium and magnesium can also precipitate. Nodular deposits may arise from chloride contents higher than 0.44 g/L whereas pitting on the plated surface may be a result of organics found in the composition of electrolytes (Davis, 2001).

Instead of tap water, distilled or deionized water may be used in the process. Avoiding tap water use, eliminates building up of natural contaminants in plating operations (calcium, magnesium, iron, manganese, chlorine, carbonates, phosphates etc.) (USEPA/742/B-97/005, 1997). These contaminants for plating baths may result in decreased efficiency of rinsing and decreased recovery of drag-out and more frequent wasting of the plating bath (USEPA/742/B-97/005, 1997). Moreover, sludge production is less in the processes using deionized water instead of tap water (SBEAP, 2007). Another disadvantage of using low-quality of water is breaking down of some plating parts (RAC/CP, 2000).

Among distilled water and deionized water, deionized water is more advisible in preparing bath formulations (IAMS and WRATT, 1996). In addition, deionized water is mostly recommended qualified water type for electroplating processes in terms of reducing the waste (URL6). However, it may not always be economically feasible in large scale applications because tap or well water is much more cheaper than deionized or distilled water. Regional Activity Centre for Cleaner Production (RAC/CP) (2000) gives some examples of water quality class for specific electroplating steps:

- For alkaline baths and rinses, it is advised to use soft water.
- For hot baths, demineralized (or decarbonated) water is highly recommended.
- For final rinses, strictly controlled quality of water is needed in order not to have any stains or corrosion on the finished product.

Another material that can be replaced in the process is anode. Anodes used in electroplating may lead to contamination in the plating baths because of the impurities they have in their composition (USEPA/742/B-97/005, 1997). Generally, the more pure the anode is, the more adventageous it is and hence the more it is recommended (Davis, 2001). There are two main factors for this outcome: (1) anodes of less purity contaminate the baths and result in heavy sludges, (2) the roughness of the deposit obtained by electroplating is directly affected by the purity of the anodes (Davis, 2001). A disadvantage of higher purity anodes are their cost. They can cost more than the low purity anodes (USEPA/742/B-97/005, 1997). Sometimes low purity anodes are used on purpose. A good illustration for this is using phosphorized copper anodes. Phosphorized copper anodes are being used for only acid copper plating in order to reduce sludge and to promote anode corrosion (Schlesinger, 2001).

The replacement of hazardous chemicals with more environmentally friendly ones is one of the most important issue to apply in terms of pollution prevention in electroplating industry. Chemical substitution may result in a decrease in hazardous waste generation and lesser contribution of hazardous wastes in waste streams. In metal finishing industry, USEPA targeted four materials in order to reduce or eliminate wastes; these are chlorinated solvents, cadmium, cyanide and chromium (Cushnie, 1994). The surveys revealed that crucial steps have been taken so far in management of these four Cs in terms of either reduction or elimination in this industry (Cushnie, 1994).

In 1997, USEPA mentioned that cyanide was probably the most toxic component in electroplating processes. There are alternatives of non-cyanide baths for silver, cadmium, zinc, gold and copper (Ford, 1994). These applications commonly require reformulation of the electroplating bath composition. The non-cyanide alternatives for some electroplating processes are given in Table 2.10. However, these baths does not offer an absolute replacement for all processes. Each alternative has different characteristics like uniformity of the deposition, plating quality, plating efficiency, toxicity, stability and process design requirements. Further investigation is needed to be done for each specific electroplating process. In gold plating, for example, the applicability of alternatives for gold cyanide baths, that are gold sulfite and cobalt hardened gold plating, is still under examination (USEPA/742/B-97/005, 1997).

Table 2.10 Alternatives for Cyanide Including Electroplating Baths (USEPA/742/B-97/005, 1997).

Cyanide Including Plating Bath	Alternatives
Copper cyanide plating	Copper Alkaline Solution Copper Acid Sulfate Copper Fluoroborate Solution Copper Pyrophosphate Solution
Silver cyanide plating	Ammonium silver Amino or thio-complex silver Halide silver No free cyanide silver
Cadmium cyanide plating	Cadmium neutral or acid sulfate Cadmium acid fluoroborate Zinc-nickel alkaline Zinc-nickel acid Zinc-cobalt acid Zinc-cobalt alkaline Zinc-iron acid Tin-nickel acid or near neutral Tin-zinc acid, alkaline or neutral and so on
Zinc cyanide plating	Zinc alkaline Zinc acid chloride
Gold cyanide plating	Gold Sulfite Solution Cobalt-hardened Gold Solution

As well as the studies being carried on the alternatives found in the pollution prevention guidelines, new bath formulations also being tested. Ballesteros et. al. (2011) worked with a bath containing 0.1 M CuCl$_2$ (copper(II) chloride), 1.0 M KCl (potassium chloride) and 0.3 M KC$_4$H$_5$O$_6$ (potassium bitartarate) for non-cyanide alkaline copper electrodeposition on a glassy carbon electrode. Deposited copper was found to be homogeneously distributed (Ballesteros et al., 2011). In an another study, copper cyanide, sodium cyanide, sodium carbonate and tartarate containing copper cyanide plating solution is also compared with five different combinations of EDTA copper plating solutions including potassium citrate or potassium sodium tartarate as an additional complexing agent. As a result of the experiments, the use of EDTA electrolytes was promoted because of the strengths obtained in plating uniformity, current efficiency and decreasing voltage applied (Fu et al, 2012). In 1990, Kline obtained an electrolyte composed of copper acetate, an organophosphonate as a chealating agent, potassium carbonate as a buffer, potassium hydroxide to adjust pH and two additives to improve quality and adhesion of the deposit and patented this product as a substitute for alkaline copper cyanide plating solution. It is important to point out that the replacement of cyanide electroplating baths generally needs a change in the pretreatment of base metal to enable more throughly cleaning because of the lack in cyanide bath's cleaning ability (Noyes, 1993).

It is an unavoidable fact that new bath formulations are also needed to be tested further. For example, Yang et al. (2012) studied on non-cyanide gold electroplating using a complexing agent. They observed the effect of plating time and organic additives in a non-cyanide plating bath. The substitution concept is very much dependent on the process because electroplating has a wide application field and every plating work is case specific. However, some generalizations can be made according to properties of material to be plated, structural performances, applied current, desired quality of deposition etc. Chen et al. (2012) claimed that cyanide containing electrolytes are the preferable silver plating baths and they result in good plating in terms of sticking to the base metal, appearance and silver crystallization. However, they also pointed out the environmental concern about cyanide use. So, in their study they deposited silver over copper electrode using cyanide-free electrolyte and termed their plating as "successful" for the ability of silver adhesion to copper and the levelling ability of copper over silver. On the other hand, there are some cases that some substitutions are very successful and have applications for a long time. Gernon et. al. state that substitution of fluoroboric acids by methane sulfonic acids (MSA) in especially tin and lead containing electrolytes in electrochemical applications dated back more than 20 years (Gernon et al., 1999). The median lethal doses (LD$_{50}$) are quoted to be 1158 mg/kg (oral, rat) for MSA and 464-495 mg/kg (oral, rat) for fluoroboric acid. OSHA has also set permissible exposure limit (PEL) for hydrofluoric acid concentration of 2.5 mg/m^3 and fluoroboric acid containing electrochemical processes have the ability of producing HF. There is no associated PEL level for MSA set by OSHA. The waste generated in lead involving electroprocessing is mentioned as less toxic and easily manageable. It is biodegradable and acts as a natural component in sulfur cycle (Gernon et al., 1999). These factors enables to categorize MSA as a more environmentally friendly application. MSA application as an electrolyte has also been investigated in silver, nickel, copper, cadmium and zinc electroplating (Balaji and Pushpavanam, 2003).

ii. Bath-life extension

Monitoring the chemical composition and operating parameters of a plating bath offers an extended lifetime of the bath and a standart quality in the plating work. To be able to monitor the bath, critical parameters have to be decided at the very begining. Although there are recipes that describes how the baths are prepared and operated which are supplied by manufacturers of the chemicals, it is advised that parameters should be optimized according to the process of concern. In terms of chemical concentrations, optimization is needed because many chemical suppliers usually recommend the use of higher concentrations than necessary for an effective operation (USEPA/742/B-97/005, 1997). The reason underlying is to guarantee the end product's quality and to get highest yield from a bath (RAC/CP, 2000). On the other hand, the higher the concentration is, the higher the viscosity of it. If the viscosity is increased, more solution sticks onto the surface of the workpiece which then tend to leave the process while it is being withdrawn from the bath (Cushnie, 2009). The solution that sticks to the surface of the workpiece while leaving the bath is called drag-out whereas the solution coming from the previous process is called drag-in (IPPC, 2006). More concentration in the plating bath, therefore, leads to large and concentrated volume carried to the rinsing stages. Therefore, more water would be consumed at consequent rinsing stages; more fresh water is polluted (Cushnie, 2009). If inadequate rinsing is applied, the following baths would be contaminated, shortening the bath-life of other stages. As a result, more waste is generated.

One of the critical parameters apart from the chemical concentrations is the pH of the solution. pH should be maintained within the proper range in the bath. The importance of maintaining pH differs depending on the process. In alkaline cyanide processes, for example, the pH should be kept in the alkaline range, otherwise hydrogen cyanide evolves from the solution which is very toxic to humans (USEPA 530-R-94-037, 1994). On the other hand, copper pyrophosphate solutions are susceptible to excessive decomposition of pyrophosphate to orthophosphate at pHs lower than recommended. Also, the throwing power of the solution decreases at these pHs. At higher pHs anode efficiency is decreased in pyrophosphate baths (Davis, 2001). The pH change in the plating bath is a sign of either microbial contamination or impurity dependent accumulation (WSDoE, 2005).

The temperature is another critical parameter to be taken into the consideration while operating baths. RAC/CP (2000) recommends operating the electroplating baths at the highest temperature possible in order to increase its viscosity, but it is also mentioned that solution must not let to dry on the surface of the workpiece. While increasing the bath temperature, evaporation loss should not be underestimated.

After setting optimum limits for parameters, these should be held constant as much as possible. Monitoring the parameters and keeping the records of these data enables to have knowledge on what is missing in the bath, so just adjusting the component overcomes complete dumping of the bath, resulting in larger wastestreams and large amount of resource requirement. Therefore, the effects of each change in the parameter can be clearly identified, the adverse effects can be overcomed and the conditions can be properly maintained (WSDoE, 2005; IAMS and WRATT, 1996). The optimum parameters should be determined taking also into account the quality of the end product (RAC/CP, 2000).

Common inaccurate practice in the electroplating industry is to limit the monitoring of the baths to a single component such as alkalinity or conductivity, because this is deemed simpler. To illustrate, the way alkalinity used in quality determination is that when alkalinity is decreased in plating, fresh electrolyte is added. Therefore, degraded components are compensated, however, other components are accumulated in the bath. To be informative more components should be checked (Cushnie, 2009). These components should be monitored regularly and the records should be kept in order to make a clear log of the process.

Another application to extend life-time of the plating bath is the use of high purity chemicals. The additives can be degraded more easily in low quality solutions because of the impurities in the components used. Moreover, if the bath is open to bacterial attack, low quality solutions are more susceptible to biological contamination. Low quality metal working fluids decreases the resistivity against contamination (WSDoE, 2005).

Preventing contamination entering the bath is one of the major tasks to increase the lifespan of the plating bath in many large scale applications. Contamination problem mainly arises from racks, anodes, drag-in from previous operations, make-up water and/air. Racks may be abraded or salts may build up on racks which may eventually pollute the bath. Using higher purity materials (such as using demineralized or distilled water instead of tap water and more pure anodes etc.) help reduce contamination of baths by means of impurities they involve. Moreover, the workpiece needs to be cleaned throughly at the rinsing stage to overcome the drag-in contribution to the bath (Noyes, 1993).

Filtration is commonly applied in many electroplating shops to enable further use of the bath. Bhatgadde and Mahapatra (1998) used continuous filtration in order to filter the impurities caused by additive breakdown while plating in a copper pyrophosphate bath. Periodical or continuous filtering (generally through a 10 µm filter) significantly prolongs the life of a plating bath and decreases the sludge generated (Noyes, 1993). Fitration is also a reuse concept for electroplating baths.

iii. Drag-out reduction/recovery

Drag-out reduction or recovery enables less water consumption in the rinsing process. Moreover, due to the preservation of the more chemicals in the bath, less raw materials are consumed. In terms of waste management, treatment or disposal costs are also decreased with the help of drag-out reduction (Noyes, 1993).

Drag-out reduction applications have no meaning if the impurities in the solution are not removed. The impurities in the solution causes sludge generation, reduction in deposition quality, shortening the lifetime of the bath resulting in frequent discarding; therefore, these factors would render the benefits obtained by drag-out reduction useless (Noyes, 1993).

Drag-out quantity is related to the following factors (Noyes, 1993):

- time to withdraw the plated product and time allowed to drain,
- surface tension of the bath,
- viscosity of the solution,
- shape and area of the workpiece.

There are several applications to reduce drag-out (Babu et al., 2009):

- slowly removing the workpiece from the process bath and waiting for a while to enable drainage,
- using less concentrated plating baths,
- operating at higher temperatures,
- using wetting agents,
- using a structure to enable drainage (like drain boards),
- using barrels with larger holes,
- spinning the workpiece above the process bath or appropriate positioning of the workpiece.

Withdrawal speed of a workpiece and time to enable draining back to the solution effects the quantity of drag-out being carried to the other processes. When a workpiece is being taken out of the solution, the rate should be slow. To enable drainage, the workpiece should be also hold over the solution for a while, thirty seconds usually, but, if the solution tends to dry on the surface of the workpiece, the time needs to be shortened (approximately 10 seconds) for not letting the solution go dry (Noyes, 1993). Even two or three seconds letting for drainage enable 50 percent drag-out reduction (URL7).

As mentioned in the "Bath-life extension" section minimizing the chemical concentration helps to reduce the amount and denseness of the drag-out, leading to lesser amount of waste generated. Owing to reduction in viscosity and surface tension of the solution, decreasing the temperature also helps to decrease drag-out (Noyes, 1993). However, there are some disadvantages of increasing the temperature, like (Noyes, 1993):

- cyanides breakdown at higher temperatures leading to excessive carbonate formation,
- energy requirement increases,
- exposure to gases evolved increases due to evaporation,
- more make-up water is needed, thus, susceptibility to contamination increases.

An additive, wetting agent, use is also advised to decrease the drag-out, hence waste generated. A wetting agent is an additive used to decrease the surface tension of the fluids, usually a surfactant. The use of wetters is reported to decrease the drag-out by 50%. However, some platers avoid the use of wetters because of the scum produced over the bath and this scum makes the workpiece unclean (RAC/CP, 2000). Since decomposition pathways and reactions involved in additive including baths are not exact for all additives, it is not very convenient to state that the addivites prolong the lifetime of a electroplating bath. USEPA states that metals present in tap waters together with these additives may lead to contamination in plating baths, thus, additivites may be a lifetime shortener (USEPA/742/B-97/005, 1997).

For recovery of drag-out, a drain board between processes can be placed in order to direct the seeping solution back into the process bath while the workpiece is taken out from the solution. An empty tank can also be installed between plating and rinsing to collect the drainage. Furthermore, if a pre-rinsing stage is employed, water contaminated with drag-out can be used as make-up water for the plating bath (URL8).

iv. Rinse water reduction

Rinsing is applied after all steps taken in the process to clean chemicals left over the workpiece. Simple rinsing is applied by withdrawing the workpiece from the electroplating bath and washing it in another container. Water used is directly discharged therefore consuming large amounts of water (Figure 2.3).
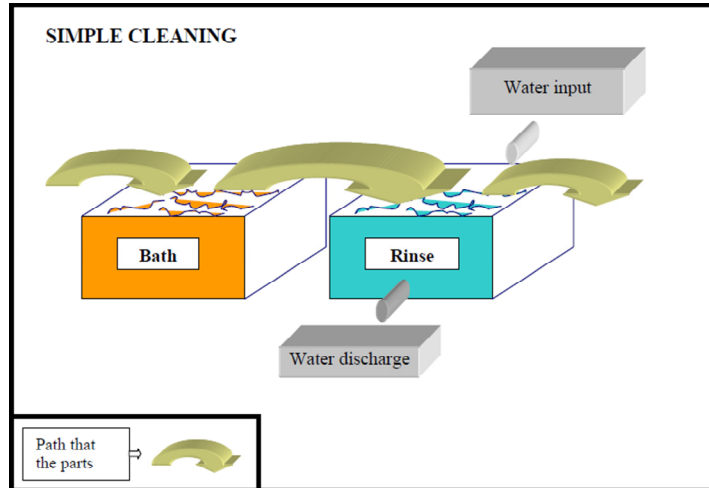
Figure 2.3 Simple rinsing diagram (RAC/CP, 2000).

There are several methods for reducing the amount of rinse water consumed for large scale applications. One opportunity is involving multiple rinsing stages such as parallel multiple rinsing and multiple cascade rinsing. In parallel multiple rinsing (Figure 2.4), workpiece is rinsed in the tanks that are designed in parallel. Water is supplied to both of the tanks and discharged directly. By adjusting the flow, significant reductions can be achieved (RAC/CP, 2000).
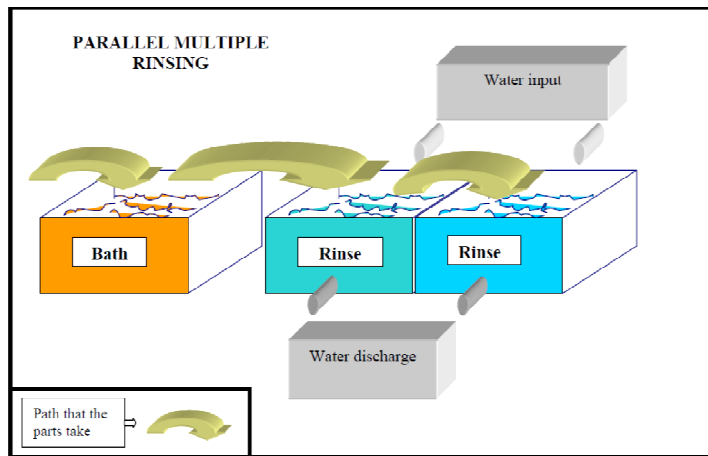
Figure 2.4 Parallel rinsing diagram (RAC/CP, 2000).

Multiple cascade system is a highly advised sytem. However, a large space is required to install multiple rinsing baths. Water input to the rinsing system is from the last rinsing tank and it reaches to the first tank by overflowing from each rinsing tank and leaves the system from the first tank. Workpiece enters from the first tank and leaves rinsing at the final tank (Figure 2.5).
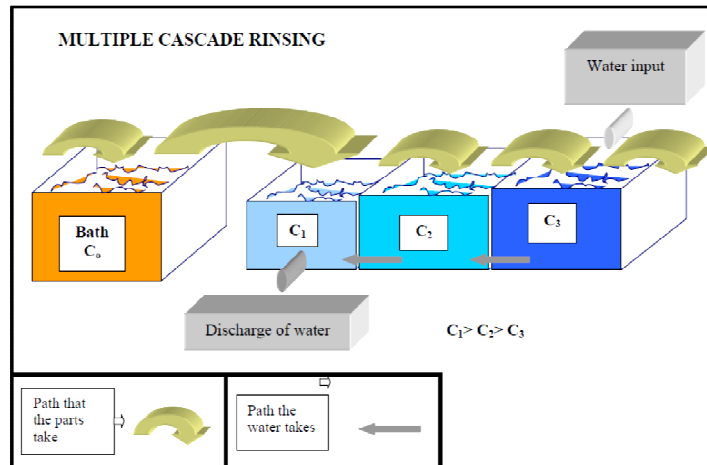
Figure 2.5 Multiple cascade rinsing diagram (RAC/CP, 2000).

In sealed recovery rinsing, another strategy for rinsing operations, tank is filled with water, some rinsing is applied and tank is then emptied. This rinsing water can be used as a bath make-up to account for evaporation loss after hot plating applications. In plating at room temperature, workpiece can be dipped into the rinsing tank which is located after the plating process, and then the plating bath. After workpiece is plated, it is rinsed in the same solution. Such an application enables the partial recovery of bath constitutents from the rinsing operation and called eco-rinsing (RAC/CP, 2000). This type of rinsing strategy can enable about 80% recovery (USEPA/742/B-97/005, 1997). In Figure 2.6, schematic diagram of eco-rinsing is presented (RAC/CP, 2000).
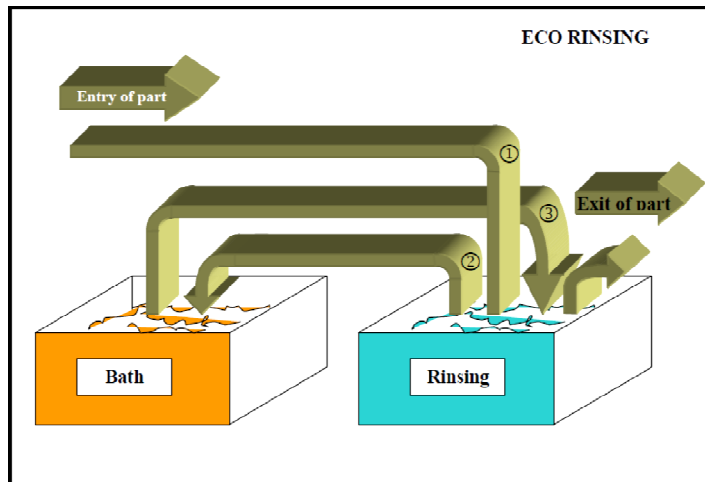
Figure 2.6 Eco-rinsing diagram (RAC/CP, 2000).

By applying spray or fog rinsing systems over the plating baths can reduce water consumption by 10-25%. However, it can not be applied to all workpieces due to required efficiency of rinsing operations which is very dependent on the workpiece geometry (USEPA/742/B-97/005, 1997).

The efficiency of rinsing can also be improved by several applications. These applications can be optimization of time required to rinse and providing agitation in rinsing. In a case study, USEPA states that a company greatly reduced the amount of water consumed by manually adjusting these two parameters (USEPA/742/B-97/005, 1997).

The measures of rinsing operations can be taken after determination of main operations, but, before the establishment of a large scale production process to gain profit from these measures as much as possible. Since it may require more space for rinsing bath installation, rinsing opportunities should be taken into consideration during process design.

2.2.2.2 Pollution Prevention Applications

According to a query made in TRI Pollution Prevention search engine (URL9), there are 52 facilities that reported their pollution prevention applications in terms of cyanide compounds in "Electroplating, Plating, Polishing, Anodizing and Coloring" category. The records are in between the years 2005 and 2012. Totally, 70 applications were created for pollution prevention about cyanide compounds. Codes pollution prevention applications in the system and the corresponding applications between 2005 and 2012 are given in Figure 2.7.

■ W13: Improved maintenance scheduling, recordkeeping, or procedures
■ W14: Changed production schedule to minimize equipment and feedstock changeovers
■ W15: Introduced an in-line product quality monitoring or other process analysis syste
■ W19: Other changes in operating practices
■ W32: Improved procedures for loading, unloading, and transfer operations
■ W33: Installed overflow alarms or automatic shutoff valves
■ W36 : Implemented inspection or monitoring program of potential spill or leak sources
■ W42: Substituted raw materials
■ W52: Modified equipment, layout, or piping
■ W53: Use of a differant process catalyst
■ W58: Other process modifications
■ W59 : Modified stripping/cleaning equipment
■ W64: Improved draining procedures
■ W67: Improved rinse equipment design
■ W89:Other product modifications

Figure 2.7 Pollution prevention applications between 2005 and 2012 in U. S (out of 70).

The majority of pollution prevention applications is about improving maintenance scheduling, record keeping or procedures. Process modifications and changes in operating practices are among the ones that are commonly be applied in order to reduce the waste. Cyanide substitution with a non-cyanide alternative is to be coded as W42 which indicates substituted raw materials. Three applications out of seventy is accounted for raw material substitution which is most probably the cyanide substitution case (2 of them clearly stated cyanide substitution).

CHAPTER 3

MATERIALS AND METHODS

In this study, copper plating was investigated from two main perspectives; the quality of the product and the change in bath composition. The outputs were evaluated from the pollution prevention point of view.

Figure 3.1 shows the flowchart of processes and analysis in context of this study that are applied to both cyanide and pyrophosphate products or bath samples. As the figure indicates, copper strike electroplating has two major components: (1) metal plated (2) plating bath. The metal to be plated is selected as aluminium because it is an electroforming application. Aluminium metal is polished and pretreated to remove dusts, oil, grease and oxides from the surface of the aluminium. As a result copper deposition on aluminium is enabled in copper strike electroplating bath. At the end of the copper deposition, the product is tested in terms of quality. Initially, a visual inspection of the product is necessary. Relying on the field of application of the finished product (copper strike application is the initial step taken for the finished product) reflectivities are of greatest concern and they are expected to be as high as possible. Due to the fact that there is a correlation between reflectivities and roughness measurements, the latter was also done on the products to understand whether it is satisfactory to have only roughness measurements despite complicated reflectivity measurements. Scanning electron microscope (SEM) imaging is taken to avoid any misleading structure forming in the early stages of the plating. All measurements related to the product quality are given to provide as much information as possible to be able to replace the bath or reduce the use of cyanide.

The second component of the copper strike electroplating is the bath. The bath formulizations are generally given by a chemical manufacturer and most of the facilities in the industry applies any of those recipes given. However, there are other formulizations present in literature. The evaluations need to be done depending on the processes and the baths need to be prepared according to the exact formulization of the process in concern. Filtration is an application before plating which should not be underestimated. During plating or after plating, bath component analysis is done to control the components of the bath, so that the life-time of the bath can be extended by regular adjustments depending on the problematic component. pH, conductivity, refractive index, voltage and chemical concentrations (copper, cyanide, Rochelle and carbonate for copper cyanide strike bath; copper and pyrophosphate for copper pyrophosphate strike bath) are the parameters of concern to indicate any change in the composition of the bath. To estimate the measurable concentrations in the bath, titration analysis were used which is one of the most informative and most practical analyses that can be performed in electroplating processes.
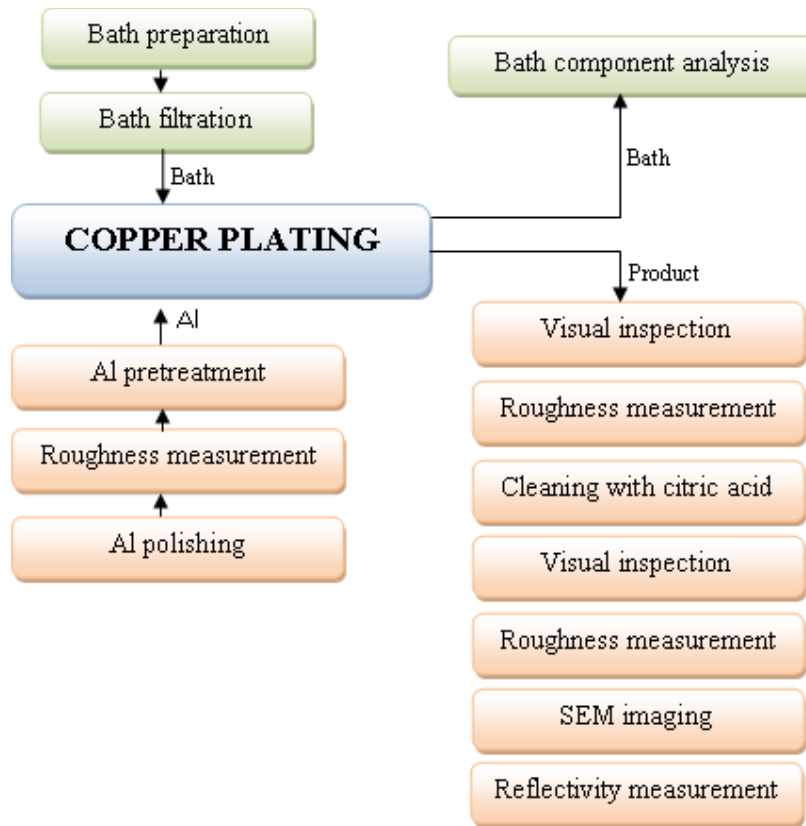
Figure 3.1 Flowchart of processes and analysis in context of this study.

3.1 Aluminium Handling

One of the most troublesome plating options is plating on aluminium metal. The reasons behind are very rapid oxidation of aluminium and the ability of aluminium to melt in baths that are either acidic or alkaline. Therefore, chemical reactions that are not desirable can take place in electroplating baths (Palanna, 2009). Oxides or any other undesirable reactants probably decreases adherence between aluminium and the metal to be plated. It is obvious that even oxides are a major factor to prevent a good deposition; therefore, aluminium should be thoroughly cleaned prior to any plating operation. In order to overcome these problems pretreatment of aluminium, which consists of several steps, is required. The main aim of the pretreatment is to cover aluminium metal with zinc so that it would avoid interacting with oxygen and other acidic/alkaline mediums. This zinc layer would then perform ion exchange with copper inside the electroplating bath (Palanna, 2009).

Aluminium samples were made ready to be pretreated using metallographic specimen preparation techniques in the laboratories of a private company. 7075 grade aluminium samples were first polished with colloidal silica abrasives with an average size of 1 micrometer.

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After polishing, alkaline-acidic cleaning and zincating are mainly applied pretreatment steps for preparation of polished aluminium before plating and the detailed steps taken are as follows (ASTM, 2011):

1. Washing aluminium parts with hot water and soap,
2. Rinsing with water,
3. Ultrasonic cleaning for approximately 3 min in acetone,
4. Rinsing with water,
5. Applying 50 g/L sodium hydroxide (NaOH) solution at 50°C approximately from 30 seconds to 1 minute (until full-gassing occurs),
6. Rinsing with water,
7. Acid cleaning (I) approximately for 15 seconds in 75% nitric acid (HNO_3 - density: 1.4 g/mL) and 25% hydrofluoric acid (HF - density: 1.16 g/mL),
8. Rinsing with water,
9. Submerging in zincate solution which is composed of 525 g/L sodium hydroxide (NaOH) and 100 g/L zinc oxide (ZnO) for 45 seconds. In this step, a thin zinc layer is formed by the removal of oxides over the aluminium surface.
10. Rinsing with water,
11. Acid cleaning (II) approximately for 1 minute in 50 % nitric acid,
12. Rinsing with water,
13. Zincating in the solution identical to the one in step 9 for approximately 30 seconds,
14. Rinsing with water.

In each rinsing stage, clean deionized water was used to avoid any other interaction that will affect bath performance. Resting the workpiece in deionized or distilled water is not recommended, because the zinc layer dissassociates back into the water. Therefore, after aluminium pretreatment workpieces are immediately used in the next step, that is copper deposition.

From the pollution prevention point of view, there are two aspects. First one is that, the adherence of copper on the aluminium is very much dependent on the pretreatment phase. So, if the pretreatment is not effective enough, the quality of the plating may be reduced resulting in more rejected parts and increasing total solid waste amount. Secondly, if the cleaning of the aluminium surface is not very much successful, the dirt on the aluminium may enter to the plating bath, decreasing the life-time of the bath. Therefore, more frequent treatment or disposal of the bath may be required leading to more contribution to hazardous waste streams.

3.2 Product Quality Oriented Experiments

The main objective of this setup was to compare several copper strike applications in terms of the quality of products.

Most of the industrial practices are being performed by a recipe supplied from a chemical manufacturer. This was also how the laboratory works related to this study was started. The starting point of conducting product quality oriented experiments was to decrease or completely eliminate the cyanide consumption at the very beginning, before full establishment of a copper strike electroplating process. If a satisfactory product quality could be achieved with different bath formulations other than the recipe of a commercial brand, then the chemical consumption would be reduced, thus the hazardous content of the waste streams would be also be decreased. Less chemical consumption would also result in less treatment or disposal costs. Moreover, if cyanide baths could be replaced with a non-cyanide alternative, a toxic component would be fully eliminated. Therefore, hazardous waste generation from laboratory works would be decreased.

3.2.1   Chemical Compositions of Electroplating Baths

Five different formulations were used in preparation of electroplating baths to apply a strike layer onto an aluminium metal, that are;

BATH A -   Commercial brand's case specific copper cyanide strike bath
BATH B -   Copper cyanide strike solution given by Schlesinger and Paunovic (2010)
BATH C -   Copper cyanide strike solution with sodium carbonate addition given by Schlesinger and Paunovic (2010)
BATH D -   Copper pyrophosphate strike solution formulated with lower limits given by Barauskas (2011)
BATH E -   Copper pyrophosphate strike solution formulated with upper limits given by Barauskas (2011)

Table 3.1 gives the concentrations for bath formulations in terms of purity of the chemicals used.

Table 3.1 Composition of electroplating baths in product quality oriented experiments.

BATH	Component		Concentrations given in formulations	Purity (%)	Concentrations used
A	Copper cyanide	CuCN	53.00 g/L	99.70	53.16 g/L
	Potassium cyanide	KCN	103.00 g/L	99.25	103.78 g/L
	Rochelle	$KNaC_4H_4O_6.4H_2O$	15.00 g/L	100.00	15.00 g/L
B	Copper cyanide	CuCN	22.00 g/L	99.70	22.07 g/L
	Potassium cyanide	KCN	43.00 g/L	99.25	43.32 g/L
	Rochelle	$KNaC_4H_4O_6.4H_2O$	15.00 g/L	100.00	15.00 g/L
C	Copper cyanide	CuCN	22.00 g/L	99.70	22.07 g/L
	Potassium cyanide	KCN	43.00 g/L	99.25	43.32 g/L
	Rochelle	$KNaC_4H_4O_6.4H_2O$	15.00 g/L	100.00	15.00 g/L
	Sodium karbonate	Na_2CO_3	15.00 g/L	100.00	15.00 g/L
D	Copper pyrophosphate trihydrate	$Cu_2P_2O_7.3H_2O$	25.00 g/L	100.00	25.00 g/L
	Potassium pyrophosphate	$K_4P_2O_7$	95.70 g/L	96.00	99.69 g/L
	Potassium nitrate	KNO_3	1.50 g/L	100.00	1.50 g/L
	Ammonium hydroxide	NH_3	0.50 mL/L	25.00	0.60 mL/L
E	Copper pyrophosphate trihydrate	$Cu_2P_2O_7.3H_2O$	30.00 g/L	100.00	30.00 g/L
	Potassium pyrophosphate	$K_4P_2O_7$	176.00 g/L	96.00	183.33 g/L
	Potassium nitrate	KNO_3	3.00 g/L	100.00	3.00 g/L
	Ammonium hydroxide	NH_3	1.0 mL/L	25.00	1.20 mL/L

For making up the baths, deionized water was heated up to 40-50°C. For copper cyanide bath make-up, Rochelle salt, potassium cyanide and copper cyanide is dissolved in deionized water in given order. For copper pyrophosphate bath preparation, potassium nitrate, potassium pyrophosphate, copper pyrophosphate and ammonia solution is mixed in deionized water.

2000 mL of bath solutions were prepared for each formulization (A, B, C, D and E). These baths were filtered through 125 mm Whatman filter. 2000 mL baths were separated into three 600 mL baths to be used in low, medium and high current density runs. The remaining 200 mL were used for bath composition analysis.

3.2.2 Operating Parameters and Calculations

In order to strike a copper deposit onto aluminium, current density and the time required to plate needs to be calculated. Faraday's law is used to calculate both (Askeland et al., 2011).

$$W = \frac{m.I.t}{n.F} \tag{1}$$

W : deposited weight (g)

W = volume deposited (V, cm^3) x density of copper (ϱ, 8.94 g/cm^3)

n   : valence of dissolved metal in solution (eqv/mole)

    for copper cyanide n=1

    for copper pyrophosphate n=2

F   : Faraday's constant = 96485 A.sec

m   : molecular weight of copper (63.546 g)

I   : current (A)

t   : time required to plate (sec)

Using Farady's law time versus current density equations to strike a deposit of 2 µm thick (theoretically) copper are derived as follows:

$$time = \frac{W.n.F}{m.I} = \frac{V.\varrho.\, N.F}{m.I} \tag{2}$$

$$time = \frac{area(cm^2) x plating\ thickness(\mu m)\ x10^{-3}(cm/\mu m)\ x8.94(g/cm^3) x n x 96485(A.sec)}{63.546\ (g)\ x\ I\ (mA)\ x\ 0.001\ (A/mA)} \tag{3}$$

$$time = \frac{1357.40\ x\ area\ (cm^2)\ x\ plating\ thickness\ (\mu m)\ x\ n}{I\ (mA)} \tag{4}$$

$$time = \frac{1357.40\ x\ area\ (cm^2)\ x\ plating\ thickness\ (\mu m)\ x\ n}{Current\ density\ (mA/cm^2)\ x\ area\ (cm^2)} \tag{5}$$

$$time = \frac{1357.40\ x\ plating\ thickness\ (\mu m)\ x\ n}{Current\ density\ (mA/cm^2)} \tag{6}$$

For copper cyanide valence is 1. So, the equation becomes;

$$time = \frac{1357.40\ x\ plating\ thickness\ (\mu m)}{Current\ density\ (mA/cm^2)} \tag{7}$$

Strike deposits are generally offered to plate up to 2.5 µm thicknesses. The theoretical thickness of copper is accepted as 2 µm for all deposits obtained in these sets, therefore;

$$\text{time} = \frac{1357.40 \times 2 \ (\mu m)}{\text{Current density (mA/cm}^2)} \tag{8}$$

$$\boxed{\text{time} = \frac{2714.80}{\text{Current density (mA/cm}^2)}} \tag{9}$$

Aluminium parts to be plated are 3 cm in diameter, thus, the surface area to plate are 7.07 cm² each. The current densities were applied according to the ranges given in sources as low, medium and high current density to be comparable. Time requied to plate 2 µm copper layer were calculated and given in Table 3.2.

Table 3.2 Operating parameters calculated for copper cyanide strike baths.

BATH	Exp No	Current Densities (mA/cm²)		Plating Area (cm²)	Current Applied (mA)	Time to Plate
A	1	Low	10.0	7.07	71	4 min 32 sec
	2	Medium	35.0	7.07	247	1 min 18 sec
	3	High	60.0	7.07	424	45 sec
B	4	Low	5.0	7.07	35	9 min 3 sec
	5	Medium	22.5	7.07	159	2 min 1 sec
	6	High	40.0	7.07	283	1 min 8 sec
C	7	Low	5.0	7.07	35	9 min 3 sec
	8	Medium	22.5	7.07	159	2 min 1 sec
	9	High	40.0	7.07	283	1 min 8 sec

For copper pyrophosphate valence is two. The equation for copper pyrophosphate is then;

$$\text{time} = \frac{1357.40 \times \text{plating thickness (}\mu m) \times 2}{\text{Current density (mA/cm}^2)} \tag{10}$$

Theoretically plating 2 µm copper over aluminium;

$$\text{time} = \frac{2714.8 \times 2 \ (\mu m)}{\text{Current density (mA/cm}^2)} \tag{11}$$

$$\boxed{\text{time} = \frac{5429.6}{\text{Current density (mA/cm}^2)}} \tag{12}$$

The surface area to plate was the same as for copper cyanide strike baths, that is 7.07 cm². Depositions were done under three current densities; low, medium and high. Results of calculations are given in Table 3.3.

Table 3.3 Operating parameters calculated for copper pyrophosphate strike baths.

BATH	Exp No	Current Densities (mA/cm^2)		Plating Area (cm^2)	Current Applied (mA)	Time to Plate
D	10	Low	6.0	7.07	42	15 min 5 sec
	11	Medium	10.5	7.07	74	8 min 37 sec
	12	High	15.0	7.07	106	6 min 2 sec
E	13	Low	6.0	7.07	42	15 min 5 sec
	14	Medium	10.5	7.07	74	8 min 37 sec
	15	High	15.0	7.07	106	6 min 2 sec

After copper layers were deposited on polished aluminium samples, product quality was tested. In addition, even if the main scope of this setup is not to identify the changes in bath parameters, bath parameters were also analyzed.

3.2.3   Product Quality Determination

Product quality was tested by visual inspection, measurement of roughness and reflectivity, as well as scanning electron microscope (SEM) imaging.

3.2.3.1 Visual Inspection

First decision of deposited coppers on polished aluminium metal was done by visual inpection. Bubble forming, brightness of plated copper, presence of any peeling or any defect, etc were evaluated and photographs were taken for further evaluation.

3.2.3.2 Roughness

Roughnesses of samples were measured with Mitutoyo Surftest SJ.401 device present in METU Department of Metallurgical and Materials Engineering laboratories. In order to measure roughnesses, two measures are taken perpendicularly for each sample with 0.5mm/s speed for 1.5 cm length and averages of these two measurements were taken to determine the average roughness of a single workpiece.

3.2.3.3 Scanning Electron Microscope (SEM) Imaging

SEM images of samples were taken with FEI Nova Nano SEM 430 device present in METU Department of Metallurgical and Materials Engineering laboratories . Resolution of the device is 1.8 nm and 1.4 nm in low and high vacuum modes, respectively.

3.2.3.4 Reflectivity

Perkin Elmer-Lambda 950 UV/VIS spectrophotometer in the laboratories of a private company was used for specular reflectance measurement. By applying different wavelengths in the range of 900 nm and 2200 nm, 130 measurements were recorded for each sample. In order to measure UV/VIS integrating sphere values Perkin Elmer 150 mm integrating sphere was used in the same equipment. Under 129 wavelengths 129 measurements were taken for each sample between the interval of 900 nm and 2190 nm for integrating sphere measurements.

Fourier transform infrared spectroscopy (FTIR) specular reflectivity measurements were performed using a Perkin Elmer-Frontier Optica FTIR in the laboratories of a private company. FTIR measurements were performed between the 2000 nm and 16000 nm wavelength interval. 4375 reflectivity values were obtained for each sample.

3.3 Bath Composition Oriented Experiments

The main objective of this setup was to determine the changes in the composition of the two selected baths; one cyanide and one pyrophosphate bath; during four hour long plating operation. Tracking the bath parameters is essential in terms of lengthening the lifetime of the bath. If the bath is compensated for missing components, then the lifetime is extended, therefore, less amount of bath is discarded or treated reducing the amount of hazardous waste generation.

3.3.1 Chemical Compositions of Electroplating Baths

In the beginning, two strike baths were selected; one among copper cyanide strikes; Bath B and the other from copper pyrophosphate strikes; Bath D. Therefore, the baths with lower chemical concentrations would have a chance to be compared in terms of their performances (Table 3.4).

Table 3.4 Electroplating bath compositions prepared for monitoring baths.

BATH	Component		Concentration given in formulations	Purity (%)	Actual concentration used
B	Copper cyanide	CuCN	22.00 g/L	99.70	22.07 g/L
	Potassium cyanide	KCN	43.00 g/L	99.25	43.32 g/L
	Rochelle	$KNaC_4H_4O_6.4H_2O$	15.00 g/L	100.00	15.00 g/L
D	Copper pyrophosphate trihydrate	$Cu_2P_2O_7.3H_2O$	25.00 g/L	100.00	25.00 g/L
	Potassium pyrophosphate	$K_4P_2O_7$	95.70 g/L	96.00	99.69 g/L
	Potassium nitrate	KNO_3	1.50 g/L	100.00	1.50 g/L
	Ammonium hydroxide	NH_3	0.50 mL/L	25.00	0.60 mL/L

3.3.2   Operating Parameters and Calculations

Two baths (each having a volume of 1825 mL) were operated for 4 hours and every thirty minutes 75 mL sample is taken for analysis of components. This way, no more than 30% of the total volume of bath was used in sampling and analysis during plating. Cyanide bath was operated between 50-55°C. All measurements related with cyanide bath and pyrophosphate bath were done at room temperature which is around 26°C. The current densities applied were decided according to the results of the product quality oriented experiments. It was observed that lowest voltage variances had shown up at the lowest current densities. Therefore, use of lowest current densities that are applicable was beneficial in terms of minimizing the effect of large voltage variances.

The theoretical thicknesses expected at the end of 4 hours can be calculated from the derived equations for copper cyanide and copper pyrophosphate baths as given in Section 3.2.2.

For copper cyanide bath:

$$\text{time} = \frac{1357.40 \text{ x plating thickness } (\mu m)}{\text{Current density } (mA/cm^2)} \tag{13}$$

$$\text{plating thickness } (\mu m) = \frac{\text{time x Current density } (mA/cm^2)}{1357.40} \tag{14}$$

For copper pyrophosphate bath:

$$\text{time} = \frac{2714.8 \text{ x plating thickness } (\mu m)}{\text{Current density } (mA/cm^2)} \tag{15}$$

$$\text{plating thickness } (\mu m) = \frac{\text{time x Current density } (mA/cm^2)}{2714.8} \tag{16}$$

Theoretical thicknesses were calculated using the equations given above and results are presented in Table 3.5.

Table 3.5 Operating parameters for extended plating.

BATH	Current Densities	Plating Area	Current Applied	Time to Plate	Theoretical Thickness (μm)
B	5.0 mA/cm^2	7.07 cm^2	35 mA	4 h	53.04
D	6.0 mA/cm^2	7.07 cm^2	42 mA	4 h	31.83

Each sample taken was analyzed to determine parameter changes throughout the four-hour duration of both cyanide and pyrophosphate baths. The analyses of product quality were also performed additionally.

3.3.3 Parameters Measured For Plating Bath Composition

Plating Electronic pe86CB-20-5-25-S/GD pulse reverse power supply was used for supplying electrical current and voltages were read from the related screen of this equipment. Operating range for power supply is between 0 and 20 volts. Maximum current supplied in direct current is 5 A and in pulse reverse 25 A.

Portable Oakton 300 series pH meter and Hach HQ 40d conductivity meter were used in pH and conductivity measurements.

Concentration measurements are most commonly and practically done by measuring refractive index or by titration analysis (NEWMOA, 2001). 0-90 brix % hand-type refractometer was used in measuring refractive index. This index gives an idea about the concentration change in fluids if a correlation between composition and refractive index can be held (IAMS, 1995). Titration analysis procedures are given in sections 3.3.4 and 3.3.5. Duplicate samples were taken from baths and averages were presented.

3.3.4 Procedures for the Analysis of Components of Copper Cyanide Electroplating Baths

In copper cyanide electroplating baths, copper, titratable cyanide, Rochelle salt and carbonate analysis were conducted. All of the four analysis were titrimetric methods.

3.3.4.1 Copper

The reagents involved in copper analysis are (URL10);
- ammonium persulfate $((NH_4)_2S_2O_8)$
- concentrated ammonia solution
- 30 % hydrogen peroxide (H_2O_2)
- 0.1 M Ethylenediaminetetraacetic acid (EDTA) solution
- 1-(2-pyridylazo)-2-naphthol (PAN) indicator

Titration procedure of the analysis of copper content is as follows (URL10):

- 2 mL of bath sample is taken into a 250 mL Erlenmeyer flask,
- 25 mL deionized water is added,
- 2 mL hydrogen peroxide is mixed into the diluted bath sample,
- The mixture is stirred for five minutes and after stirring it is boiled for fifteen minutes,
- 2-3 g ammonium persulfate and 5 mL concentrated ammonia solution is put.
- 50 mL deionized water is added,
- PAN indicator is introduced in the mixture in 4-6 drops,
- End mixture is titrated with EDTA solution of 0.1 M. The color should be observed as changing from blue to green-grey.

The amount of EDTA consumed is recorded. Calculation of copper concentration is done by considering the equality;

$$1 \text{ mL } 0.1 \text{ M EDTA} = 0.00637 \text{ g Cu} \tag{17}$$

Then, copper concentrations are calculated by;

$$\text{Copper content (g/L)} = \frac{0.00637 \text{ g Cu x EDTA (mL) x 1000 mL /1 L}}{1 \text{ mL EDTA x 2 mL}} \tag{18}$$

3.3.4.2 Titratable Cyanide

Most appropriate term to use for the measurement of the cyanide is the "titratable cyanide". Actually, silver nitrate is titrated to form silver cyanide complexes with free cyanides in the solution. However, if there are other metal ions such as zinc, cadmimum or copper, free cyanides would be found in complexation with these metals. The partial or complete dissociation of cyanide from these metal cyanide complexes may prevent to measure the real free cyanide (CN^- and HCN) content of the solution. Hence, silver nitrate titration is a measure of available cyanides for titration (Delgado et al., 2008).

The reagents involved in cyanide analysis are (URL10):

- 0.1 N silver nitrate solution
- 10% ammonia solution
- 1-2 g potassium iodide

Titration procedure of the analysis of titratable cyanide content is as follows (URL10):

- 10 mL of bath sample is taken into a 250 mL Erlenmeyer.
- 100 mL deionized water is added.
- drops of 10% ammonia solution is introduced into the diluted bath sample.
- 1 or 2 g potassium iodide is added after ammonia solution and dissolved.
- The mixture is titrated with 0.1 N silver nitrate solution. Color of the solution shows up a white coloudy appearance when the titration is completed.

Silver nitrate consumed is recorded. Titratable cyanide can be calculated by the equation below:

$$\text{Titratable cyanide (g/L)} = \text{consumption of silver nitrate (mL) x 1.3} \tag{19}$$

3.3.4.3 Rochelle Salt

There are two common methods applied in Rochelle salt determination, first, titration with potassium permanganate ($KMnO_4$) (URL10) and second, titration of excess $KMnO_4$ with sodium thiosulfate ($Na_2S_2O_3$) (Langford and Parker, 1971). The first method was found to be unreliable because color change could not be stabilized. Twenty or thirty seconds stabilized color change would have considered as enough, however, there were not any dedication to the time to wait in any of the sources addressing to the first experiment. Therefore, the second method for Rochelle salt determination was used. The reagents involved in the second method are (Langford and Parker, 1971):

- Concentrated hydrochloric acid (HCl)
- 2 g zinc dust (Zn)
- 1 g magnesium sulfate ($MgSO_4$)
- 25 % sulphuric acid (H_2SO_4)
- 0.1 N potassium permanganate ($KMnO_4$)
- 3 g potassium iodide (KI)
- 0.1 N sodium thiosulphate ($Na_2S_2O_3$)

The procedure of the Rochelle salt titration is given below (Langford and Parker, 1971).

- 5 mL bath sample is taken into a 250 mL Erlenmeyer
- 5 mL concentrated hydrochloric acid is added into the bath (poisonous gasses evolves, perform inside a fumehood)
- Without completely vaporizing, sample is boiled (takes about 5 minutes)
- At room temperature 2 g of zinc dust is added and left for 30 minutes to react.
- After 30 minutes it is filtered using deionized water through Whatmann 40 filter paper.
- 1 gram of magnesium sulphate is put into the filtrate.
- From 25% sulphuric acid, 10 mL is taken into the filtrate.
- Exactly 50 mL of 0.1 N potassium permanganate is added.
- The mixture is left at 80-90oC for about 30 minutes and allowed to cool down to room temperature.
- 3 g of potassium iodide is added.
- Titration is done with 0.1 N sodium thiosulfate. The color change is from dark brown to colorless.

Sodium thiosulphate consumed is recorded. Rochelle salt concentration can be calculated using following formula:

$$\text{Rochelle salt (g/L)} = \text{mL consumption of } KMnO_4 \times 0.9375 \qquad (20)$$

3.3.4.4 Carbonate

Carbonate analysis was performed in all cyanide baths, even if the reagents did not included any carbonate, to be able to examine atmospheric adsorption of carbon dioxide during plating which is the only period bath was left open. The reagents involved in carbonate analysis are (URL10):

- 30% barium chloride solution
- 1 N hydrochloric acid (HCl)
- 1 N sodium hydroxide (NaOH) solution
- Methyl orange indicator

Carbonate titration procedure is as follows (URL10):

- 10 mL bath sample is taken into a 250 mL Erlenmeyer.
- 100 mL deionized water is added and diluted sample is heated.
- 30 mL barium chloride is put into heated sample.
- The mixture is allowed to precipitate for about half an hour.
- Precipitate is filtered through a Whatmann 40 filter.
- To wash the precipitate on the filter, Erlenmeyer is rinsed by hot water and poured onto filter paper twice.
- Filter paper is taken and carefully ripped apart, placed into a clean Erlenmeyer.
- 100 mL deionized water is added.
- 1 N HCl is added at an exact amount of 25 mL.
- 4-6 drops of methyl orange indicator is put.
- While titrating with 1 N NaOH, color changes from pink to yellow.

Potassium carbonate (g/L) = (25- consumption in mL) x 6.91   (21)

3.3.5 Procedures for the Analysis of Components of Copper Pyrophosphate Electroplating Baths

In copper pyrophosphate plating baths, copper and pyrophosphate concentrations were also measured by titrimetric methods.

3.3.5.1 Copper

Reagents involved in copper analysis for copper pyrophosphate electroplating baths are (URL11):

- concentrated ammonium hydroxide
- 0.1 M EDTA
- PAN indicator

Copper titration procedure is given below (URL11):

- 2 mL of bath sample is taken into 250 mL Erlenmeyer.
- Sample is diluted with 100 mL deionized water.
- Concentrated ammonium hydroxide is added until color appears to be deep blue.
- The mixture is heated to 60oC.
- PAN indicator is added in 4-6 drops.
- Solution is then titrated with 0.1 M EDTA. Color change observed is from purple to greenish grey.

Recorded EDTA consumption is used in the formula following:

$$\text{Copper content (g/L)} = \frac{\text{EDTA in mL x 4.236 x molarity of titrant x 8.217 g/L}}{1 \text{ oz/gal}} \qquad (22)$$

3.3.5.2 Pyrophosphate

Reagents involved in pyrophosphate analysis are (URL11):

- 1 N hydrochloric acid (HCl)
- 1 N sodium hydroxide (NaOH)
- 20% zinc sulphate ($ZnSO_4$)

Pyrophosphate titration procedure is given below (URL11):

- 5 mL of bath sample is diluted with 100 mL deionized water.
- 1 N HCl is added drop by drop until pH is 3.8 (if pH falls too much, 1 N NaOH is added drop wise to increase pH)
- Mixture is agitated for 5 minutes and pH is checked once more to ensure pH falls between 3.6 and 3.8.
- 50 mL 20% ZnSO4 is added, this addition decreases the pH.
- For 10 minutes, mixture is stirred again.
- Using 1 N NaOH, mixture is titrated drop wise until pH is 3.8 again. This consumption is noted for pyrophosphate concentration calculation.

$$\text{Pyrophosphate content (g/L)} = \text{ (consumption in mL x 17.4) + (g/L Cu x 1,37)} \qquad (23)$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Product Quality Oriented Experiments

The first setup was about comparing several strike baths for their performances in copper electroplating. There were two major aims to compare copper depositions in terms of quality (USEPA/742/B-97/005, 1997):

- Commercial suppliers of chemicals may provide a bath formulation which is in higher concentration than needed.
- Cyanide baths may be replaced by non-cyanide alternatives.

Baths and corresponding aluminium sample codes plated are given in Table 4.1. Polished aluminium samples were deposited with copper by applying low, medium and high current densities in their applicable ranges, as was given in Table 2.1 and Table 2.3 in sections 2.1.1.2 and 2.1.2.2, respectively.

Table 4.1 Baths and corresponding plated polished aluminium samples by low, medium and high current densities.

BATH	Exp. No	Current Densities	Al No
A - Commercial brand's case specific copper cyanide strike bath formulation	1	Low	19
	2	Medium	20
	3	High	21
B - Copper cyanide strike solution given by Schlesinger and Paunovic (2010)	4	Low	18
	5	Medium	17
	6	High	16
C - Copper cyanide strike solution with sodium carbonate addition given by Schlesinger and Paunovic (2010)	7	Low	12
	8	Medium	14
	9	High	15
D - Copper pyrophosphate strike solution formulated with lower limits given by Barauskas (2011)	10	Low	26
	11	Medium	27
	12	High	28
E - Copper pyrophosphate strike solution formulated with upper limits given by Barauskas (2011)	13	Low	22
	14	Medium	24
	15	High	25

Plating quality was first observed visually for each sample. Roughness and reflectivity measurements were also done. SEM images were taken and bath components were analyzed. Outputs of these analyses were evaluated for each parameter in the following sections.

4.1.1   Visual Inspection

Resultant deposited copper layers on polished aluminium samples are demonstrated in Figure 4.1. No major defects were observed after copper deposition using neither copper cyanide nor copper pyrophosphate electroplating baths. However, blackening of the surface during plating in copper cyanide baths were remarkable, especially on the ones from carbonate included copper cyanide strike (samples 12,14 and 15) and two of the Bath B products (samples 17 and 18). The spotting out or staining of the workpiece in cyanide solutions is a random trouble, as discussed by Graham (1971). Cyanide solution is entrapped inside the small gaps of the metal to be plated or inside the deposited metal. When the workpiece is left to dry, water evaporates but salts are left. These salts are then decomposed using humidity of the ambient air and decomposes releasing gas. On the surface of the deposited layer, these gasses interact with the surrounding environment and a stain is left on deposition as a result of reactions that occur. Improving smoothness, ultrasonic cleaning and weak acid cleaning are advised to overcome such stains (Graham, 1971). These blackened copper depositions were then cleaned with citric acid and a better surface was obtained. Figure 4.2 shows the parts after this cleaning.

On the other hand, finished products obtained in pyrophosphate baths were significantly brighter when compared to the others, without application of any cleaning. This inspection led to an outcome that a satisfactory brightness could be achieved in a pyrophosphate bath without any brightening additive. In addition, the appearance of products obtained in cyanide baths were quite variable in quality with respect to the different current densities applied, while more consistent product quality could be obtained in copper pyrophosphate baths.
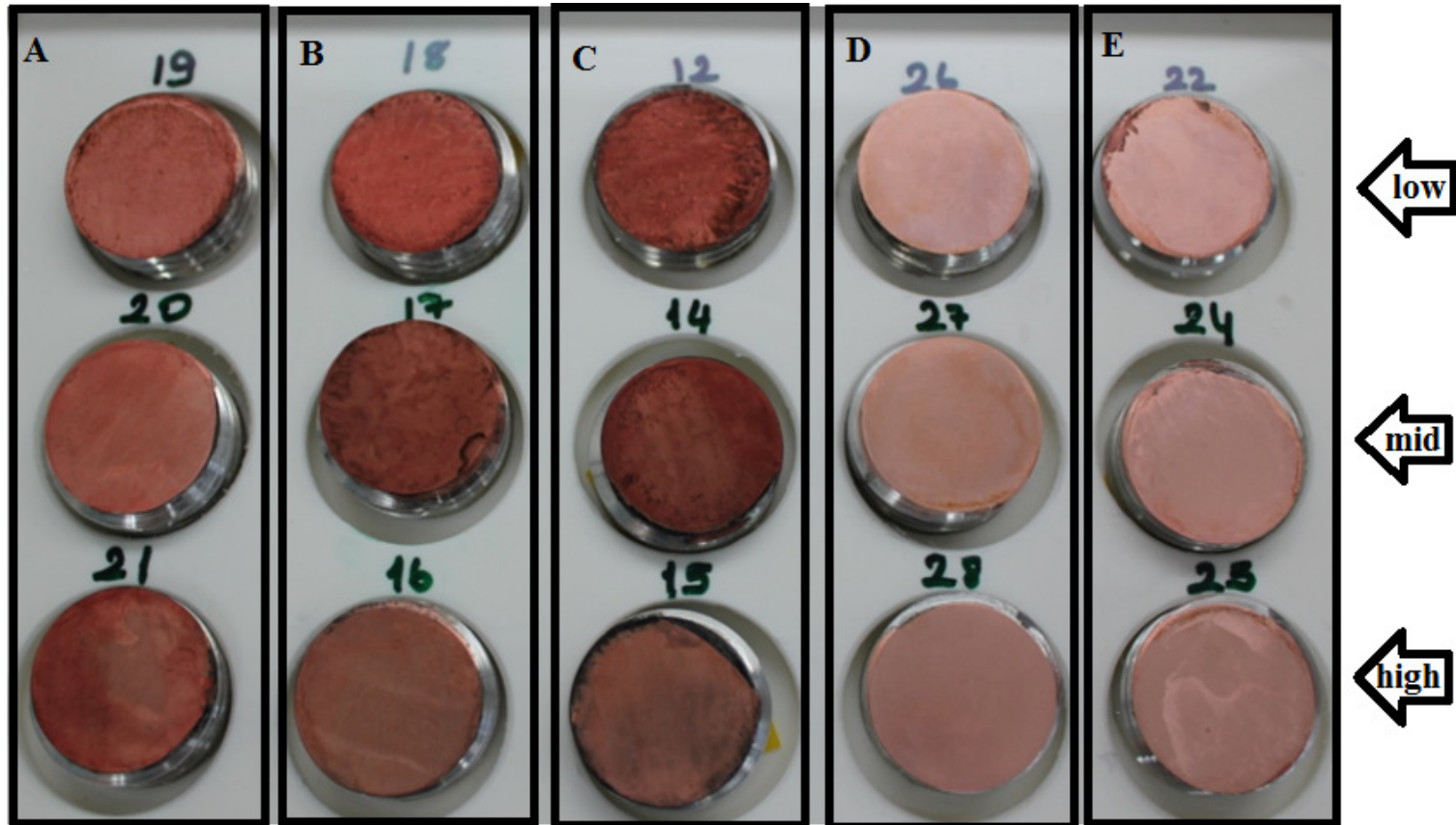
Figure 4.1 Copper plated aluminiums with several electroplating strike baths before cleaning with citric acid.
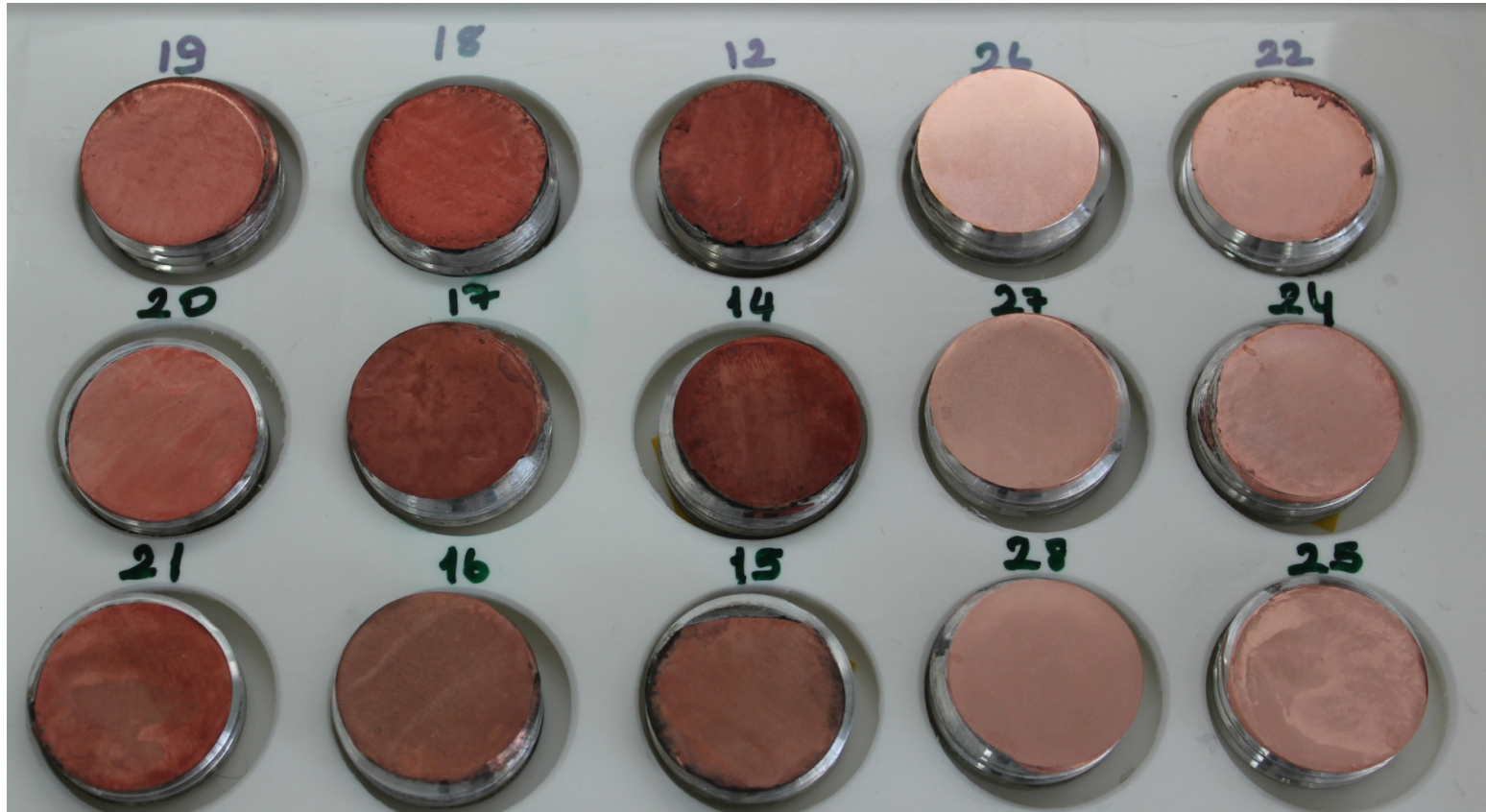
Figure 4.2 Copper plated aluminiums with several electroplating strike baths after cleaning with citric acid.

4.1.2 Roughness

One major expectation from this study is that the plated surface should be as smooth as possible to enhance the reflectivity in terms of specular measurements (Birkebak et al., 1964). This is especially important if, as in this case, more electroplating is going to be performed on the same product in subsequent steps.

Initially, the specific roughnesses of bulk aluminium workpieces was measured, so that a good comparison can be made after copper plating was performed on them. Aluminium workpieces had been smoothened with colloidal silica abrasives before any plating process. The average roughness of a bulk aluminium workpiece was found to be 0.047 ± 0.02 µm. In addition, two perpendicular measurements in a single workpiece did not vary too much. Therefore, it can be concluded that satisfactory smoothening was accomplished using collodial silica abrasives. Table 4.2 shows in the second column the two perpendicular roughness values of each bulk aluminium workpiece and the average roughness is given in the third column.

Table 4.2 Roughnesses of bulk aluminium workpieces before plating.

Sample	Ra (µm)	Average (µm)	Sample	Ra (µm)	Average (µm)
a	0.03 0.04	0.035	h	0.07 0.07	0.070
b	0.07 0.06	0.065	i	0.05 0.05	0.050
c	0.03 0.03	0.030	j	0.04 0.03	0.035
d	0.03 0.03	0.030	k	0.03 0.04	0.035
e	0.04 0.04	0.040	l	0.11 0.08	0.095
f	0.03 0.03	0.030	m	0.06 0.05	0.055
g	0.04 0.03	0.035	TOTAL AVERAGE ROUGHNESS		0.047± 0.02

Secondly, the roughness of copper plated aluminium products were measured by the same procedure before and after cleaning with citric acid. These values are presented in Table 4.3. For cyanide baths, roughnesses of Bath A products range between 0.10-0.15 µm, Bath B between 0.10-0.21 µm and Bath C between 0.10-0.17 µm before cleaning.

In pyrophosphate baths, pre-cleaning roughnesses ranges between 0.08 and 0.13 µm for Bath D and between 0.08 and 0.12 µm for Bath E. These roughnesses are lower than those obtained in cyanide baths. Among the cyanide baths, smoothest surfaces were obtained at high current density for Bath A and Bath B and at medium current density for Bath C (all 0.10 µm).

Furthermore, cyanide baths generally showed up more difference between the two consecutive measurements in a single piece. To illustrate, the most rough result among cyanide baths; Bath B with low current application (sample 18); had 0.11 µm difference between two measurements whereas among pyrophosphate baths; Bath D with low current application (sample 26); had 0.04 µm difference between the two. Since two perpendicular measurements were performed during roughness measurement, the difference between two perpendicular measurements indicates the homogeneity of the surface coating. The fact that pyrophosphate bath samples show much lower differences indicate the good levelling ability of pyrophosphate baths.

Cleaning with citric acid had a considerable effect on roughness measurements especially in rough deposits, so mostly cyanide platings were positively affected from cleaning process. Only two average roughness values out of nine remained the same after cleaning in cyanide baths; that are experiments 5 and 6 (samples 17 and16, respectively). However, it was not possible to determine whether citric acid cleaning improves the surface or not because the roughness of some products increased after cleaning. No significant change was observed in the roughness of the products plated from pyrophosphate baths. An additional comment on roughness measurement is that most rough surfaces occured at low current density applications in both pyrophosphate and cyanide baths.

Table 4.3 Roughness measurements of copper plated products for quality comparison.

Al No	Exp No	Bath	Current density	Before Cleaning Ra (µm)	After Cleaning Ra (µm)
19	1	A	low	0.13	0.10
			low	0.16	0.14
			low average	0.15	0.12
20	2	A	medium	0.13	0.16
			medium	0.17	0.15
			medium average	*0.15*	*0.16*
21	3	A	high	0.10	0.09
			high	0.09	0.09
			high average	*0.10*	*0.09*
18	4	B	low	0.26	0.39
			low	0.15	0.20
			low average	*0.21*	*0.30*
17	5	B	medium	0.11	0.11
			medium	0.11	0.10
			medium average	*0.11*	*0.11*
16	6	B	high	0.10	0.10
			high	0.09	0.09
			high average	*0.10*	*0.10*
12	7	C	low	0.18	0.21
			low	0.16	0.21
			low average	*0.17*	*0.21*
14	8	C	medium	0.09	0.09
			medium	0.11	0.09
			medium average	*0.10*	*0.09*
15	9	C	high	0.12	0.13
			high	0.12	0.12
			high average	*0.12*	*0.13*
26	10	D	low	0.11	0.11
			low	0.15	0.09
			low average	*0.13*	*0.10*
27	11	D	medium	0.08	0.08
			medium	0.08	0.07
			medium average	*0.08*	*0.08*
28	12	D	high	0.11	0.11
			high	0.10	0.12
			high average	*0.11*	*0.12*
22	13	E	low	0.11	0.12
			low	0.12	0.12
			low average	*0.12*	*0.12*
24	14	E	medium	0.07	0.07
			medium	0.08	0.08
			medium average	*0.08*	*0.08*
25	15	E	high	0.07	0.08
			high	0.08	0.08
			high average	*0.08*	*0.08*

4.1.3   Scanning Electron Microscope (SEM) Images

Scanning Electron Microscope (SEM) images were taken for samples from baths A, B, C (cyanide bath products) and D (pyrophosphate bath product) at a magnification of 10000x and 20000x. The images for Bath E components were visually inspected at the laboratory and a similiar structure to Bath D products was observed. In general, copper depositions from cyanide baths form a granular, almost spiky structure and can be best figured out by sample no 18 -20000x (Figure 4.4). Copper formations from pyrophosphate baths appear much smoother and can be best figured out by sample no 26 -20000x (Figure 4.6).

While pittings and large nodules can be observed in Bath A and Bath B samples, none or very small nodular deposits could be seen in Bath D samples. Sample 20, for example, has a very large nodule in Figure 4.3 at 20000x magnification whereas sample 28 has a very little one as seen from Figure 4.6. According to EDX analysis of the same equipment used for SEM imaging, nodules observed are 100% copper.

Schlesinger and Paunovic (2010) states that pittings are caused by hydrogen gas evolved in copper cyanide electroplating. Large nodules in copper cyanide baths may also be a result of bubbles because of hydrogen gas evolving during deposition or may be a result of insufficient levelling ability of cyanide plating baths. The most probable choice is the buble formation, since bubbles attach on the surface for a short period of time and when they attach local growth of deposition takes place in bubble-free segments.This fact causes irregularities in the deposition. On the other hand, copper pyrophosphate plating baths seem to result in more consistently homogeneous plating. This result can be derived from the smoothness and little failure containing structure of the platings and the similarity of the images of the products obtained by applying three different current densities.

In cyanide baths, grain sizes get smaller as the applied current density is increased which can be observed from 20000x magnification samples more clearly. No major grain size differentiation can be made for pyrophosphate bath products at 20000x.

Carbonate added Bath C samples (12,14,15), have a smoothener surface structure than cyanide products but not as smooth as pyrophosphate bath products (Figure 4.5).

Al no: 19 - 10000x	Al No: 19 - 20000x
Al no: 20 - 10000x	Al no: 20 - 20000x
Al no: 21 - 10000x	Al no: 21 - 20000x
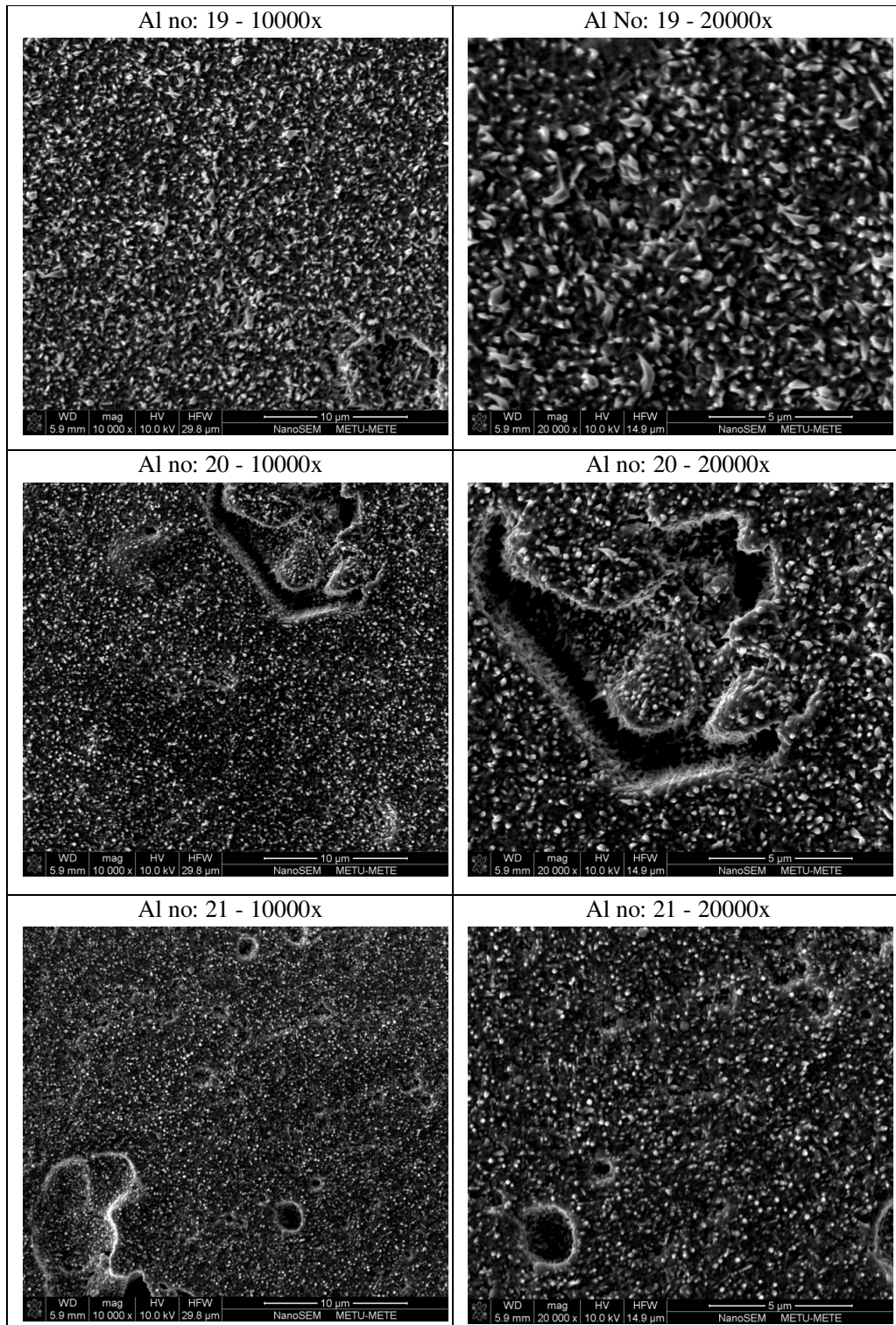
Figure 4.3 SEM images of Bath A products magnified by 10000x and 20000x.

Al no: 18 - 10000x	Al no: 18 - 20000x
Al no: 17 - 10000x	Al no: 17 - 20000x
Al no: 16 - 10000x	Al no: 16 - 20000x
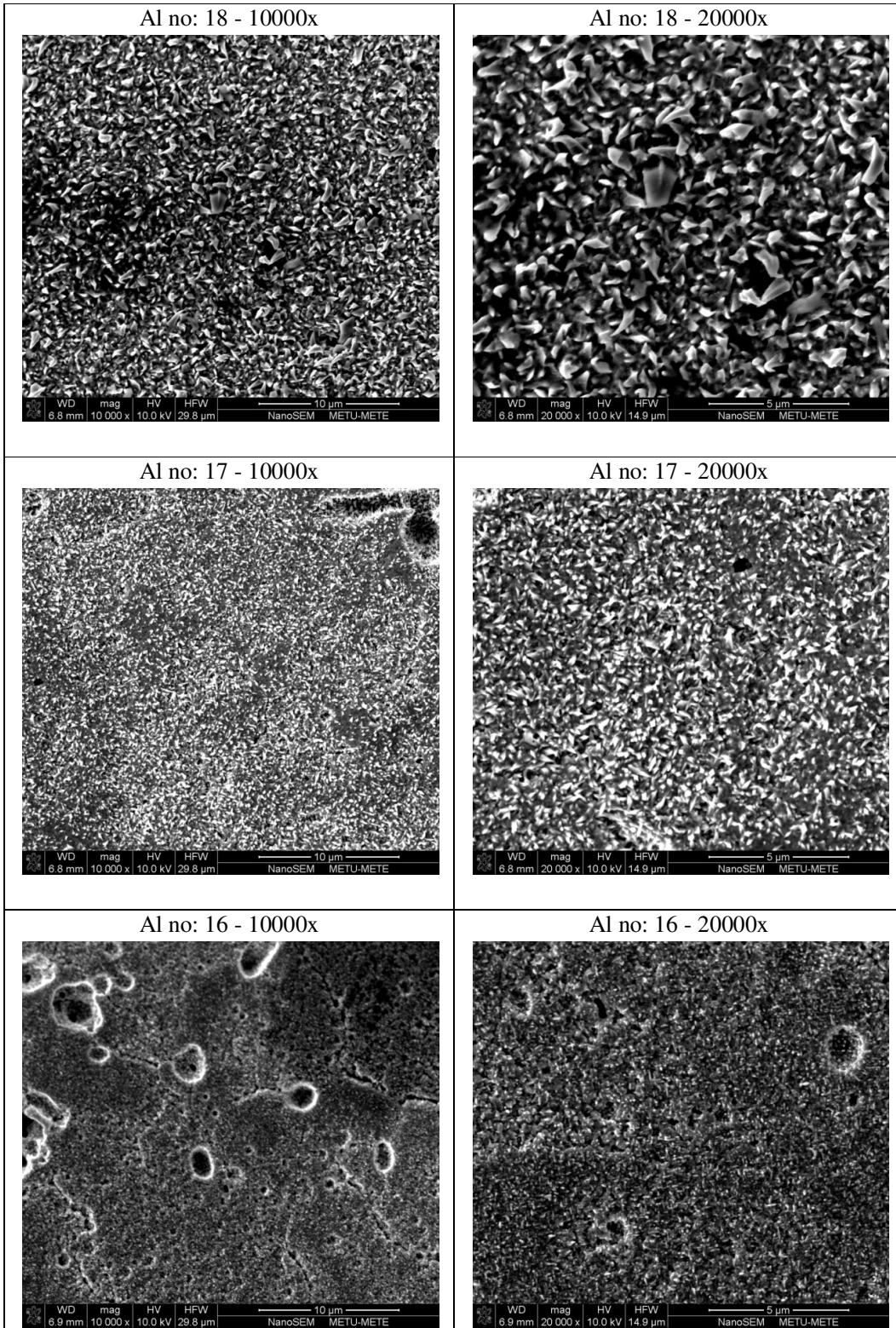
Figure 4.4 SEM images of Bath B products magnified by 10000x and 20000x.

Al no: 12 - 10000x	Al no: 12 - 20000x

Al no: 14 - 10000x	Al no: 14 - 20000x

Al no: 15 - 10000x	Al no: 15 - 20000x
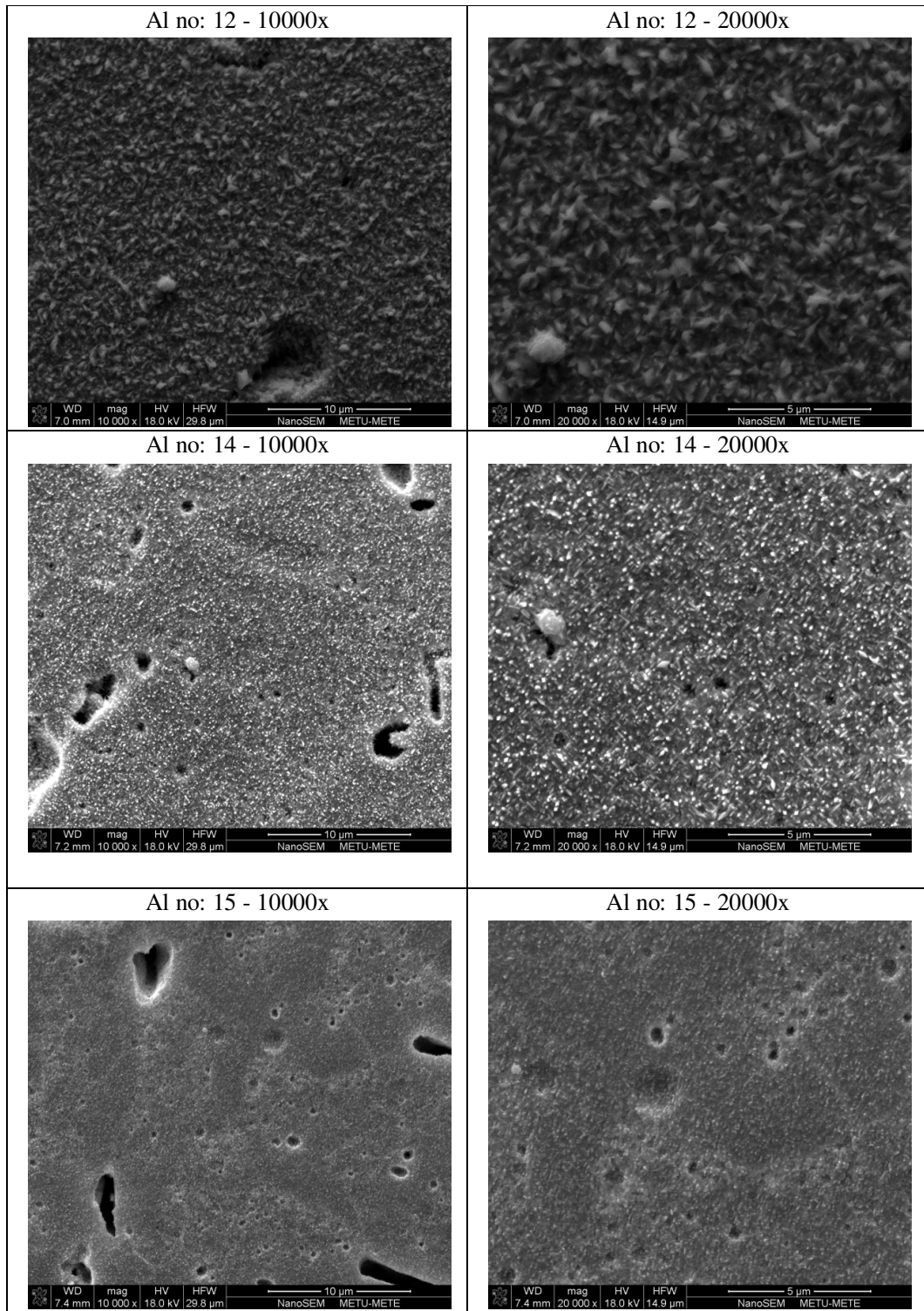
Figure 4.5 SEM images of Bath C products magnified by 10000x and 20000x.

Al no: 26 - 10000x	Al no: 26 - 20000x
WD 6.7 mm · mag 10 000 x · HV 10.0 kV · HFW 29.8 µm · 10 µm · NanoSEM METU-METE	WD 6.7 mm · mag 20 000 x · HV 10.0 kV · HFW 14.9 µm · 5 µm · NanoSEM METU-METE
Al no: 27 - 10000x	Al no: 27 - 20000x
WD 6.6 mm · mag 10 000 x · HV 10.0 kV · HFW 29.8 µm · 10 µm · NanoSEM METU-METE	WD 6.6 mm · mag 20 000 x · HV 10.0 kV · HFW 14.9 µm · 5 µm · NanoSEM METU-METE
Al no: 28 - 10000x	Al no: 28 - 20000x
WD 6.6 mm · mag 10 000 x · HV 10.0 kV · HFW 29.8 µm · 10 µm · NanoSEM METU-METE	WD 6.6 mm · mag 20 000 x · HV 10.0 kV · HFW 14.9 µm · 5 µm · NanoSEM METU-METE

Figure 4.6 SEM images of Bath D products magnified by 10000x and 20000x.

4.1.4 Reflectivity

Before plating polished aluminium samples were first tested for their reflectivities under varying wavelengths. Reflectivities of copper depositions are of great concern for the field of application of the finished product. The product of concern is a cold shield which is a part of an optoelectronic device. High absorption at the inner surface and high reflection at the outer surface is desired in cold shields. Therefore, reflectivities after plated with copper are expected to be as high as possible. The first test applied was UV-Vis integrating sphere measurements. Integrating spheres is able to measure reflected light in all directions. Figure 4.7 gives these measurements from polished aluminium samples in graphical form. Maximum reflection in polished aluminiums was observed to be 88.41% and minumum was 77.63%. All polished aluminium samples follow the same trend in terms of reflectivities.
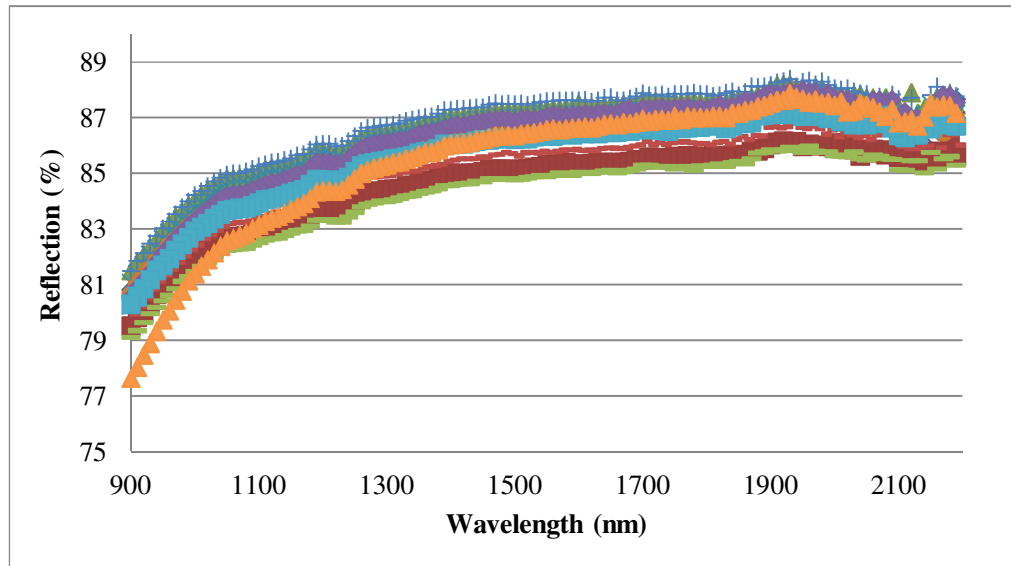
Figure 4.7 UV-Vis integrating sphere measurements of polished aluminium samples.

In mirror reflection, light incoming to surface makes an angle with the surface normal and it is reflected by preserving the same angle with the surface normal but in opposite direction. Likewise, specular reflection is the measurement of light reflected from the surface as in mirror reflection. In Figure 4.8, UV-Vis spectrophotometry and in Figure 4.9 FTIR specular reflectances are shown for polished aluminium surfaces. The maximum specular reflectivities are 83.45% and 95.29% for UV-Vis spectrophotometry and FTIR measurements, respectively. Minumum measurements are 65.25% and 80.05% for UV-Vis and FTIR for polished aluminium samples.

UV-Vis specular reflectivity measurements were done in 900-2200 nm band and FTIR measurements were performed in 2200-16000 nm band. These measurements are expected to be a continuation of each other. However, there can be errors even in placing the workpiece in FTIR apparatus which can be as much as 10%. Therefore, these facts should be taken into the consideration while evaluating the records and the placement problem in FTIR device should be overcomed for further studies.
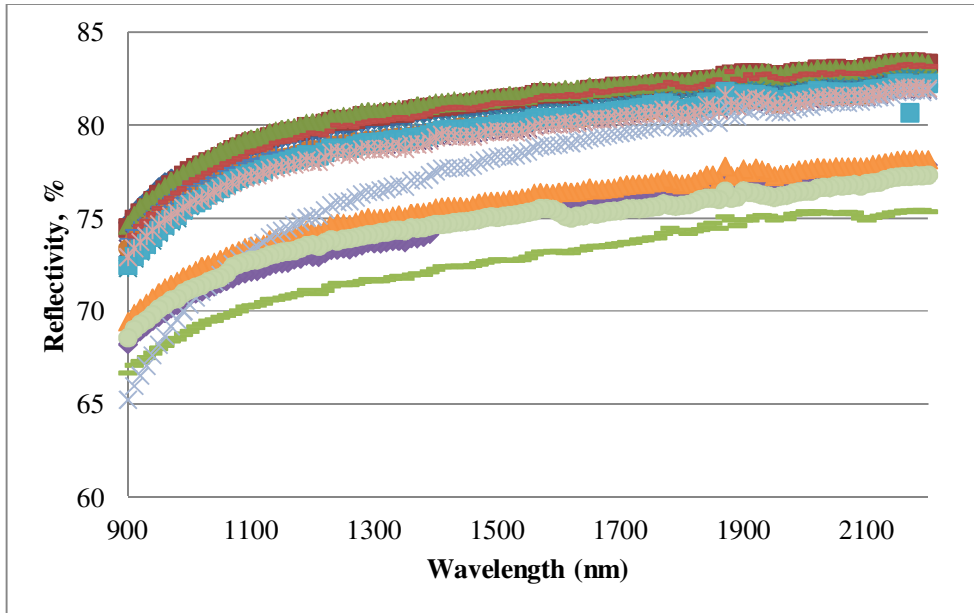
Figure 4.8 UV-Vis specular reflectance measurements of polished aluminium samples.
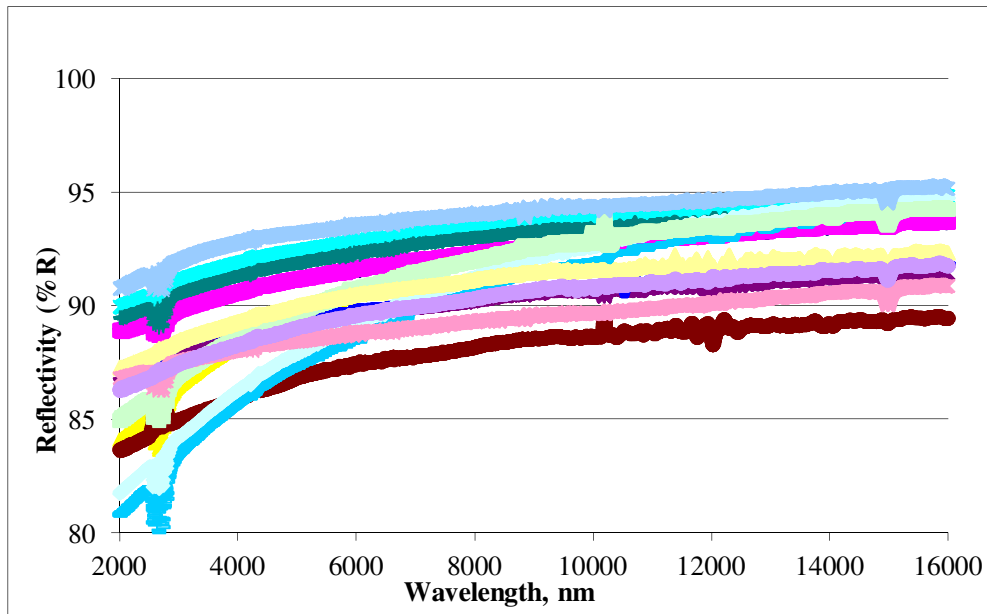
Figure 4.9 FTIR specular reflectance measurements of polished aluminium samples.

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In Table 4.4, in seventh column, maximum and minimum measured values of UV-Vis integrating sphere analysis are used to calculate the percent change of reflectivities under whole applied range of wavelengths. So, minimum change represents less variation in reflectivities under different wavelengths.Therefore, products obtained from Baths D and E (pyrophosphate bath products) showed more consistent reflectivities at different wavelengths according to integrating sphere measurements between 900 nm and 2190 nm. Moreover, the minimum and the maximum reflectances are in between 91.30% and 93.60% in pyrophosphate products which are very high compared to the cyanide products (min 58.37%; max 91.75%). So, use of pyrophosphate bath ends up with high and stable reflectivity under different wavelengths as depicted by integrating sphere measurements.

Among cyanide baths, the product of commercial brand bath (sample no 19) is the one showing lowest change in reflectivities under different wavelengths but not the one with the highest reflectivity. Highest reflectivity observed in sample 15 which was produced in the carbonate added bath. In cyanide baths at low current applications (samples 19, 18, 12), it is observed to have much less variances in reflectivities under different wavelengths.

Table 4.4 Minimum and maximum measurements of UV-Vis integrating sphere and their corresponding wavelengths.

BATH	Sample	Min (%)	Wavelength (nm)	Max (%)	Wavelength (nm)	Percent deviation (%)
A	19	82.46	900	88.88	2150	7
	20	74.10	900	91.07	2160	19
	21	72.73	900	90.80	2150	20
B	18	79.14	900	89.08	2120	11
	17	58.37	900	81.43	2150	28
	16	65.95	900	90.80	2120	27
C	12	73.15	900	84.63	2120	14
	14	60.87	900	85.67	2180	29
	15	74.62	900	91.75	2080, 2150	19
D	26	91.63	910	93.02	2180	1
	27	92.33	1220, 1230	93.51	1910	1
	28	91.91	1140	93.50	2170	2
E	22	91.30	900	93.21	2090	2
	24	91.83	1130	93.08	1990	1
	25	91.69	900	93.59	2150	2

UV-Vis specular reflectances are also favoring the findings of integrating sphere measurements of products (Table 4.5). Maximum reflectances obtained are 72.39% and 60.57% for pyrophosphate and cyanide products, respectively. Pyrophosphate bath products have a minimum of 60.10% while it is 32.53% for cyanide ones. This means, the surface of the pyrophosphate products are more like a mirror in terms of smoothness because mirror-like reflection is favored by these products. Furthermore, percent deviations of pyrophosphate products are much lower than others except for sample 22. After cleaning with citric acid, sample 22 was noted to appear worse than before cleaning. Such a case may be a result of this cleaning action which was done before the measurements of reflectivities.

Table 4.5 Minimum and maximum measurements of UV-Vis specular reflectance.

BATH	Sample	Min (%)	Wavelength (nm)	Max (%)	Wavelength (nm)	Percent deviation (%)
A	19	19.54	900	53.18	2200	63
	20	20.98	900	46.75	2200	55
	21	35.41	900	58.88	2200	40
B	18	6.12	900	32.53	2200	81
	17	17.39	900	50.04	2200	65
	16	29.83	900	57.56	2200	48
C	12	9.14	900	42.72	2200	79
	14	29.93	900	60.57	2200	51
	15	33.97	900	53.63	2200	37
D	26	47.93	900	69.61	2200	31
	27	53.85	900	70.64	2200	24
	28	47.65	900	64.56	2200	26
E	22	28.68	900	60.1	2200	52
	24	54.72	900	72.39	2200	24
	25	36.4	900	65.93	2200	45

Maximum and minimum records of FTIR measurements and their percent deviations are given in Table 4.6. These records are also supporting the previous results that pyrophosphate products shows better reflectivities under different wavelengths applied. As a generalization, percent deviations are lower in the wavelength interval of FTIR measurements than UV-Vis specular range.

Table 4.6 Minimum and maximum measurements of FTIR specular reflectance.

BATH	Sample	Min (%)	Wavelength (nm)	Max (%)	Wavelength (nm)	Percent deviation (%)
	19	54.3	2000.0	91.2	15945.6 - 15974.4	40
A	**20**	47.9	2000.0	87.5	15996.8 - 16000.0	45
	21	46.2	2000.0	88.6	16000.0	48
	18	32.1	2000.0	83.2	16000.0	61
B	**17**	48.2	2000.0	92.1	15996.8 - 16000.0	48
	16	60.5	2000.0 - 2003.2	91.4	16000.0	34
	12	40.7	2000.0	89.8	16000.0	55
C	**14**	63.7	2000.0	93.1	15996.8 - 16000.0	32
	15	51.3	2000.0 -2003.2	89.3	15987.2 - 16000.0	43
	26	70.5	2000.0 - 2003.2	93.0	15782.4 - 15795.2	24
D	**27**	76.6	2000.0 - 2003.2	97.6	11664.0 - 11686.4	22
	28	68.9	2000.0	95.6	15993.6 - 16000.0	28
	22	60.3	2000.0	96.5	14972.8 - 14992.0	37
E	**24**	75.8	2000.0 - 2003.2	96.3	14953.6 - 14979.2	21
	25	67.5	2000.0	95.1	14979.2 -14988.8	29

Correlation of reflectivity measurements with roughness measurements needs to be done where major roughness differences were observed in order to prevent contradictory information. Because measurement methods are completely different from each other and only two roughness measurements were taken from each sample, whereas UV-Vis measurements were done under many different wavelengths. Hence, Bath A samples in Figure 4.10, Bath D samples in Figure 4.13 and Bath E samples in Figure 4.14 just demonstrate the reflectivity changes on the surface of the samples because of their very close roughness values.

The difference between UV-Vis integrating sphere and UV-Vis specular measurements is being expressed by difracted reflections. Actually this difference is expected to be proportional to the roughness. For example, in Figure 4.11, the difference between these two measurements for sample 18 is much larger than others, displaying the largest roughness over the surface (measured roughness is given in section 4.1.2 as 0.30 µm). In Figure 4.15, UV-Vis specular reflectance measurements were subtracted from integrating sphere measurements for randomly selected samples (18, 12, 19 and 25). The roughnesses of these samples are 0.30, 0.21, 0.12 and 0.08 µm, respectively. As a result difractions are decreasing with the decrease in roughnesses. Therefore, there is a correlation between the roughness and reflectivity measurements and this correlation can be further improved to pre-determination of product quality in terms of roughness measurements which are easier to perform in a laboratory than reflectivity measurements.

As a general comparision, specular reflectances of UV-Vis spectrophotometry for polished aluminium samples are all higher than plated surfaces because none of the plated surface has a lower roughness value than 0.047μm (Table 4.2) which is the average roughness of polished aluminium. Moreover, as an expected result from roughness measurements, copper pyrophosphate products show better reflection ability compared to cyanide products.

Figure 4.10 Reflectivities for products obtained using Bath A by low, medium and high current densities.

Figure 4.11 Reflectivities for products obtained using Bath B by low, medium and high current densities.
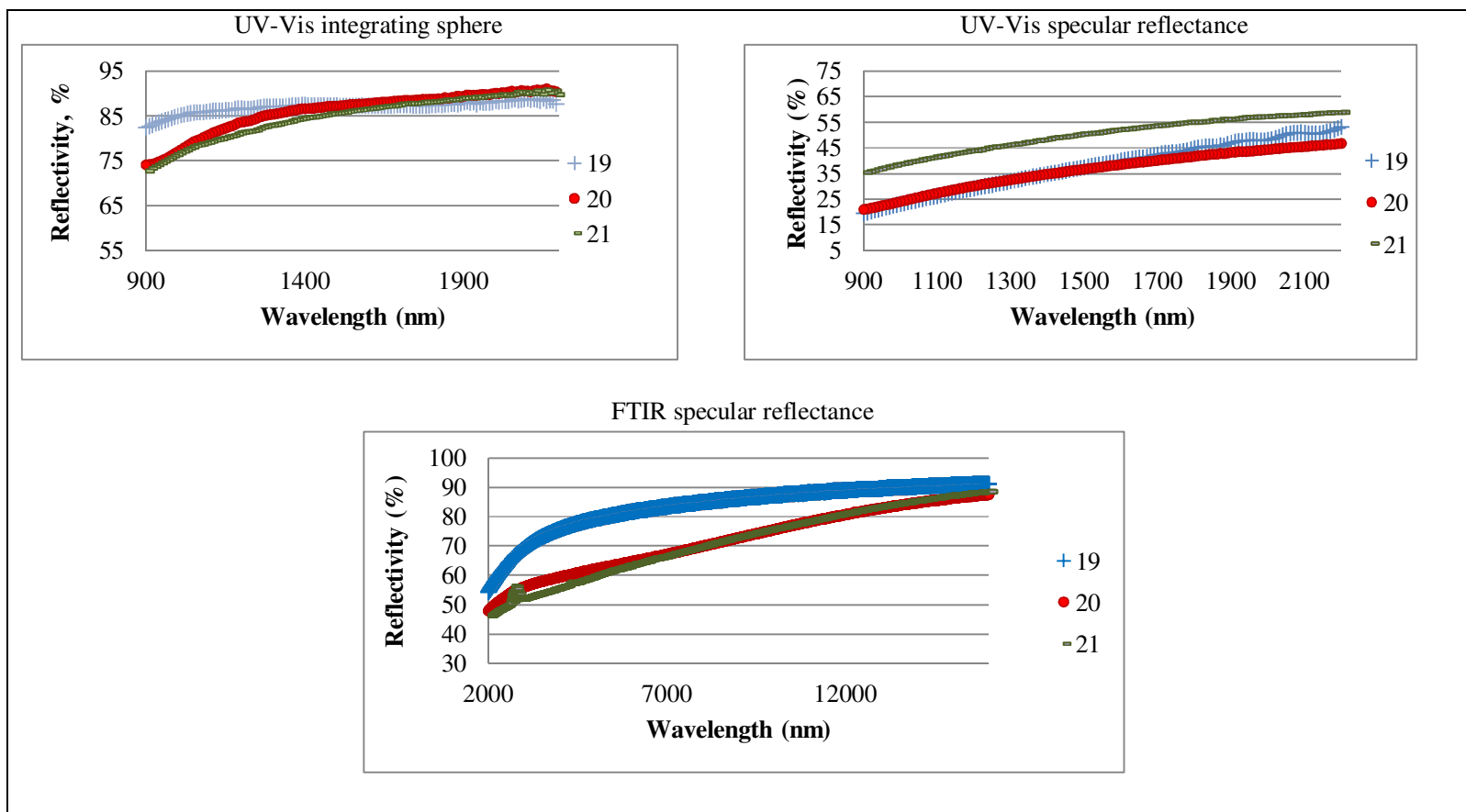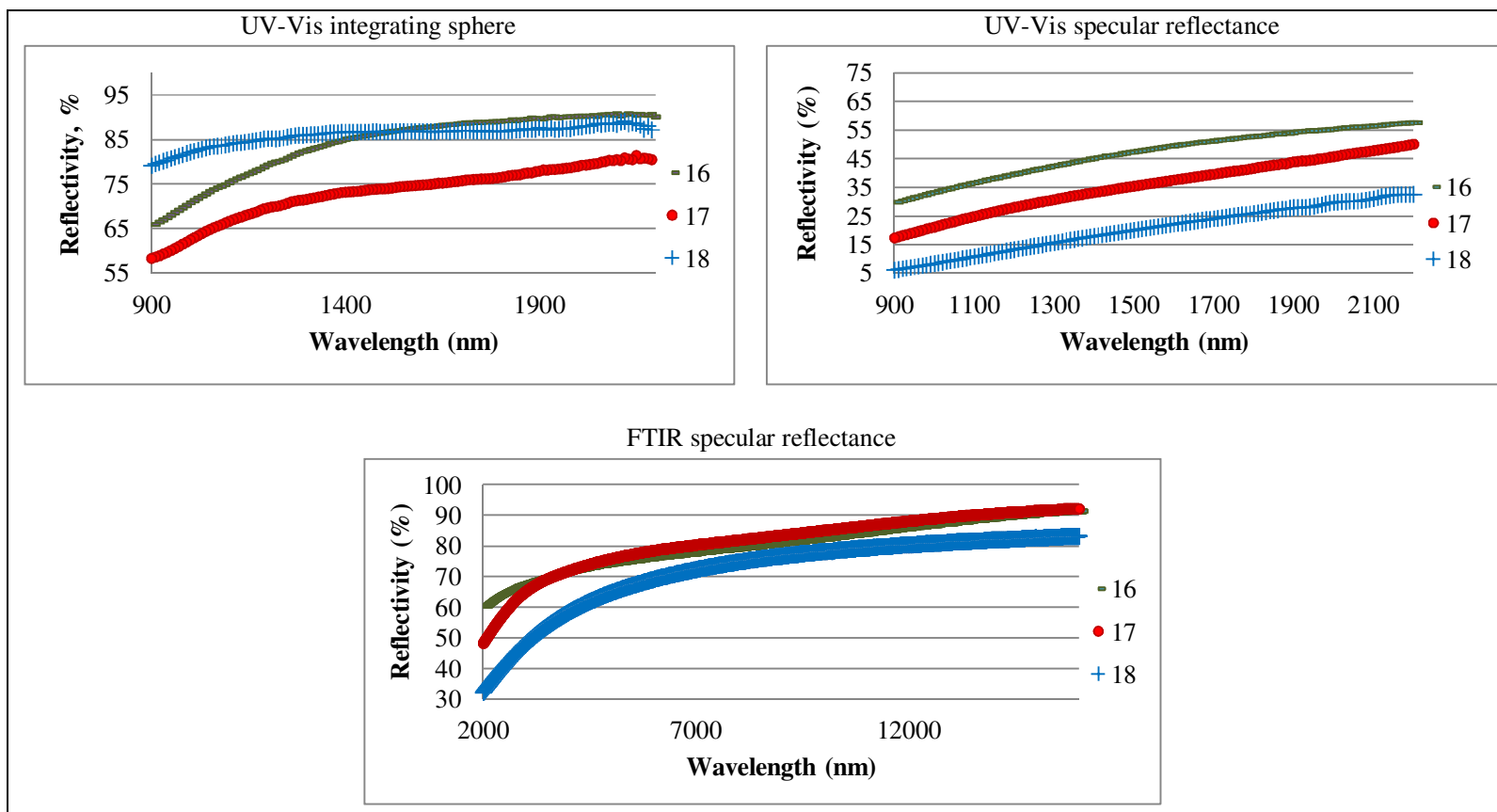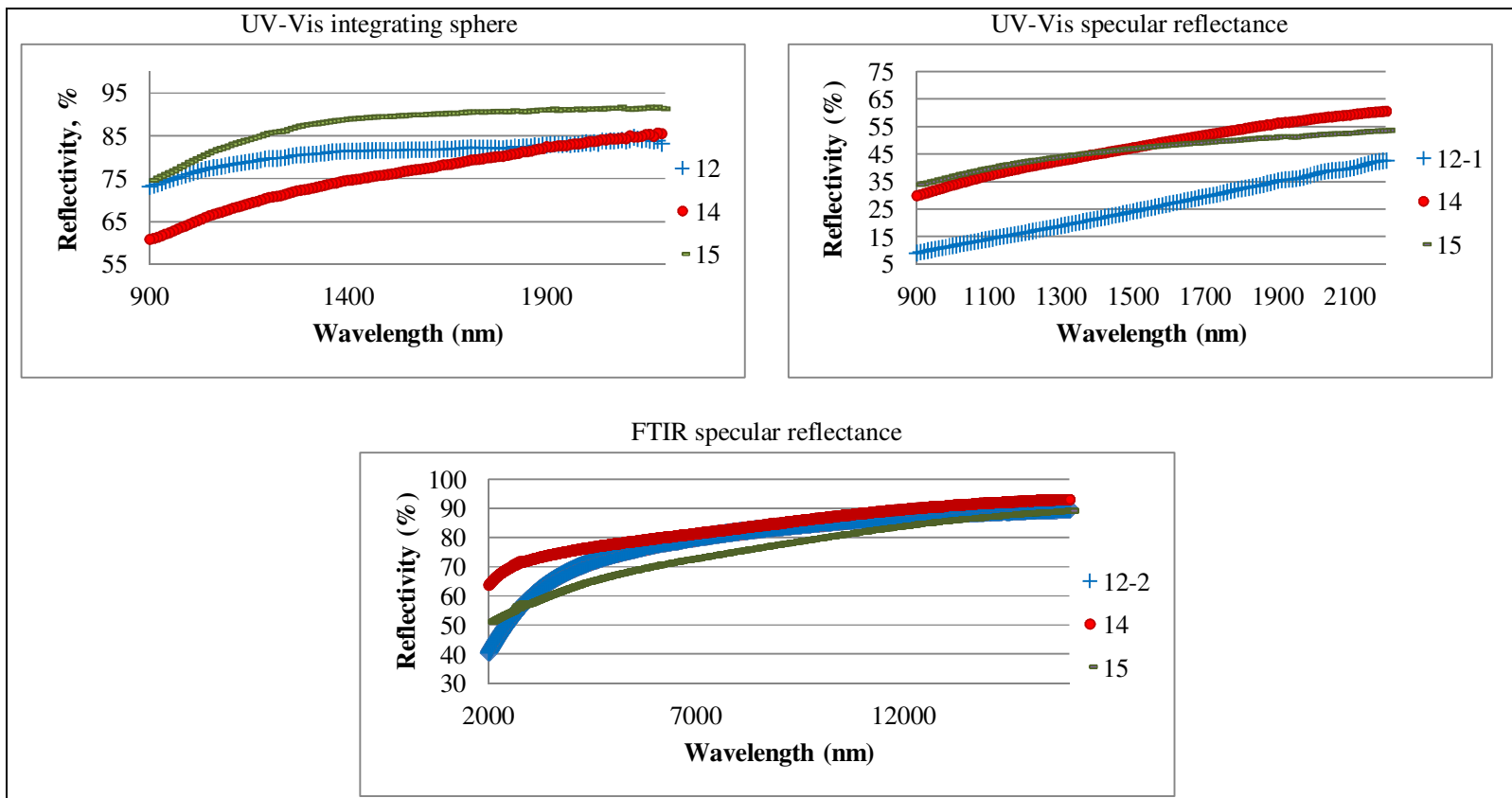
Figure 4.12 Reflectivities for products obtained using Bath C by low, medium and high current densities.
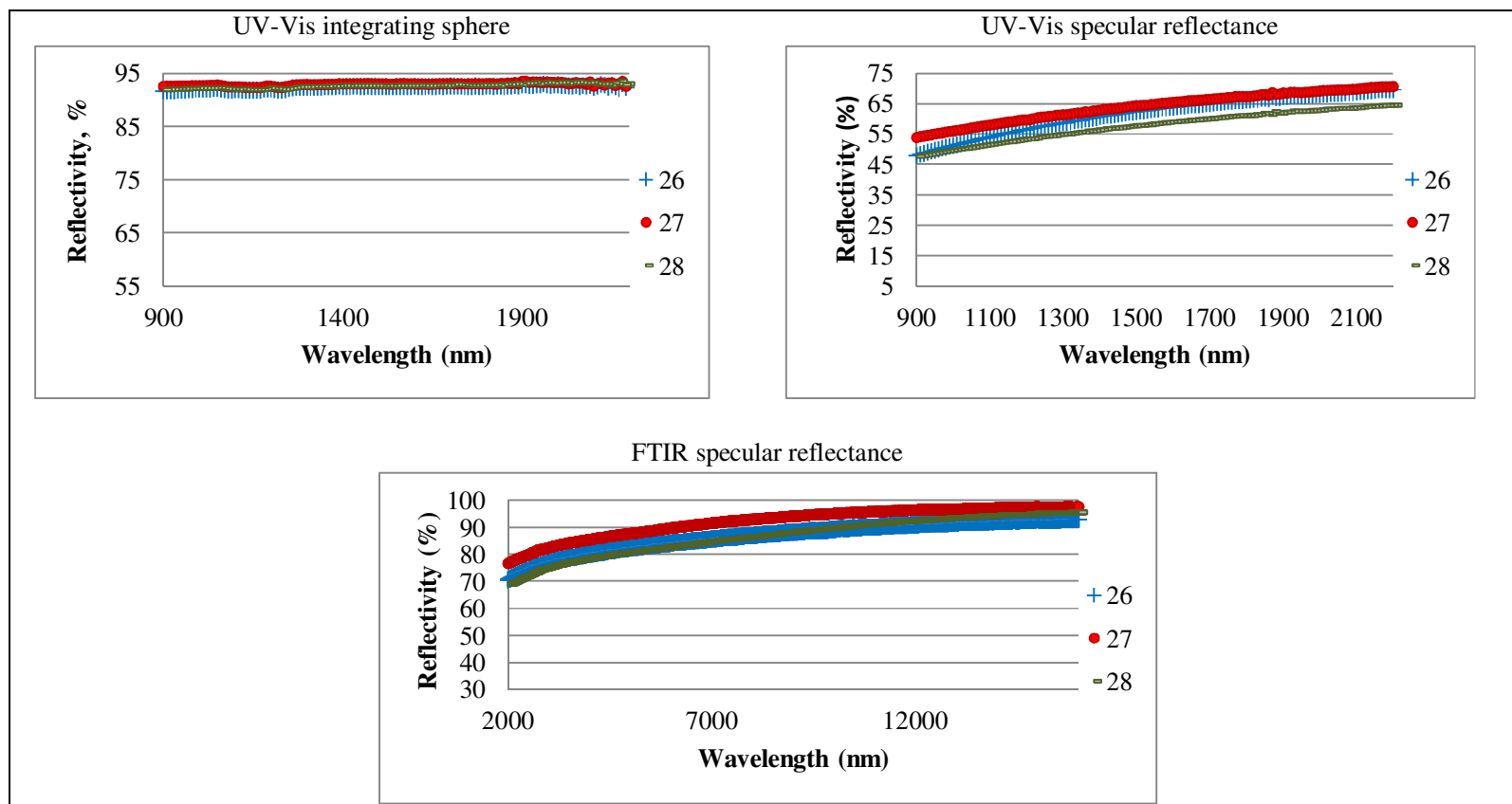
Figure 4.13 Reflectivities products obtained using Bath D by low, medium and high current densities.
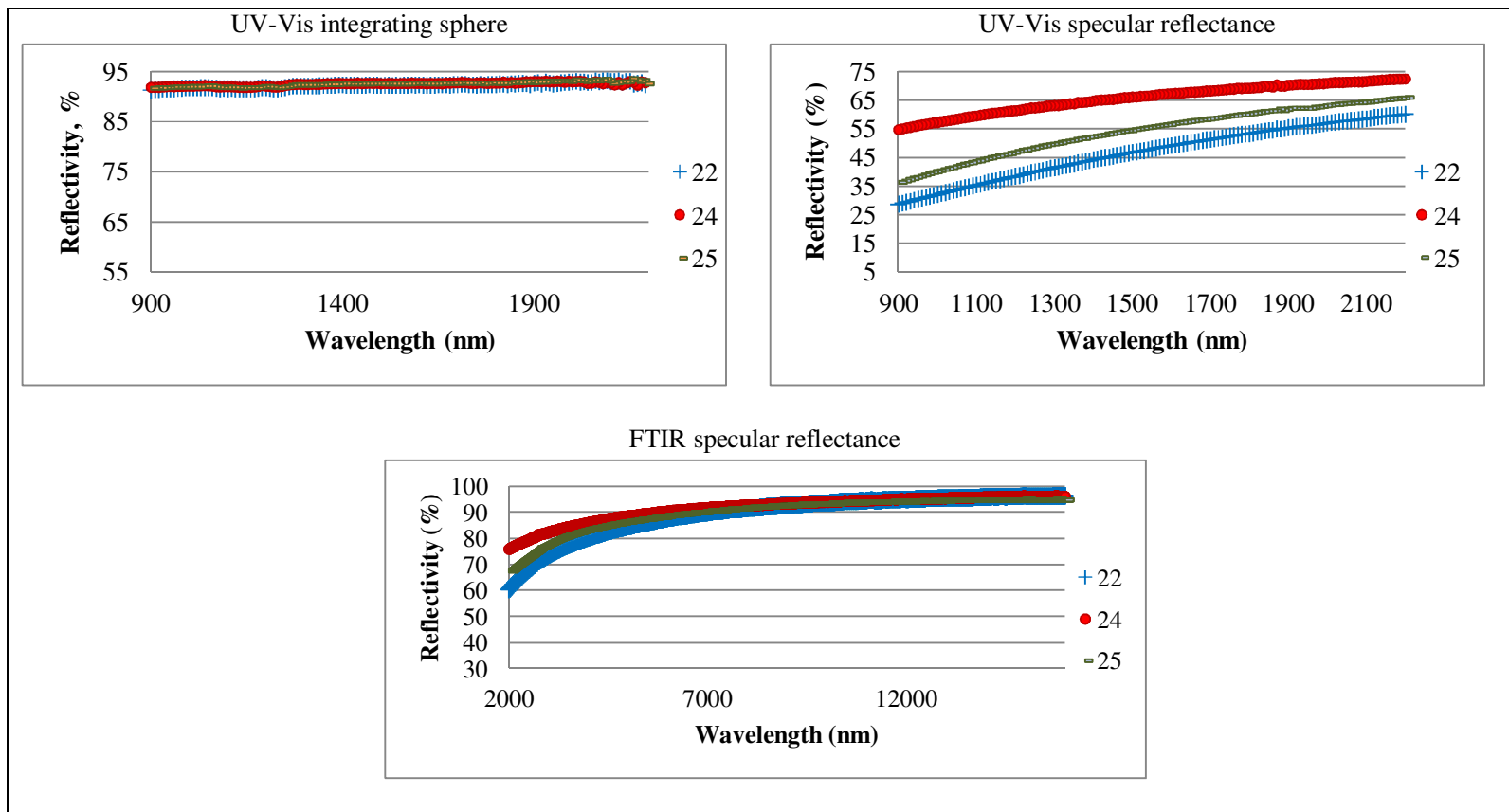
Figure 4.14 Reflectivities products obtained using Bath E by low, medium and high current densities.
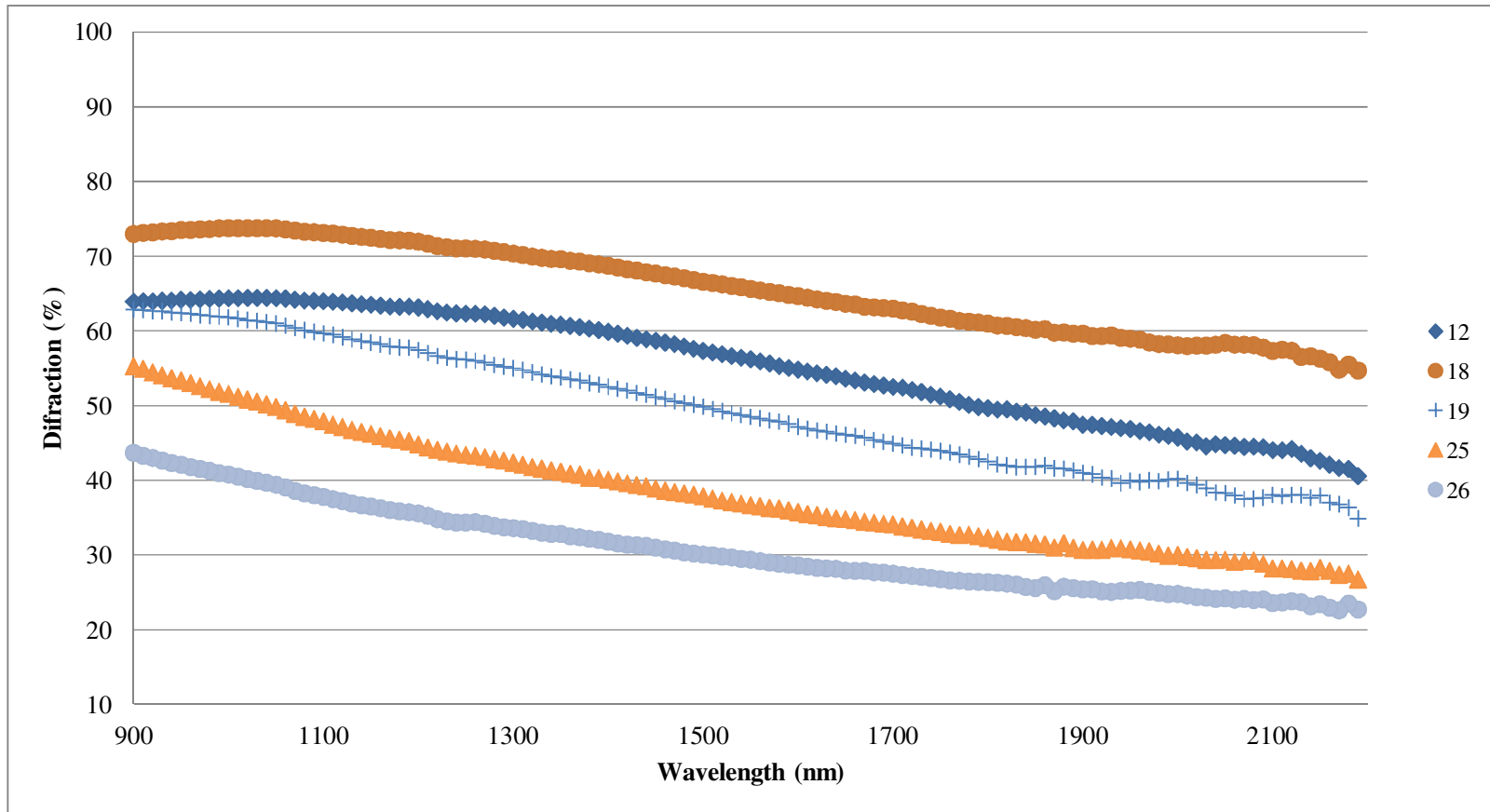
Figure 4.15 Difracted reflections calculated for UV-Vis spectrophometry measurements.

4.1.5 Analysis of Bath Components Before and After Plating

Even though analysis of bath components in two micrometer plating processes was not the major aim of product quality determination setup, these analyses were performed to provide a basis for monitoring bath components. The parameters of fresh baths were first measured. For each plating a new fresh bath was used and after plating copper, parameter change was observed for each bath used.

4.1.5.1 General Parameters

The fact that only 2 microns deposition were done on each polished aluminium sample, there is no major change in parameters. However, general trend in copper cyanide baths (Bath A, B and C) is that pH, conductivity and refractive index increase with respect to the ones of fresh baths (Figure 4.16). In Baths D and E (pyrophosphate baths) on the other hand, refractive index remains constant after plating, regardless of plating under low, medium or high current density. pH and conductivity parameters do not show a general trend in Baths D or E, except conductivity in Bath D, which tends to show a decreasing trend. (The definitions of baths are shown on page 47)

	pH				Conductivity (mS/cm)				Refractive Index (% Brix)			
BATH A	A 12.42	1 12.42	2 12.44	3 12.44	A 153.7	1 154.0	2 155.6	3 155.8	A 15.5	1 16.0	2 16.0	3 16.0
BATH B	B 11.87	4 11.99	5 11.86	6 11.94	B 74.7	4 76.4	5 78.5	6 77.9	B 7.5	4 8.0	5 8.0	6 8.0
BATH C	C 11.70	7 11.70	8 11.71	9 11.69	C 87.7	7 89.1	8 88.7	9 89.1	C 9.5	7 10.0	8 10.0	9 10.0
BATH D	D 8.49	10 8.49	11 8.50	12 8.51	D 70.70	10 70.20	11 70.00	12 70.00	D 10.0	10 10.0	11 10.0	12 10.0
BATH E	E 8.70	13 8.65	14 8.68	15 8.70	E 111.8	13 111.7	14 111.6	15 111.7	E 16.2	13 16.2	14 16.2	15 16.2

Figure 4.16 Variances in general parameters after plating in five different bath compositions.

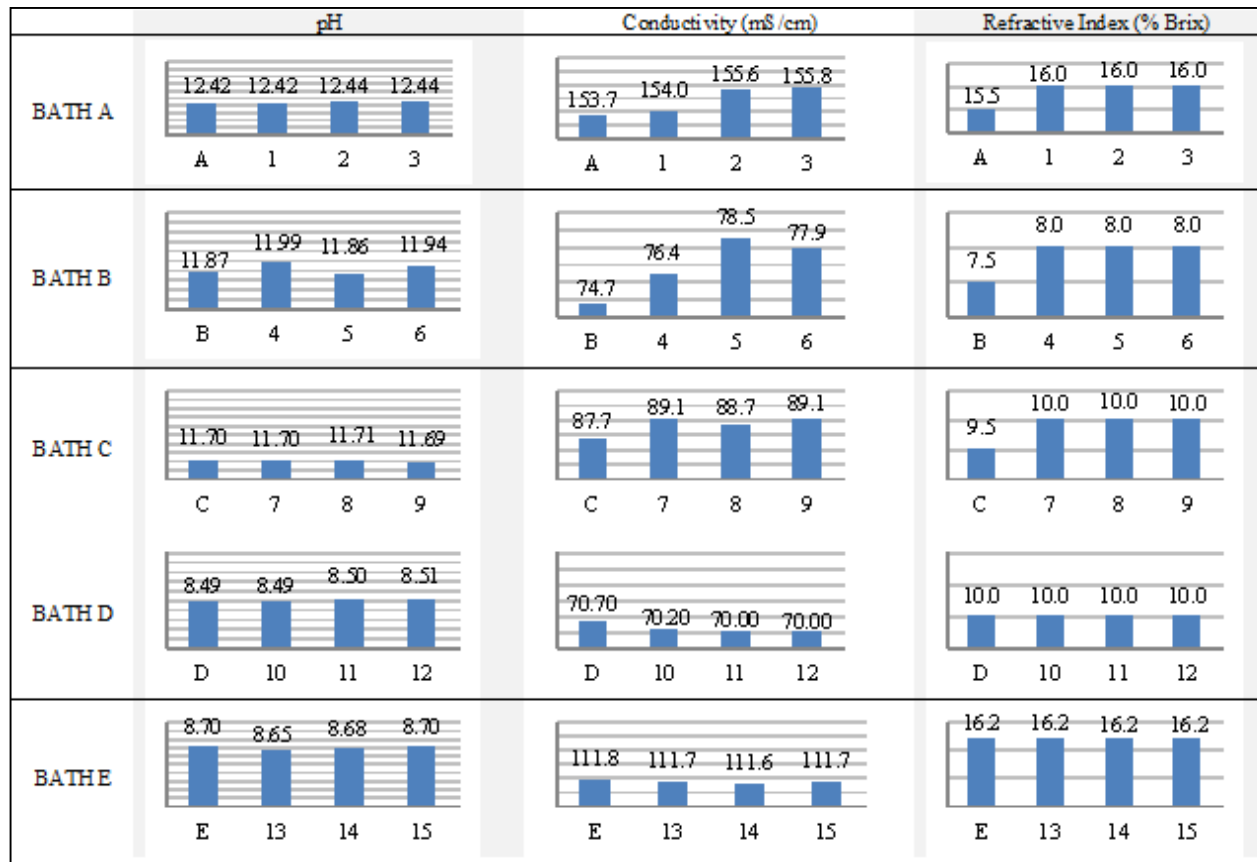During plating, voltages were observed to be fluctuating (Table 4.7). The least voltage fluctuations occur when the lowest current density was applied. Moreoever, the difference between maximum and minimum voltages observed were higher in cyanide baths. This voltage differences were considered as a result of excessive bubble formation in cyanide baths during plating. Excessive bubble formation increases the voltage applied (Demirci and Karakaya, 2007).

Table 4.7 Before, after or during plating measurements of minimum and maximum voltage observed for five different baths formulations.

Bath	Al No	Exp No	Current density	Min Voltage (V)	Max Voltage (V)
A	-	A	-	-	-
	19	1	Low	0.67	0.70
	20	2	Medium	1.06	1.20
	21	3	High	1.29	1.52
B	-	B	-	-	-
	18	4	Low	0.60	0.63
	17	5	Medium	0.98	1.20
	16	6	High	1.52	1.63
C	-	C	-	-	-
	12	7	Low	0.58	0.60
	14	8	Medium	0.99	1.13
	15	9	High	1.53	1.60
D	-	D	-	-	-
	26	10	Low	0.82	0.84
	27	11	Medium	1.10	1.12
	28	12	High	1.29	1.31
E	-	E	-	-	-
	22	13	Low	0.74	0.76
	24	14	Medium	0.84	0.96
	25	15	High	1.09	1.12

4.1.5.2 Changes in Copper Cyanide Bath Components

In Table 4.8 and Figure 4.17 concentrations of the corresponding bath components after titration analysis are shown. Gridline intervals in Figure 4.17 are 1 units for each figure. According to these results, there is no clear trend regarding the change in concentrations. A more detailed discussion is made for four hour long runs using cyanide and pyrophosphate baths.

Table 4.8 Copper, cyanide, Rochelle and carbonate titration results.

Bath	Al No	Exp No	COPPER (g/L)	CYANIDE (g/L)	ROCHELLE (g/L)	CARBONATE (g/L)
A	-	A	36.79	26.65	15.47	5.39
	19	1	38.22	26.52	16.41	6.47
	20	2	38.70	27.11	16.41	6.11
	21	3	38.06	26.91	17.34	5.39
B	-	B	15.61	11.31	17.81	6.11
	18	4	16.08	11.38	15.47	4.67
	17	5	15.93	11.83	15.47	4.31
	16	6	16.56	11.70	17.81	5.39
C	-	C	15.45	11.18	16.41	25.15
	12	7	15.29	11.38	14.53	23.72
	14	8	15.61	11.18	16.88	25.87
	15	9	15.29	11.44	15.47	24.79

Figure 4.17 The changes in copper, cyanide, Rochelle and carbonate concentrations.

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4.1.5.3 Changes in Copper Pyrophosphate Bath Components

Copper concentrations, in general, tend to increase after each plating and pyrophosphate concentrations decrease after depositions end (Table 4.9 and Figure 4.18). Further discussion were done in four hour long deposition characterization.

Table 4.9 Copper and pyrophosphate concentrations.

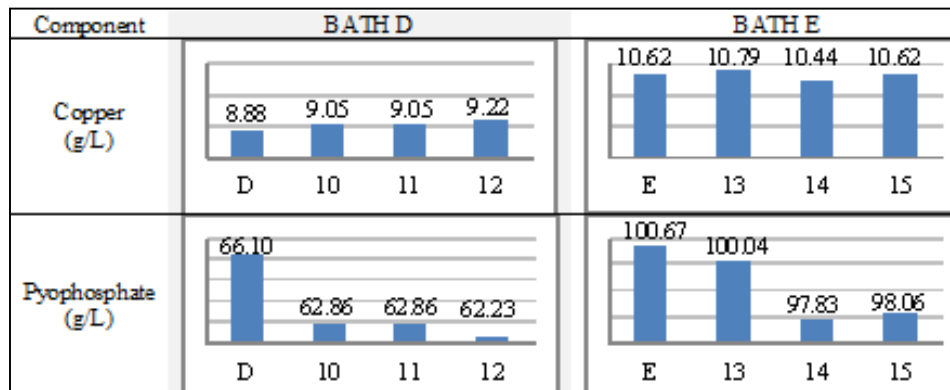| Bath	Al No	Exp No	COPPER (g/L)	PYROPHOSPHATE (g/L)
D	-	D	8.88	66.10
	19	1	9.05	62.86
	20	2	9.05	62.86
	21	3	9.22	62.23
E	-	E	10.62	100.67
	18	4	10.79	100.04
	17	5	10.44	97.83
	16	6	10.62	98.06

Figure 4.18 The changes in copper and pyrophosphate concentrations.

4.2 Bath Composition Oriented Experiments

In bath composition oriented experiments, the parameters of two baths were analyzed for extended electroplating processes; one copper cyanide bath in Bath B composition and one copper pyrophosphate bath in Bath D composition. Therefore, the baths with lower chemical concentrations would have a chance to be compared in terms of bath parameters.

Tracking changes in bath parameters is essentially recommended by most of the pollution prevention guidelines because of the improvements achieved in (USEPA/742/B-97/005, 1997; IAMS and WRATT, 1996; IPPC, 2006; RAC/CP, 2000; WSDoE, 2005):

- extending bath life
- waste minimization
- product quality
- drag-out reduction
- less raw material consumption
- preserving energy

In order to apply one of the priority concerns in waste minimization study, analysis of bath components were done.

The main parameters involved for plating processes are given in Table 4.10. Current densities were the lowest current densities given in applicable ranges in literature to avoid high fluctuations in voltage. Anodes used were oxygen-free anodes as recommended in several sources (Barauskas, 2011; Davis, 2001; Schlesinger and Paunovic, 2010; Tilburg and Chester, 1960; URL12; URL13). Figure 4.19 gives the setup for copper cyanide electroplating and Figure 4.20 gives the setup for copper pyrophosphate electroplating.

Table 4.10 Parameters for extended plating.

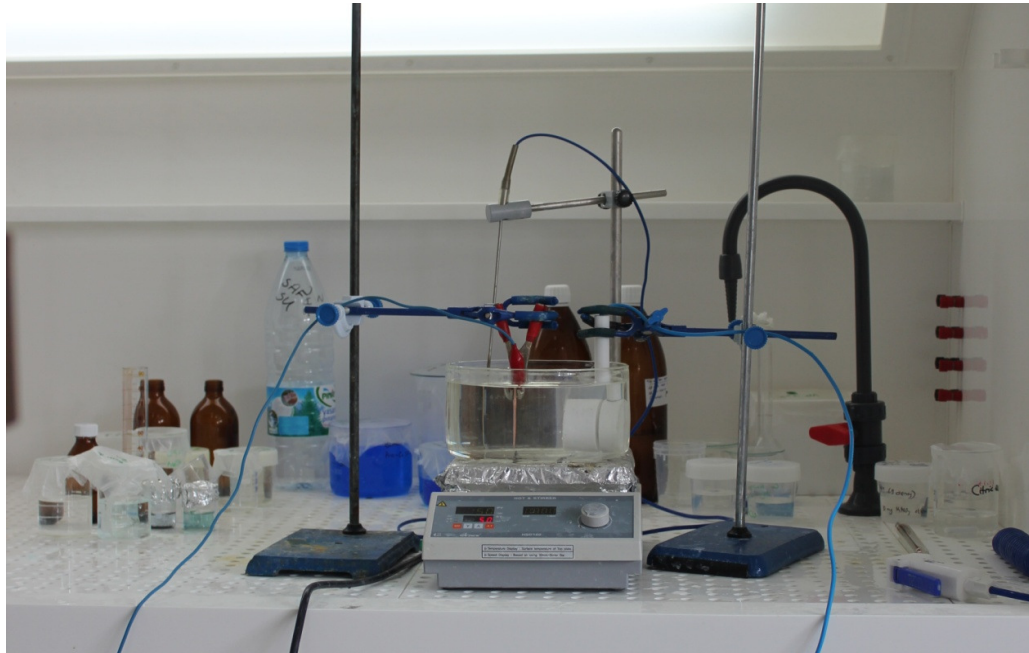| Parameter	Cyanide Bath	Pyrophosphate Bath
Zincated weight of aluminium	20138.4 mg	20145.8 mg
Current density	5 mA/cm^2	6 mA/cm^2
Plating area	7.07 cm^2	7.07 cm^2
Current applied	35 mA	42 mA
Anode area	2 x 18.49 cm^2	2 x 18.49 cm^2
Anode-cathode distance	4 cm	4 cm
Bath composition	Copper cyanide Potassium cyanide Rochelle	Copper pyrophosphate trihydrate Potassium pyrophosphate Potassium nitrate Ammonium hydroxide

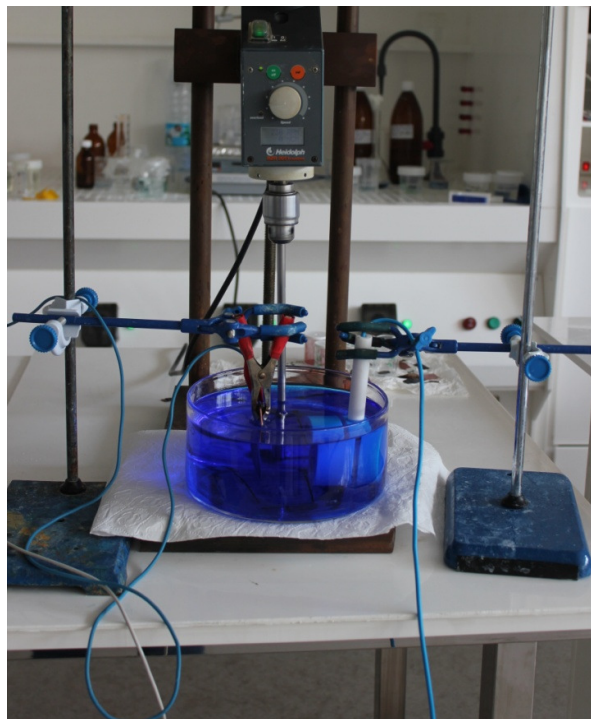Figure 4.19 Copper cyanide electroplating setup.

Figure 4.20 Copper pyrophosphate electroplating setup.

4.2.1 Visual Inspection

During extended plating, cyanide bath evolves hydrogen gasses, leading to bubble formation (Figure 4.21). Hydrogen gasses are formed in cyanide processes as a result of the difference between anode (95-100 %) and cathode (10-60%) efficiencies of these strike baths. In pyrophosphate strike baths these efficiencies are both 100%. Thus, no bubble formation is observed in pyrophosphate baths (Schlesinger and Paunovic, 2010). Eventhough the surface of the base metal was perfectly smoothened, these small bubbles by attaching and detaching during plating causes irregular deposits on the surface, therefore a rough surface is obtained. This is one of the reasons for using additives in bath compositions, especially wetting agents, to reduce surface tension. Better adhesion is provided by using these additives. In Figure 4.22, copper pyrophosphate bath during plating can be observed. Even inside the bath, the product gives a shiny appearance.
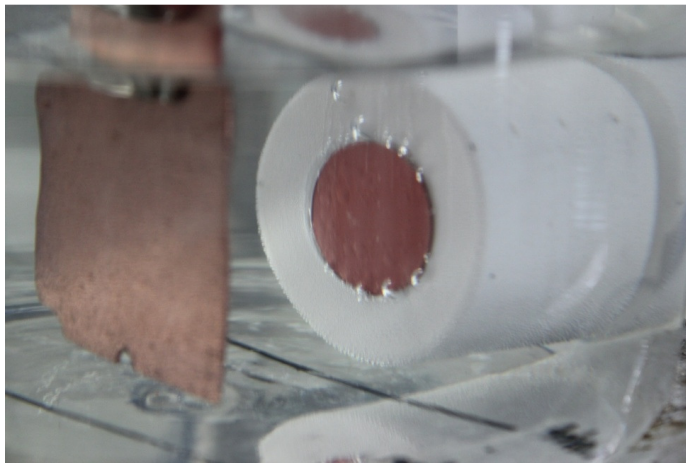
Figure 4.21 Bubbles evolving in copper cyanide plating process.
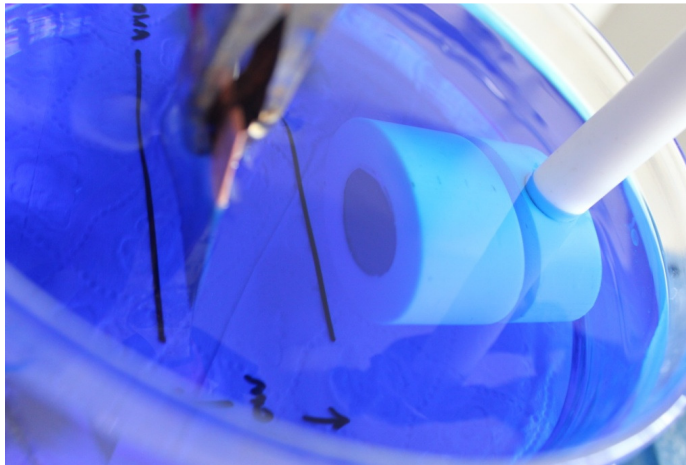
Figure 4.22 Copper pyrophosphate plating process.

In Figure 4.23, photographs after extended plating operations are displayed. The irregularities caused by bubbles in copper cyanide deposition can easily be observed. Luster of pyrophosphate product is one of the major distinctions between the two baths.
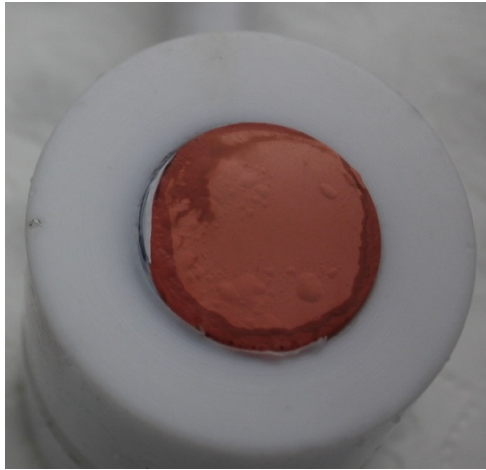
(i) Copper plated with cyanide bath   (ii) Copper plated with pyrophosphate bath

Figure 4.23 Samples plated with copper after 4 hours operation.

In addition to the products, anodes also differ in cleanliness after being used. Anodes used in copper cyanide electroplating bath gets blackened whereas the ones used in copper pyrophosphate baths gets brighter (Figure 4.24).

(i) Anodes after cyanide bath   (ii) Anodes after pyrophosphate bath
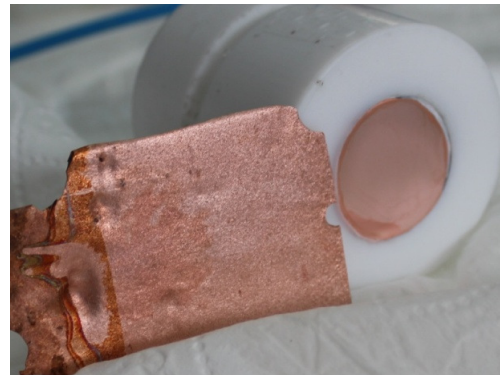
Figure 4.24 Anodes used in 4 hours operation.

4.2.2   Roughness

Roughnesses shows a predictable result because of the bubbles attaching and detaching to the surface to be plated during plating. Average roughness of cyanide bath is 2.52 µm while that of pyrophosphate bath is 0.21 µm (Table 4.11). Pyrophosphate bath is able to conserve the smoothness more in extended plating compared ro cyanide product since roughness obtained after 2µm plating in the same bath was 0.11 µm. Copper cyanide bath, however, is adding more to the roughness as plating goes on. The roughness value obtained for 2 µm plating was 0.26 µm, which is much smoother than the extended plating product in cyanide bath.

Table 4.11 Roughness measurements after four hours of operations.

Bath type	Sample	Ra (µm)	Average (µm)
Cyanide	30	2.91	2.52
		2.13	
Pyrophosphate	29	0.22	0.21
		0.19	

4.2.3   Scanning Electron Microscoper (SEM) Images

Overlapping depositions and almost spiky formations in copper cyanide baths stand out in relief, especially in 10000x magnification for extended plating (Figure 4.25). Smooth copper layer formations in copper pyrophosphate baths are preserved in extended plating Figure 4.26.
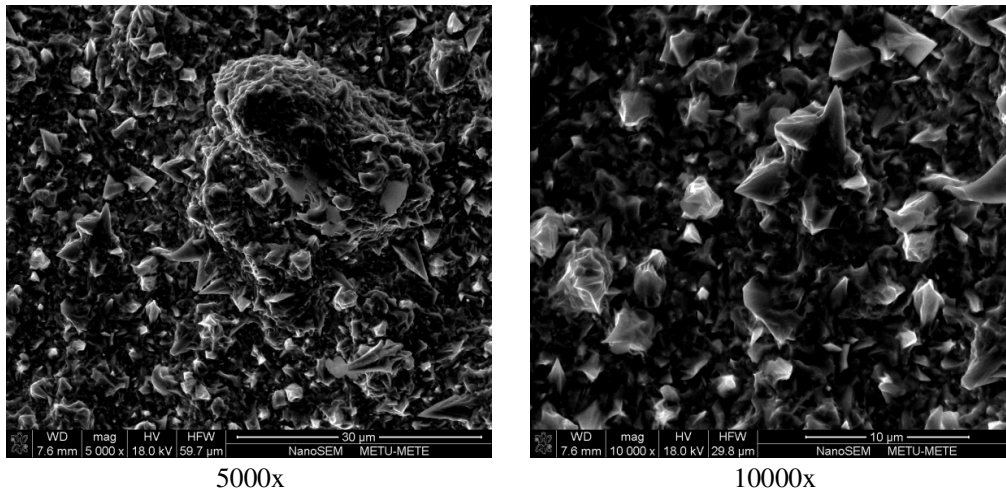
5000x   10000x

Figure 4.25 Copper cyanide product SEM image for extended plating at magnifications 5000x and 10000x.
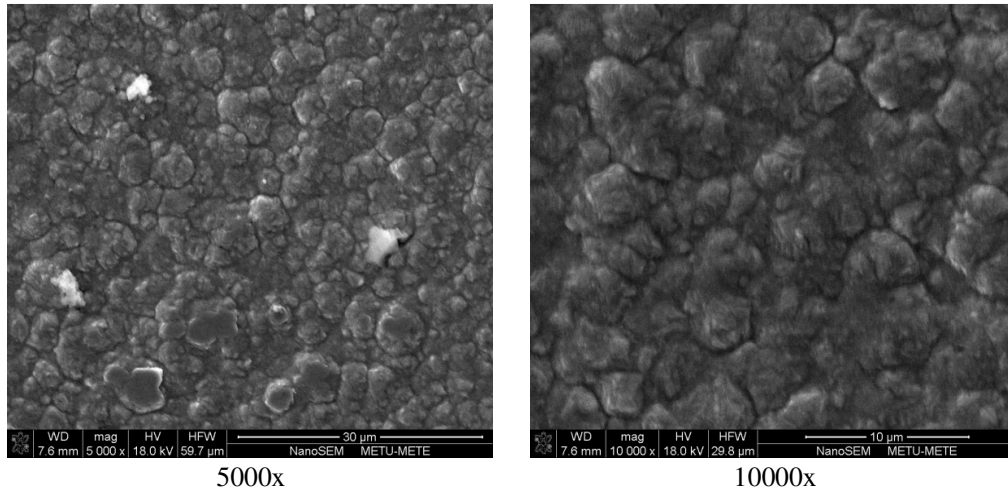
5000x	10000x

Figure 4.26 Copper pyrophosphate product SEM image for extended plating at magnifications 5000x and 10000x.

4.2.4 Reflectivity

The difference between UV-Vis integrating sphere and specular reflectances are higher in the product of cyanide bath than the product of pyrophosphate bath (Figure 4.27). The reason behind is that because of product obtained from cyanide bath has a rougher surface, light could not be reflected as in mirror reflection, but difracted from its reflection angle.

UV-Vis integrating sphere

UV-Vis specular reflectance

FTIR specular reflectance
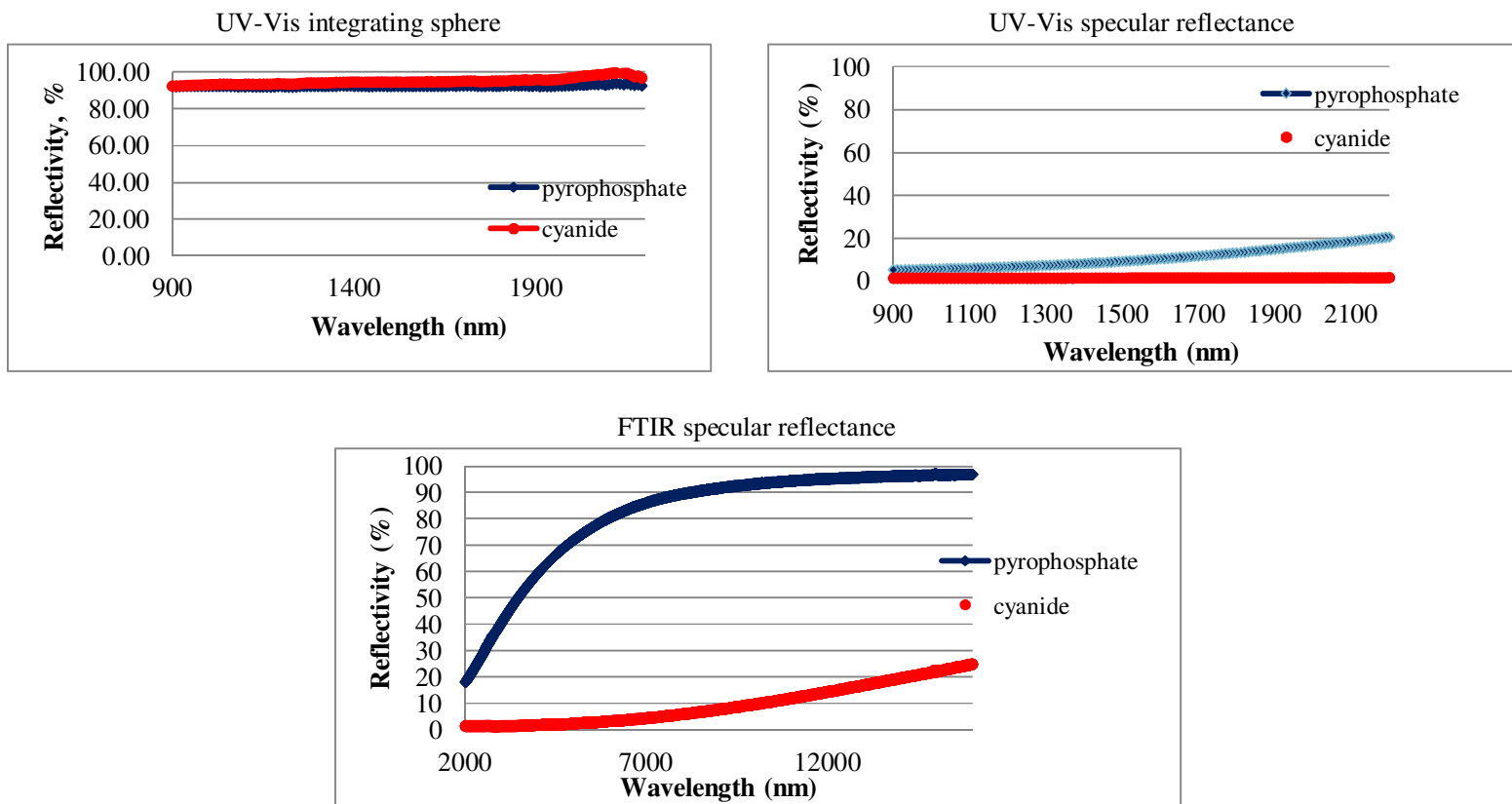
Figure 4.27 Reflectivity measurements of extended plating for cyanide and pyrophosphate bath samples.

4.2.5 Analysis of Cyanide and Pyrophosphate Bath Components Before and After Long Run Plating

4.2.5.1 Changes in Copper Cyanide Bath Components for Long Run Plating

Table 4.12 gives the change in general parameters for thirty minute intervals for extended plating. Figure 4.28 represents these changes in graphical form.

Increasing free cyanide and copper contents in a cyanide bath leads to a raise in conductivity of the solution (Davis, 2001). In Table 4.13 and in Figure 4.29, results of the titrations to determine copper, cyanide, rochelle salt and carbonate are shown for long run of cyanide bath. The results are shown in grams/liter because the exact molecular formula of the compounds in the solution is not known. Among these results, there is an obvious increase in both copper and cyanide content of the bath. The most important point to draw attention is that free cyanide and copper contents were within the acceptable ranges when the bath was first set-up. Table 2.1 gives the ranges for copper content as 11-21 g/L with a typical value of 16 g/L and cyanide content as 6-11 g/L with a typical value of 9 g/L. By analysis, copper content was found to be 15.45 g/L and free cyanide was 11.31 g/L when the bath was first made-up. The point is that there needs to be another driving force for increasing free cyanide content; that is temperature. Free cyanide content at elevated temperatures is more than lower temperatures because of the dissociation of metal-cyanide complex to free cyanide at the temperatures needed for activation of such dissociation (Kojima et al., 2005). Excess free cyanide increases anode efficiency, leading to more copper dissolution into the bath and cathode become unable to bind all copper ions in the solution, due to efficiency of cathode being lower than 100%. As a result copper tends to accumulate in the bath (Schlesinger and Paunovic, 2010).

In copper cyanide bath, there is a trend towards to an increase in voltage. The overall voltage applied by power supply can be expressed as follows (URL14) :

$$V_T = E_0 + \eta + iR$$

where;
V_T = overall voltage
E_0 = reaction voltage
η = overpotential for anode and cathode
iR = resistivity voltage

According to the formula presented above, voltage increase may be a result of three factors: reaction voltage, overpotential or resistivity voltage increase. Resistivity voltage, in this case, is rather decreasing because of the increasing copper and cyanide concentrations in the solution, thus the increasing conductivity. Overpotential is not expected to change because it is related to the potential required to start the redox reactions. Therefore, the increase in voltage is most probably due to the reaction potentials. As time passes more metal cyanide complexes are predicted to be decomposed, hence voltage increases. The concentration changes are also represented by measurements made by refractometer.

Rochelle salts are predicted to form temporary complexes with copper ions in electroplating baths via interacting with electrolysis products (Schlesinger and Paunovic, 2010). The fluctuations in Figure 4.29 (iii) may be a result of bonding and non-bonding of these salts. Schlesinger and Paunovic (2010) states also that use of Rochelle salts helps to improve the quality of the plating by the help of salt formation likely to be present in the cathode film which means it probably participates in the structure of the copper deposition. To clearly decide on whether any participitation in deposition is present, longer period continuous plating analysis needs to be performed. Since, in four hours net change in Rochelle concentration is about just 1 g/L with fluctuations over time.

Even if salts of carbonates are not included in the bath make-up, they can be absorbed from the atmosphere or they can be formed as a result of cyanide hydrolysis in the bath (Schlesinger and Paunovic, 2010). Carbonate is a parameter that build up in the bath as shown in Figure 4.29 (iv). However, the increase is not linear. It is probably as a sign of interacting species with carbonate.

Table 4.12 The change of general parameters in extended process for cyanide bath.

Exp. no	Time (min)	pH	Conductivity (mS/cm)	Refractive index (Brix %)	Voltage (V)
16	0	11.56	75.8	7.8	0.55
17	30	11.65	77.4	8.0	0.56
18	60	11.75	78.7	8.2	0.59
19	90	11.78	79.9	8.2	0.58
20	120	11.87	82.9	8.3	0.60
21	150	11.93	82.6	8.5	0.60
22	180	11.95	83.6	8.5	0.60
23	210	11.98	85.1	8.8	0.60
24	240	12.04	88.6	9.0	0.62

Table 4.13 Results of titration analysis of cyanide electroplating bath.

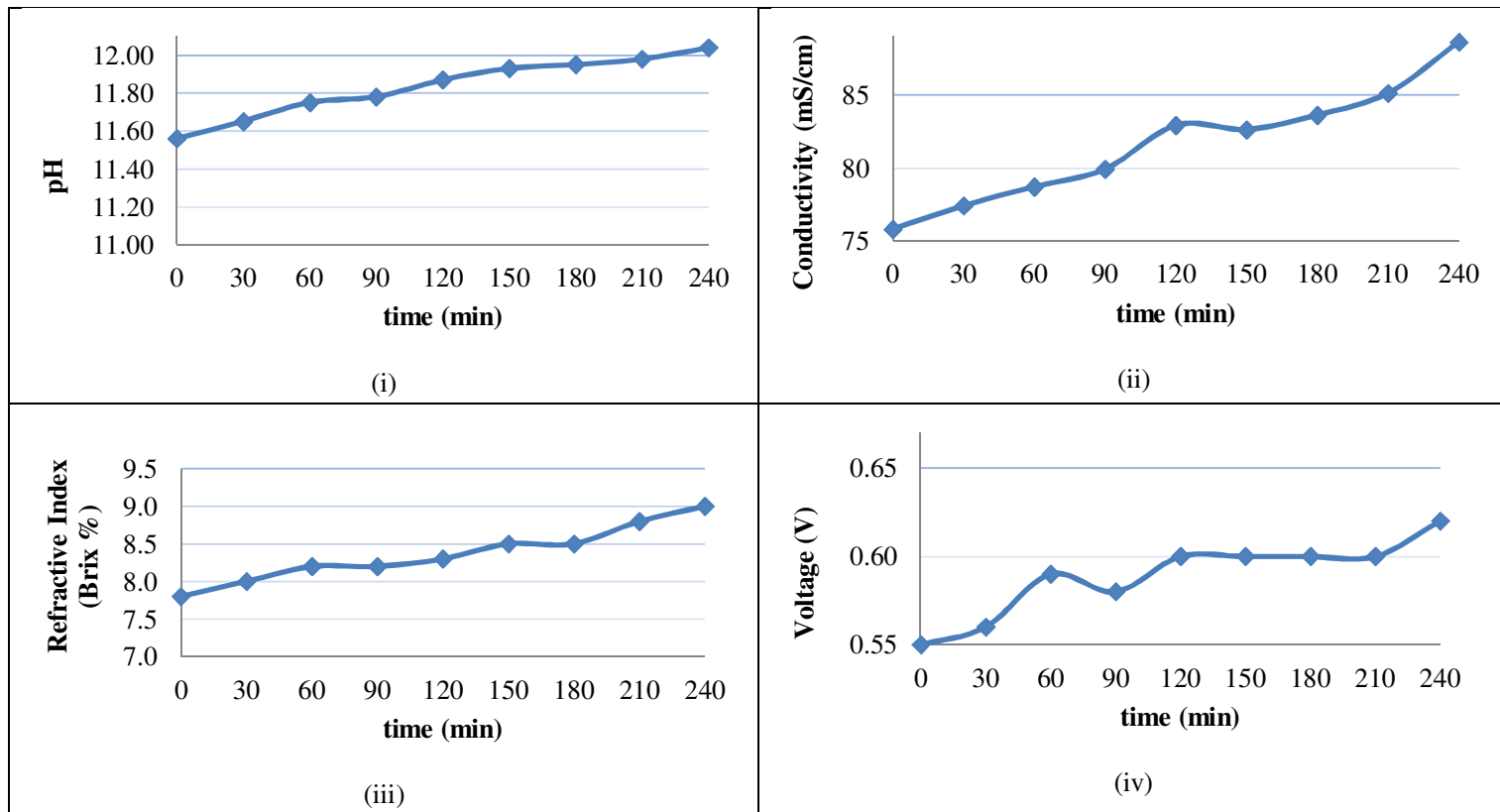| Exp. no	Time (min)	COPPER (g/L)	CYANIDE (g/L)	ROCHELLE (g/L)	CARBONATE (g/L)
16	0	15.45	11.31	17.34	8.98
17	30	16.56	11.44	17.81	8.62
18	60	16.56	11.64	16.88	8.98
19	90	16.56	11.64	16.88	8.62
20	120	17.20	11.70	16.88	9.34
21	150	17.52	12.03	15.94	8.62
22	180	17.52	11.96	15.00	9.70
23	210	18.15	12.03	15.94	9.34
24	240	18.15	12.61	16.41	9.34

Figure 4.28 Four hours plating with cyanide bath (i) pH, (ii) conductivity, (iii) refractive index, (iv) voltage.
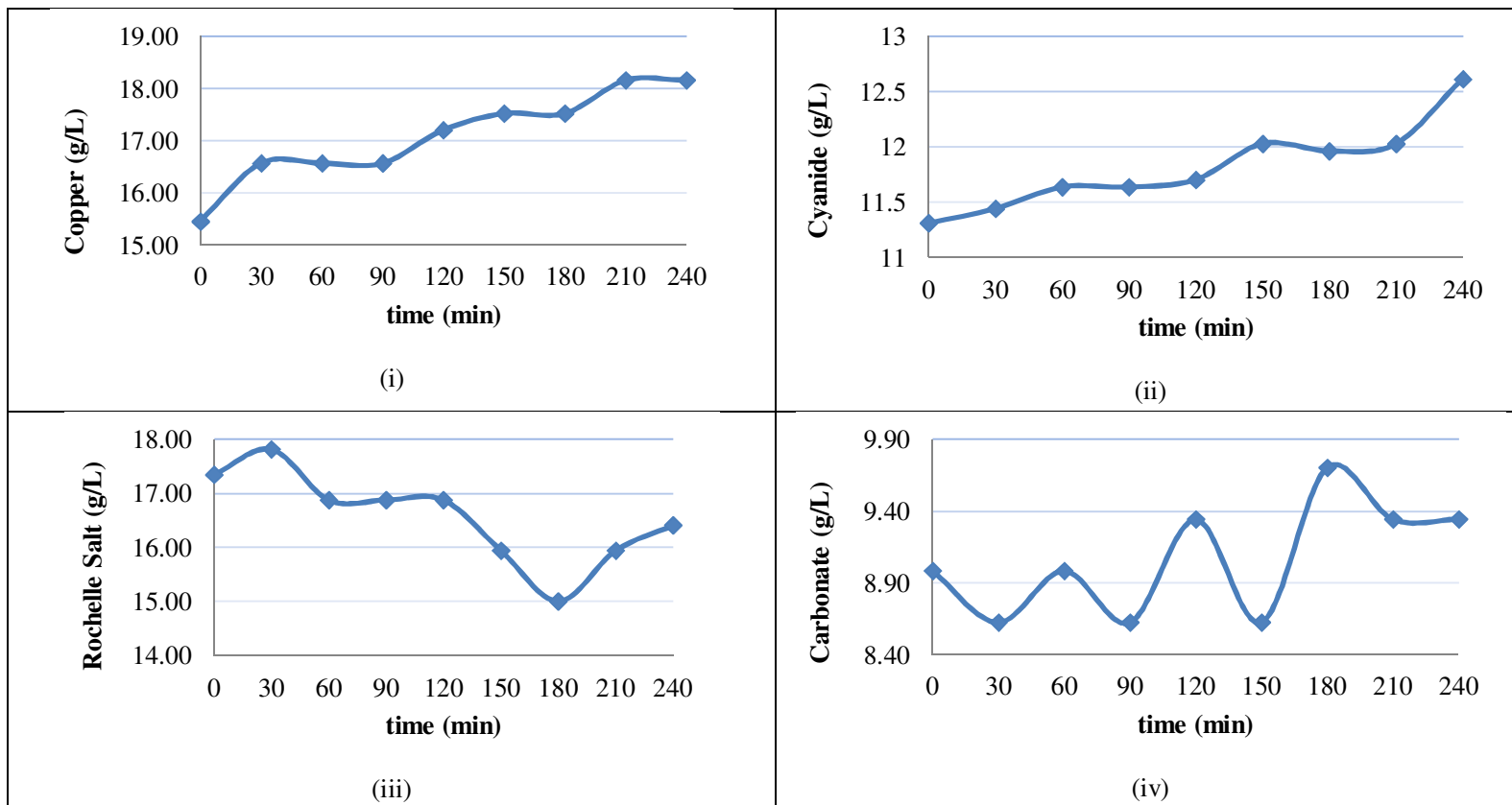
Figure 4.29 Bath composition change during four hours plating with cyanide bath (i) copper, (ii) cyanide, (iii) Rochelle (iv) carbonate.

4.2.5.2 Changes in Copper Pyrophosphate Bath Components for Extended Plating

In Table 4.14, results of monitoring the parameters in copper pyrophosphate bath are given. Conductivity of the bath is increasing by 2 mS/cm during extended plating. Related increase is 12.8 mS/cm in copper cyanide plating bath. Likewise, pH and refractive index of the solution are balanced more in pyrophosphate bath. These two parameters are not steadily increasing as in cyanide bath. pH value fluctuates over time between 8.45 and 8.39 and refractive index which is a measure of concentration change in the solution is 9.8 % when the bath is first made-up and remains constant at 10% throughout the plating operation for four hours.

Average copper concentrations were observed to change between 9.22 and 9.75 g/L over four hours. 9.22 g/L copper concentration is observed at time 0, 90 min and 240 min. Pyrohosphate concentrations are also fluctuating between 61.36 and 62.94 g/L. The changes in both copper and pyrophosphate concentrations are not considered as significant changes due to the fact that titrations are not very sensitive measurement methods for plating operations in which grams per liter concentrations are being used to form a plating bath composition.

In conclusion, an outcome that states pyrophosphate bath is more stable than cyanide bath can easily be made according to the measurements of general parameters like pH, conductivity, refractive index, voltage and titration analysis results. These results suggest that copper ions from anodes dissolves in solution, then goes and get deposited onto cathodes at 100% current efficiency, without accumulating in the bath.

Table 4.14 The change in parameters of extended process for copper pyrophosphate bath.

| Exp. no	Time (min)	pH	Conductivity (mS/cm)	Refractive index (Brix %)	Voltage (V)	COPPER (g/L)	PYROPHOSPHATE (g/L)	Cu/P_2O_7
25	0	8.45	69.4	9.8	0.92	9.22	61.36	6.65
26	30	8.40	70.7	10	0.90	9.75	62.94	6.46
27	60	8.39	70.7	10	0.88	9.57	62.70	6.55
28	90	8.41	71.3	10	0.88	9.22	61.36	6.65
29	120	8.42	71.5	10	0.90	9.40	61.59	6.55
30	150	8.42	71.2	10	0.92	9.40	62.46	6.65
31	180	8.41	71.3	10	0.94	9.40	62.46	6.65
32	210	8.42	71.3	10	0.96	9.57	61.83	6.46
33	240	8.40	71.4	10	0.98	9.22	62.23	6.75
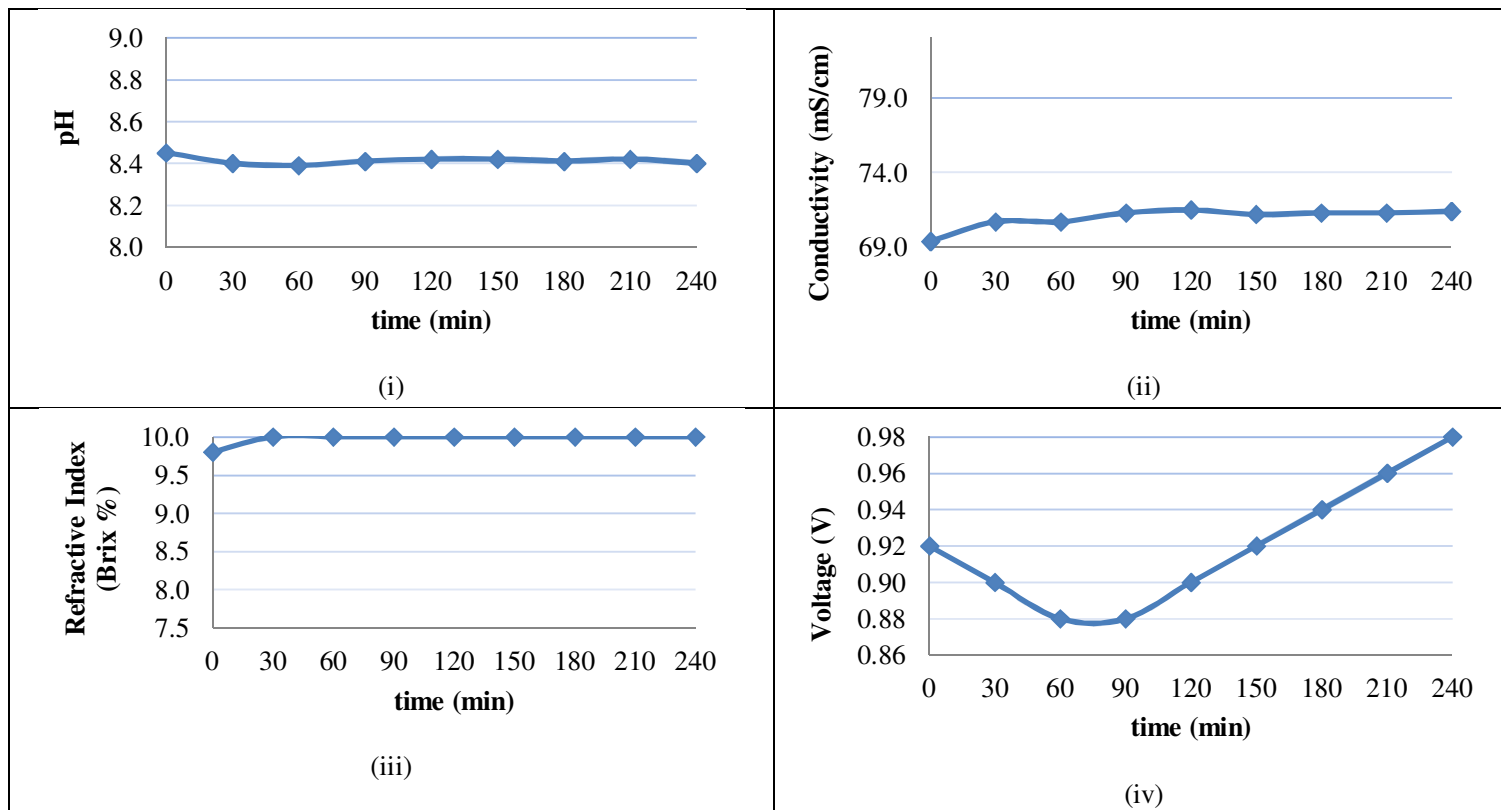
Figure 4.30 Extended plating with pyrophosphate bath (i) pH, (ii) conductivity, (iii) refractive index, (iv) voltage.
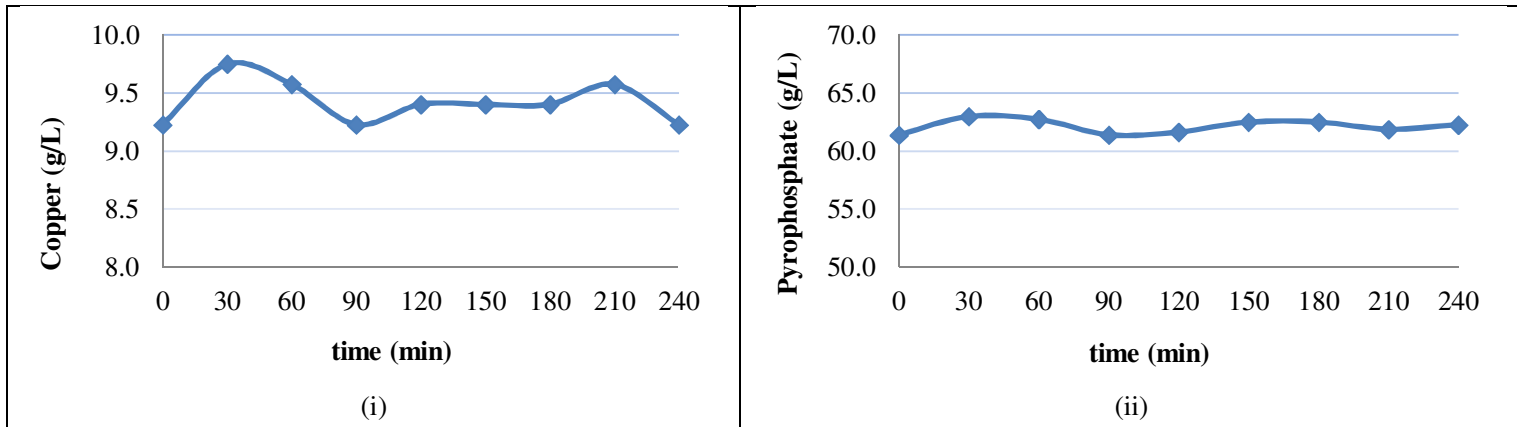
Figure 4.31 Bath composition change during extended plating with pyrophosphate bath (i) copper, (ii) pyrophosphate.

4.3 Discussion on Pollution Prevention Aims of the Study

In the electroplating industry, recipes of the bath formulizations are supplied by chemical manufacturers. Applications are done following the recommendations in these recipes. However, chemical suppliers may recommend high amount of chemical consumption than required for a specific process or the bath parameters may need an adjustment depending on the process. Moreoever, a manufacturer may heavily rely on the bath type in which much more experience was accumulated previously, thus, is the more advisable for the manufacturer. This study has revealed that the guidelines of pollution prevention strategies present an excellent roadmap to optimize, and even develop a new production method. Because, as well as minimizing the waste, they are the tools for setting a completely controlled process. This study has initiated from the two waste minimization strategies: (1) chemical substitution assessment and (2) bath-life extension. Following sections include the discussion on pollution prevention approaches of the results.

4.3.1   Evaluation of Substitution of Cyanide Baths

Possibility of the substitution of cyanide baths has two different approaches:

(1) substitution with low concentrated cyanide baths,
(2) substitution with pyrophosphate baths.

In the first substitution approach, the products of the formulization of the commercial brand is compared with the products composed in the low concentrated baths. In terms of visual appearances of the plated products, product number 20 which is obtained from high concentrated manufacturer bath (Bath A) by medium current density can be replaced with the one obtained from Bath B (product number 16, by high current density). The average roughnesses before cleaning for all current densities applied as follows:

Bath A - 0.133µm
Bath B - 0.140 µm
Bath C - 0.130 µm

Therefore, in terms of roughness measurements; Bath A can be replaced by Bath C and Bath B, which have close average roughness values. Moreover, when SEM images are evaluated, the almost spiky nature of the cyanide deposition can be smoothened by carbonate addition to the system. If a smoother surface is desired, Bath A can be replaced by Bath C. Also, the percent deviation of UV-Vis integrating sphere measurements revealed that for medium and high current applications on Bath A (19, 20% respectively) can be replaced with Bath C high current application (19%). In this study, another reflectivity measurement, that is specular reflectance, is desired to be as high as possible. The highest mirror-like reflection in Bath C (60.57%) and in Bath B (57.56%) are very close to the one obtained from Bath A (58.88%). FTIR specular reflectances are also supporting the replaceability of Bath A with either Bath B or C.

In the second substitution approach, the visual appearances of pyrophosphate products shows that the extra cleaning step can be eliminated by pyrophosphate bath use. If this step is being performed by acids, this is an additional gain considering pollution prevention. If the brightness is of greater concern, cyanide products do not offer as bright surfaces as the pyrophosphate products. Therefore, substitution is possible in terms of comparison of brightness of products. When SEM images are viewed, pyrophosphate bath products have more defect free and more smooth surfaces which is very advantegeous in terms of eliminating the additives that provide more smooth and less defective product formation. These additives are commonly organic in nature and they readily breakdown in plating baths. This fact represents an environmental perspective, since the breaking down of these particles are changing the chemistry of the bath and causes more waste formation and more sludge because of frequent filtering of the organics from the bath. The replenishment of the organics in the bath is related with the raw material consumption which is also a source reduction issue. Another product quality parameter, reflectivity, has a trend to have higher values on the pyrophosphate products, thus, if the reflectivity is a crucial parameter for the process and if it is expected to be as high as possible, then pyrophosphate baths can take the place of cyanide baths.

As a result, formulization of the commercial brand can be replaced with several alternatives depending on the desired product quality. Figure 4.32 shows these substitution alternatives and the corresponding chemical reductions (given in per liters) achieved by these substitutions (green arrows indicate the bath substitution with a pyrophosphate bath and the red arrows indicate the bath substitution with a cyanide bath).
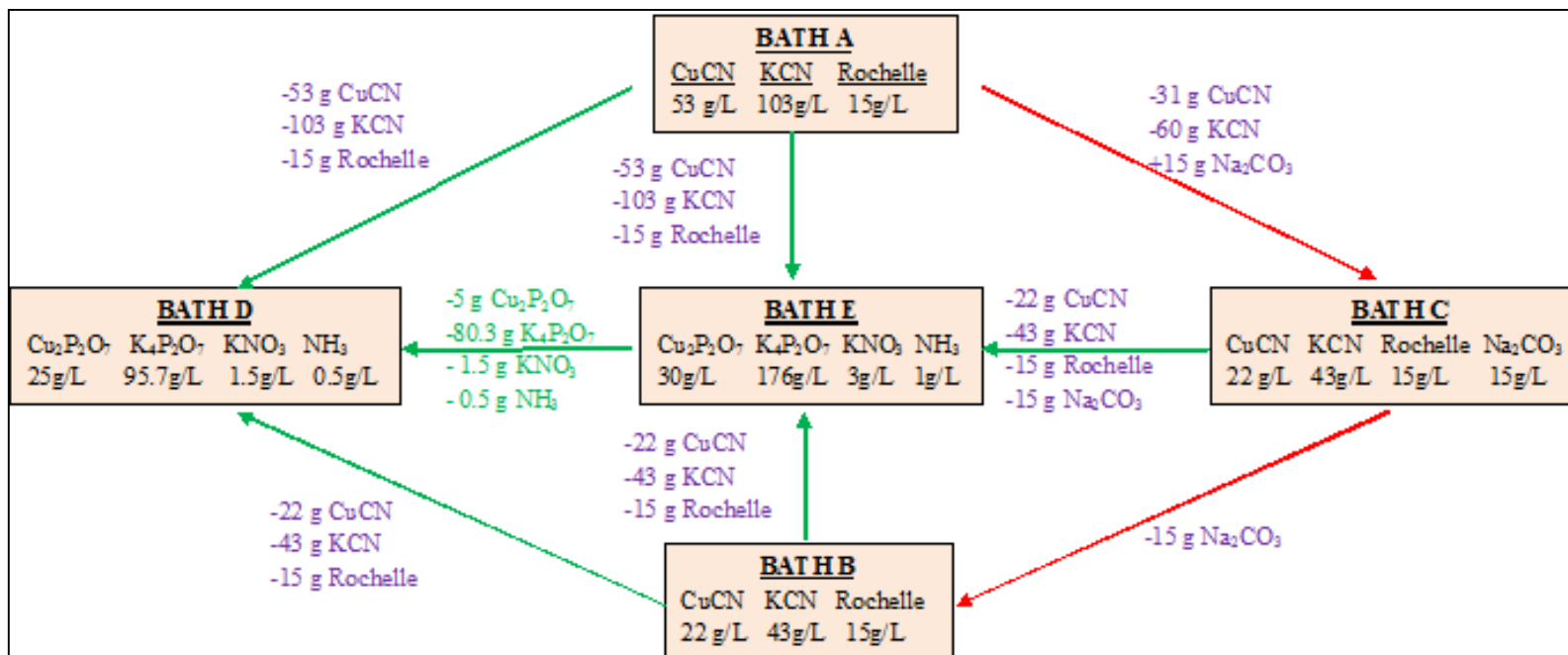
Figure 4.32 Substitution alternatives of the formulization of the commercial brand (changes are given in per liter).

4.3.2 Lifetime of Baths

The bath parameters were analyzed in order to have information about major changes in parameters during four hours of plating. These analysis revealed that copper pyrophosphate bath has a more stable bath composition during this period. Therefore, pyrophosphate bath without additives are more sustainable compared to the additive-free cyanide bath. The parameters of the cyanide baths are distinctively changing compared to the pyrophosphate baths. As a result, the lifetime of copper strike plating bath is increased by using pyrophosphate bath in this laboratory scale application.

4.4 Processes Before Plating

Filtration: During bath filtration, it was observed that some components of the baths retained at the surface of the filter paper which should not be underestimated. Therefore, filtration is an unavoidable fact for the preparation of baths.

Pretreatment - Zincating: In trial experiments (results are not shown), aluminium was used to be zincated by a commercially ready-to-use zincate solution. However, aluminium zincating was seemed to be unsuccessful. Zincate solution was then prepared as given in the standarts. It was determined that commercial ready-to-use zincate solution is not a proper way to zincate the surface of the aluminium.

Another fact is that zincate solution undergoes decomposition very rapidly with the help of drag-out from sodium hyroxide and acid cleaning stages, leading to blackening of the aluminium which can be easily confused with zincate deposition on the aluminium. This blackening is thought to be directly effecting the plating quality. In Figure 4.33, first two depositions were held after unclean zincate solution application and the last one was plated after the zincate solution had changed with clean one. The deposition of copper seems to be reflecting the underlying blackened surface as a result of decomposition of zincate solution. This factor needs to be further investigated.

Figure 4.33 Depositions before and after changing zincate solution.

4.5 Costs of Preparation of Baths

The costs of preparation of the baths were calculated and presented in Table 4.15. All chemicals used in cost calculation were high graded. Low concentrated cyanide bath (Bath B) costs almost three times more than the low concentrated pyrophosphate bath. Therefore, the make-up prices for pyrophosphate baths are lower than for cyanide baths. Non-cyanide baths are mentioned to cost more than cyanide baths (USEPA/742/B-97/005, 1997). However, the costs of using a bath should be calculated by taking account cumulative costs for each different application (make-up costs, environmental costs as disposal, effects, etc.) to be informative about the total cost of using a bath.

Table 4.15 Make-up costs for baths.

	Chemical	Grade	Unit Price	Concentration	Chemical Costs
BATH A	CuCN	≥99.0%	45 €/250 g	53 g/L	9.54 €/L
	KCN	≥98.0%	63.5 €/100 g	103 g/L	65.41 €/L
	Rochelle	99.0%	27.9 €/100 g	15 g/L	4.19 €/L
					79.13 €/L
BATH B	CuCN	≥99.0%	45 €/250 g	22 g/L	3.96 €/L
	KCN	≥98.0%	63.5 €/100 g	43 g/L	27.31 €/L
	Rochelle	99.0%	27.9 €/100 g	15 g/L	4.19 €/L
					35.45 €/L
BATH C	CuCN	≥99.0%	45 €/250 g	22 g/L	3.96 €/L
	KCN	≥98.0%	63.5 €/100 g	43 g/L	27.31 €/L
	Rochelle	99.0%	27.9 €/100 g	15 g/L	4.19 €/L
	Na_2CO_3	≥99.0%	65.7 €/500 g	15 g/L	1.97 €/L
					37.42 €/L
BATH D	$Cu_2P_2O_7.3H_2O$	100.0%	88.6 €/500 g	25.0 g/L	4.43 €/L
	$K_4P_2O_7$	97.0%	35.6 €/500 g	95.7 g/L	6.81 €/L
	KNO_3	≥99.0%	77.7 €/500 g	1.5 g/L	0.23 €/L
	NH_3	28.0-30.0%	64.2 €/1 kg	0.5 mL/L	0.02 €/L
					11.50 €/L
BATH E	$Cu_2P_2O_7.3H_2O$	100.0%	88.6 €/500 g	30 g/L	5.32 €/L
	$K_4P_2O_7$	97.0%	35.6 €/500 g	176 g/L	12.53 €/L
	KNO_3	≥99.0%	77.7 €/500 g	3 g/L	0.47 €/L
	NH_3	28.0-30.0%	64.2 €/1 kg	1 mL/L	0.04 €/L
					18.36 €/L

CHAPTER 5

CONCLUSIONS

This study aimed to apply two different priority one pollution prevention strategies on a laboratory scale production of copper deposition on polished aluminium metal, that were; cyanide bath substitution and bath-life extension by monitoring bath parameters. Because of their applicability to form strike layers, copper cyanide and copper pyrophosphate electroplating baths were used.

First experimental series were conducted for testing the plating quality of five copper strike baths. Copper pyrophosphate strike baths were found to be resulting in brighter deposits than copper cyanide strike baths, with a more clean surface. Results of roughness and reflectivity measurements were also supporting the brightness level of these deposits. SEM images revealed that pyrophosphate bath also leaves smoother deposits as desired and cyanide bath products having major failures as nodules, cracks, etc. even in 2 µm deposits. The product quality is not strictly dependent on different current density applications. It also provides more or less the same product quality in plating different bath compositions. Bubble formation is assumed to be the greatest issue in copper cyanide electroplating baths. Additive use is strongly necessary to decrease surface tension, to increase the brightness of the plated copper and to increase the levelling ability of cyanide baths.

The results of all product quality determination experiments revealed that the formulization offered by the commercial brand can be substituted with other bath formulizations according to the product quality which is desired. The commercial brand offers more chemical consumption. If this bath is replaced with Bath B, 31 g CuCN and 60 g KCN are eliminated for per liter of bath. If this substitution is done with Bath C, 15 g Na_2CO_3 is added to the solution, but the same reduction as in the case for Bath B substitute is achieved in terms of CuCN and KCN for a liter of solution. The intended substitution alternative of Bath A is with either Bath D or Bath E which are pyophosphate baths. By both of the two replacements 53 g CuCN, 103 g KCN and 15 g Rochelle is eliminated in making up a liter of solution which ends up with a complete shift in a cyanide based formulization. The difference between Bath E (high concentrated) and Bath D (low concentrated) are 5 g $Cu_2P_2O_7$, 80.3 g $K_4P_2O_7$, 1.5 g KNO_3 and 0.5 g NH_4 per liter bath. Each of the pyrophosphate formulization is found to be applicable for copper strike plating and the less concentrated one is offered in terms of raw material conservation.

As regards to the second aim; pH, conductivity, refractive index and voltage were used as the general parameters in monitoring baths. Copper, cyanide, Rochelle salt and carbonate for cyanide bath and copper and pyrophosphate for pyrophosphate baths were measured. It was very suprising that even most sources defines cyanide baths as more manageable than those containing pyrophosphate, general parameters, copper and cyanide compositions of cyanide bath were markedly changed for four hours plating compared to copper and pyrophosphate content in pyrophosphate bath. Therefore, consistent product formation was carried a step further with a consistent bath chemistry for the pyrophosphate bath. Moreover, pyrophosphate bath without additives are more sustainable compared to the additive-free cyanide bath. As a result, the lifetime of copper strike plating bath is increased by using pyrophosphate bath in this laboratory scale application.

Cost calculation for making up the baths showed that low concentrated cyanide bath (Bath B) costs almost three times more than the low concentrated pyrophosphate bath (Bath E). However, the costs of using a bath should be calculated by taking account cumulative costs for each different application (make-up costs, environmental costs as disposal, effects, etc.) to be informative about the total cost of using a bath.

The outcomes gained from this study are as follows:
- Copper pyrophosphate strike bath can be successfully plated on polished aluminium metal.
- Copper cyanide strike baths can be replaced by copper pyrophosphate strike baths for the product in concern.
- Use of additive-free pyrophosphate solution removes the necessity to use problematic additive breakdown issue in electroplating of copper on aluminium.
- Good adhesion on aluminium, good levelling ability and brighter surfaces were achieved resulting in better product quality.
- Product quality is standardized.
- A further cleaning operation (i.e. citric acid cleaning) needed for cyanide bath products are eliminated by pyrophosphate bath use.
- Because of eliminating bubble formation, rejected parts are reduced so the waste generation. Therefore, the costs related with laboratory works are decreased.
- Pyrophosphate bath life is decided to be longer in terms of tracking of critical parameters.
- Compared to cyanide baths, lesser amounts of chemicals needs to be consumed resulting in conservation of raw materials.
- Energy, a natural resource, is conserved while plating at room temperature in pyrophosphate baths, when compared to cyanide baths which are operated at 50-55°C.
- Human and environmental health and safety is improved by the elimination of copper plating using cyanide bath.

In conclusion, copper pyrophosphate baths can be used instead of copper cyanide baths resulting in both minimization of a hazardous, troublesome waste stream coupled with safer working conditions.

CHAPTER 6

RECOMMENDATIONS

In order to further investigate the subject several recommendations can be made as follows:

- Zincate bath can be optimized per zincated surface area.
- The effect of zincating step on copper pyrophosphate plating can be studied.
- Rinsing stage design can be done to eliminate excessive water consumption in laboratory.
- Deionized water should be used to avoid any other interaction that will affect the bath performances.
- Experiments can be conducted to demonstrate the effect of filtration on plating quality.
- One cyanide and one pyrophosphate bath can be runned for longer periods than four hours and bath parameters can be analyzed until pyrophosphate bath shows considerable changes in bath parameters.
- Cyanide strike bath can be operated at room temperature and the resultant product quality can be determined.
- The effects of including additives can be investigated for both bath types.

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