ELECTRO-CHEMICAL PLATING OF PLASTIC MATERIALS

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by

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ABSTRACT

The main objective of this study is to electroplate different plastic types of thermoplastic as (ABS and polystyrene) and thermosetting as (epoxy-fiberglass and phenolic) and to study the best graphite conductive colloid from particles size and binding agents to deposit graphite layer onto plastic surface. This process can make copper electroplating possible without intermediate conductive copper film deposited via electroless copper by using direct copper plating.

There are two reasons for using a copper layer. It makes the plastic component appear very bright because of its leveling and brightening properties. Furthermore, the copper layer is very soft and ductile and can compensate for the different thermal expansions between metal and plastic.

The essential variables in present work from graphite particle size, binding agent on plastic types, concentration of copper sulfate, current density, plating time and temperature of acid copper solution have two main effects:

a. Direct effect of the tests is the properties of the metal deposit on the plastics, as thickness, adhesion, surface roughness, porosity, and scratch resistance.
b. Direct effect on the performance for cathodic current efficiency has been tested for four major factors that affect the plating process. These were concentration of $CuSO_4.5H_2O$, temperature, current density, and time in acid copper plating.

The cathodic current efficiency for acid copper plating can be increased by increasing the concentration of copper, current density, and plating time. But it decreases by increasing the bath temperature. Relationships are found by using best fitting equations between these variables.

The results of this study showed that the smaller graphite particle size under 36 µm and binding agents (epoxy resin) is more suitable for the process in order to achieve uniform thickness, good adhesion, smooth surface, reduced porosity, maximum load applying in scratch resistance to see how far it is durable in decoration and industrial purposes for these surfaces which lead to a best sample was (δ =38 µm) copper electrolplating thickness at peel strength (σ_s =2kg / cm), roughness surface (R_a = 0.02 µm), porosity(φ =1.8%), scratch (2kg).The conditions of these tests are current density 3 A / dm^2, bath temperature 25 ^oC, plating time 60 min., and solution of 200 g /L $CuSO_4.5H_2O$, 50 g / L H_2SO_4.

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Variable Notation

Symbol	**Definition**	**Unit**
A	Cathode surface area	dm^2
d	Graphite particle size	µm
E	Ohmic resistance(voltage drop)	Volt
F	Faraday constant 96487	Coulomb/equiv.
G	The weight of graphite deposit	g
i	Current density	A/dm^2
I	Total current	A
J	Cathode current density	A/dm^2
K	Solution conductivity	siemens/cm
L	Length of substrate	cm
Q	Amount of electricity passed through cell	Coulomb
R	Solution Resistance	Ω
R_a	surface roughness	µm
t	plating time	second
T	Solution temperature	°C
V	Volume of electrodeposit	cm^3
w_{th}	Theoretical weight of deposit	g
Δw	Weight loss	g
Z	Atomic weight	g/mole

Greek Letters

δ	Plating thickness	µm
τ	thickness of substrate	cm
ρ	Density	g/cm^3
ξ	Cathodic current efficiency	-
σ_s	Peel strength	kg / cm
φ	Porosity	%

Chapter one

Introduction

1.1 Electroplating Plastics:

The are many advantages to be obtained from metallising of plastic. In the past their use was purely decorative, but nowadays they fulfile functional need as well. Various applications within the electronics industry, for instance, require the combination of properties derived from both the dielectric and the metal, which neither can supply alone [1].

Certain properties exhibited by metals but not possessed by plastics are sometimes desirable in products for special purposes ; this gives rise to the need for the metallising of plastics. As a result these properties may be improved electrically, physical, optically, thermally, chemically or mechanically[2].

The following lists illustrates how metallising not only upgrades the performances of plastics, but in the same cases produces improvements which can not be attended by any other methods. Other advantages of metal-dielectric combination are also cited [3].

1. By depositing a metal on the surface, the plastic becomes electrically conductive.
2. Corrosion resistance is considerably enhanced. Tests have shown that an enormous improvement is obtained when plastics are substituted for metals as the base material. A Cu – Ni – Au electroplate for example, will protect Mg for 24 hours, Al for 90 hours and plastics for thousand

hours when exposed to salt spray corrosion testing. As a result, electroplated plastics are ideally suited for marine equipment where resistance to salt water environment is essential.

3. A large saving in weight is obtained Table (A-1 Appendix A). This is particular importance in military equipment and space research applications.The saving will obviously depend on the polymer employed and on its geometric configuration, together with the specific metal deposited and thickness required.Transport costs are also reduced since they are normally based on weight.
4. Advantages are obtained over mechanical fabrication techniques in providing metal – plastic combinations in that they are cheaper, easier and quicker to manufacture and the result is more reliable (e.g., plated through holes in printed wiring boards).
5. An improvement is obtained in the mechanical properties Table(A-2 Appendix A). Tensile, flexural and impact strength, together with abrasion resistance,are higher. Elongation is the only property adversely affected.

6. When the dissipation of heat is necessary, the metal may act as a heat sink. Thin metallic films are used for their heat reflecting power. Thermal stability of the polymer is improved. The heat distortion point is also much higher, Table (A-3 Appendix).
7. Economics generally favours the utilization of electroplated plastics, which is of the utmost importance in decorative applications. As time passes this differential is likely to increase.The cost is of course dependent on a number of factors, not the least of them being the basic costs of the metal and plastics, since these vary considerably Table(A-4 Appendix A) .

8. Various polymers are dissolved or attacked by certain solvents, but a metallized coating will protect them from such an attack. Depending on the metal used, protection may be afforded from acids, bases and other chemicals. The ingress of moisture is avoided Table (A-5Appendix A) permeability to vapours and gases are also reduced.

After knowing the important of plated plastic , we must refers here the reason that plastic parts can not be easily electroplated is because plastic is a nonconductor of electricity. while electroplating requires that an electric current flow between the part being plated and the chemical solution. If the part is non-conductive then an electric current cannot flow [4]. therefore it can one plate nonconductive materials like plastic by using "electroless" plating. After an electroless coating is produced, a normal electroplating bath can be used to make the coating even thicker[5].

However, electroless plating solution have several commercial disadvantages. They require a relatively long process time. The multiple treatment baths have complex chemistry which may require constant monitoring and individual ingredients which may require separate replenishment. The conventionally used palladium/ tin activator also may require expensive waste treatment[6]. Furthermore, these electroless process baths may be highly toxic formalin, i.e. a carcinogen, is widely used as a reducing agent. Moreover, the bath contains copper ions and reductant , rendering the process inherently unstable[7].Therefore, replacing this electroless process with direct metallization process for using a method forming an organic electroconductive coating and a method applying carbon coating to a non-conductive layer [8]. In the present work is plating plastic by graphite coating prior to electroplating in acid copper plating bath by using different plastic substrates for each particle size of graphite and binding agent to gain optimum graphite conductive colloid.

1.2 Scope of the work:

1. Study the effect of
    - Particle size of graphite (36 , 75, 150 and 212um) on graphite coating, characteristics of plating.
    - Binding agent (epoxy resin, polyester resin and cyanoacrylates) on graphite coating and characteristics of plating.
    - Type of plastic (ABS, polystyrene, epoxy-fiber glass, phenolic) on graphite coating and characteristics of plating.

2. Best conditions are chosen for graphite deposition prior to copper electroplating from plating thickness, adhesion, porosity ,surface roughness, scratch resistance.

3. Cathodic current efficiency for acid copper plating under different concentration of copper , cathodic current density , temperature and time of plating .

Chapter Two

Theory of Electroplating on Plastics

2.1 History of Electroplating on Plastics

Plastics have been recognized from time immemorial and although electroplating is comparatively newcomer to engineering, metal finishing, as such, is undoubtedly thousands of years old. The earliest applications of metal coatings were on metals but, with the coming of the industrial age, it was only question of time before the search would be for applying metals to non-metallic (non-conductive) materials and only a matter of time before such methods were discovered. Techniques for metallization started as early as miror making. Charles[8] stated that Justus Von Liebig in 1835, discovered the process of coating a glass surface with metallic silver, making the glass mirror one of the earliest items being metallized. Plating other non-metallic objects grew rapidly with introduction of ABS plastic. The plastic part is first etched chemically by a suitable process, such as dipping in a hot chromic acid –sulfuric acid mixture. The etched surface is sensitised and activated by first dipping in tin (II)chloride solution, then palladium chloride solution. The processed surface is then coated with electroless copper or nickel before further plating .

This was followed by metallized samples exhibited by Jacobi in 1838 in which the non-adherent coating could be separated from the base for use as a negative mould as stated by Randolph and Nelson[9] and they also stated that in 1840 Robert Murray applied graphite to non – metallic surfaces to make them conductive and later reproduced engraved copper plates by this "galvano-plastics" method. Graphite has been employed in numerous processes for preparing a non-conducting material for a metal coating or plating, Thorn [10] stated that Alois Blank obtained a patent in 1889 for applying copper to asbestos roofing material which comprises first applying powdered plumbago (graphite) in a volatile liquid, such as varnish to the surface of the asbestos, the plumbago coated asbestos sheets are then immersed in a copper electroplating solution and electric current is applied to the coated asbestos sheet to form a thin film of copper coat. The resulting metal-coated asbestos sheet is described as being relatively flexible, a nonconductor of heat and substantially fireproof.

Pendleton [11] stated that Goldberg in 1920, was studying processes for electroplating non-conducting materials by first coating the non-conducting material with wax, then coating the wax with a slurry of finely divided particles of graphite, followed by electroplating of the dust coated surface with copper or other metal. Fleury and Vincent [12] stated that Laux in 1941, disclosed a process for electroplating a non-conductive surface by "graphiting" a thin layer onto the non-conducting surface followed by applying a copper layer electrolytically and "finally a further electrolytic deposit of another metal" is placed thereon.

Very important developments which occurred in the 1960s [13], at that time plat able plastics capable of receiving a deposit with adhesion sufficient for practical uses were developed. The first plastic to be plated on a commercial scale was ABS (acrylonitrile-butadiene-styrene) of special grade; somewhat later methods for plating on polypropylene were developed, and analogous processes are now available for polycarbonates, polysulfones, and others, although ABS and polypropylene are still dominate the field. Although the adhesion obtained is not as strong as in plating on metals, it is satisfactory for many practical applications. The process complete directly with plating on Zinc die casting, and emphasis on weight saving in cars promotes the use of lower-density plastics .

The cycle for preparation of these plastics includes: cleaning, solvent treatment, conditioning, rendering the surface catalytic, and applying the electroless or auto-catalytic deposit, usually nickel or copper.

Methods for avoiding the use of precious metals such as palladium have been proposed.

Plating on plastics is vital step in the manufacture of printed-circuit boards, and the initial motivation for the development of processes for electroplating on to plastics came from the automotive industry has consistently been by for the largest user of the product.

Once a successful process had been developed it rapidly became accepted by the industry, and by the early 1970's large areas of nickel/chromium plated plastics trim were appearing on vehicles. A whole range of components was produced in plated plastics, including radiator grilles, window trim, name badges, and front/rear lamp units.

This trend was particularly evident with vehicles manufactured in North America, where bright trim has always been more popular than in Europe.

As a fundamental result of these development, it was possible to introduce new techniques for plating on non-conductors which lead directly to the present state in 1986 by Karl L. Minten and Galine Pismennaya [14], were studying process of electroplating the non-conducting surface which is a significant improvement over the known electroless techniques. By this process, a liquid dispersion of graphite particles is first applied to the non-conductive surface; then the liquid dispersion medium is separated (i.e., evaporated) from graphite particles, thereby depositing a substantially continuous layer of graphite on the non-conductive surface, and next a substantially continuous metal layer is electroplated over the deposited graphite layer.

Improvements and modification of this Minten and Pismennaya process are shown in 1995 by Electrochemicals Co. [15]. It uses crystalline graphite as a conductor coupled with a polymer solution to promote adhesion. In 1997 the Shiply Co. [16] also developed a process in this group, which is called Graphite 200. It uses a cationic wetting agent, termed sensitizer, to modify the surface's charge state before applying a graphite colloidal solution.

At the end of 2002 [17] the throughput was about 4000 m^2. The metallization test of large area automobile interior articles made of ABS/PC T85 was also conducted without any problem based on direct plating.

In 2005[18] a direct metallization system based on unique dispersion of graphite has gained significant market share on a worldwide.

Today, a considerable amount of research is being devoted to the subject, this process to provide an even more economical and environmentally safe process for applying conductive metal layer on the surface of non–conductive layers of plastic which have been successfully electroplated and launched on the commercial market.

2.2 Electrodeposition Process

The overall electrodeposition process appears to be simple, namely metal ions in solution acquire electrons at the cathode and discharge to form metal atoms.

$$\underset{\text{Metal ion}}{M^{z+}} + \underset{\text{electrons}}{Ze^{-}} \dashrightarrow \underset{\text{deposited metal}}{M^{0}}$$

The electro deposition process is, however, very complex, consisting of several partial processes, and it depends on a number of variables related to the deposition conditions [19].

2.2.1 Simple Salt Solutions

In simple salt solutions, cations are present in bulk solution as hydrated ions having the same valence or oxidation state as the free ion. Consequently, before the cation is discharged there must be a preliminary dehydration. This process occurs in the electrical diffusion layer, and usually proceeds via several steps, whilst the energy required for dehydration depends on the metal ion. If the metal ion requires a high energy for dehydration, then the deposition process will involve a high activation polarization and a high overpotential is necessary before deposition occurs.

The overall electrodeposition process is schematically represented in Fig. 2-1. The hydrated cation reaches the cathode under the action of the prevailing electric field between the electrodes, as well as by convection and diffusion. As the ion enters the diffusion layer, its velocity is largely determined by the ionic concentration layer, its velocity is largely determined by the ionic concentration gradient across the layer. Whilst the ion migrates across the diffusion layer, the hydrating water molecules become aligned in the direction of the electric field and these water molecules are lost as the ion enters the fixed portion of the electrical double layer. When the cation has lost its hydration shell, it is discharged and adsorbed onto the cathode as an ad- atom which then diffuses across the cathode surface to a growth point. At a growth point, the ad-atom becomes incorporated into the growing crystal lattice of the electro deposit on the cathode [19].

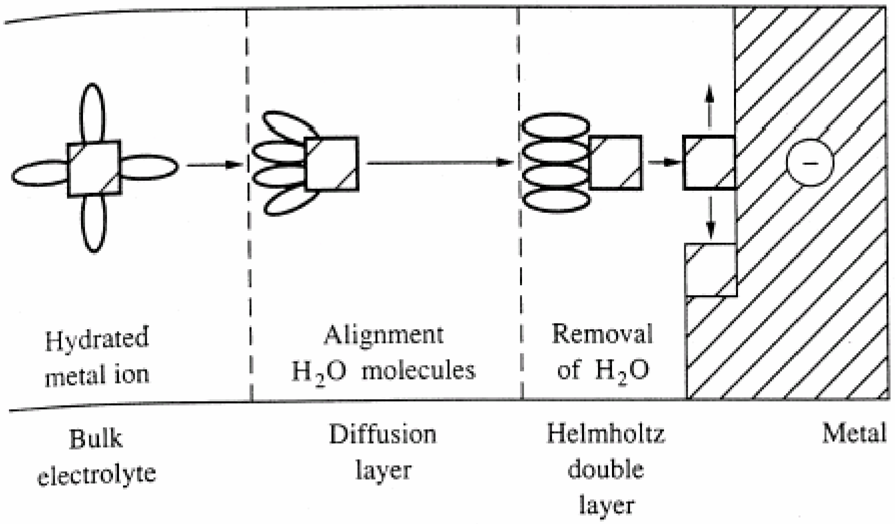


Fig.2-1 Schematic representation of the mechanism of metal deposition [18].

2.2.2 Copper Electrodeposition

Copper has met with wide acceptance as the base conductor metal in non-conductive surfaces. It has excellent electrical conductivity which is ready plated, low in cost and gives highly reliable results. Copper is ready activated, and hence good metal-to-metal bond is obtained between copper and other plated metals. The most important use of electrodeposited copper in protective coatings is as an undercoat. The three most commonly used copper solutions are pyrophosphate, acid sulfate, and acid flouroborate [20].

Plastic surface (non-conductive) plating begins commonly with a deposit of copper, from acid copper sulfate bath. This enables the part to pass the severe test more easily, and also levels roughness and imperfections in plastic [21].

2.2.3 Current Efficiency

The current efficiency, ξ, of an electrode deposition process is the ratio of the current flowing that is utilized in the electrodeposition reaction to the total current passing, expressed as a percentage. This can be expressed in another way [20]: -

$$Current\,efficincy, \xi = \frac{W\ (Weight\,of\ metal\,deposited)}{W_{th}\ (Theoretiacl\ weight\,of\ metal\,deposited)} \qquad \ldots(2.1)$$

The current efficiency is a very important factor in all electrodeposition processes and it is involved in all calculation of coating thickness and similar computations.

In applying Faraday’s law to a deposition reaction, the theoretical weight of metal deposited W_{th} is given by [18]: -

$$W_{th} = \frac{Q}{F} \times Z \qquad \ldots(2.2)$$

where W_{th} is in grams, (Q = I x t) is the amount of electricity passed through the cell and expressed in ampere second, Z is the equivalent weight of metal, and F is Faraday's constant is 96485. Substituting Equation (2.2) in Equation (2.1) the observed weight of metal deposited is obtained:

$$W = \frac{Z.Q.\xi}{100F} \qquad \ldots(2.3)$$

If, however, the cathode surface area is A (dm^2) and current density of i (A/ dm^2) is the following Equation (2.3) can be written as:

$$W = \frac{Z.i.A.t.\xi}{100F} \qquad \ldots(2.4)$$

where t is the electrodeposition time in secondes .The coating or electrodeposition thickness δ (in micrometers, μm) is given by the volume of electrodeposits (V in cm^3) divided by the surface area A (dm^2):-

$$\delta = \frac{100\,\mathrm{V}}{\mathrm{A}} \qquad \ldots(2.5)$$

But since the volume of the deposits is the weight of the metal divided by it is density, *V*= *w/ρ*, then Equation (2.5) becomes [19]

$$\delta = \frac{100W}{\rho A} \qquad \ldots(2.6)$$

and by combining Equation (2.4) and (2.6) the following equation is obtained:-

$$\delta = \frac{100\,Z.i.A.t.\xi}{100\rho\,AF}$$

$$\delta = \frac{Z.i..t.\xi}{F\rho} \qquad \ldots(2.7)$$

It can be seen from this equation that the thickness of an electrodeposit is determined by the equivalent weight of metal, and F is Faraday's constant, the quantity of electricity that passed and the current efficiency.

2.3 Methods of Electroplating (non–conductive materials) Plastics

The methods of electroplating a non–conductive material comprising indirect (classical methods) and direct method by carbon colloidal system.

2.3.1 Indirect Method (Classical)

It is the function of the electroless plating operation to metallize non conductive surface with a thin deposit of metal (usually copper) to render the surface conductive for subsequent electroplating see Appendix A.

“Electroless” implies that no current is employed in the deposition. In electroplating, electrons are obtained from a DC power source to reduce metal ions to the metallic state. In electroless plating, the mechanism is similar but the source of electrons is a chemical reducing agent. Hence, non-conductive surfaces may be metallized by employing electroless baths since the baths contain their own source of electrons, electroplating baths cannot be used for non-conductive surfaces because the electrons cannot flow [5].

2.3.2 Direct Method (Carbon Colloidal System)

A method of applying a conductive carbon coating to a non-conductive substrate. This method is to deposit a controlled and uniform coating of graphite or carbon black (which are referred to, in this specification, either together or separately as "carbon") particles on the non-conductive surface. Another object of this system is the uniformly deposit carbon coating which is adequate to eliminate the need for electroless plating prior to electroplating [22]. However, a robust direct metallization system must render the surface sufficiently conductive to enable the electrodeposition of copper to uniformly plate the surface. Certainly the electrodeposition process plays a critical role in achieving the desired uniformity. The more uniform the plating. Also, improved throwing power and surface distribution properties will reduce the cycle time in the plating process [23].

2.3.2.1 Graphite Comparison to Carbon Black:

Graphite is often compared to carbon black, a semi-conductive form of carbon. Carbon black is the main ingredient of another direct metallization system. When one compares the structure of these two forms of carbon, one notes that graphite has a highly crystalline structure, while carbon black is amorphous randomly structures. The crystalline structure enables the graphite to have higher conductivity than carbon black, which is a significant advantage in electroplating surface. The higher conductivity is explained by the fact that graphite conducts electricity anisotropically [22].

2.4 Process Stages for Graphite Based Direct Metallization

The steps of the graphite metalization system as following[22]:

1. Cleaning and conditioning
2. Graphite conductive colloid
3. Fixing
4. Drying
5. Copper electroplating

2.4.1 Cleaning and Conditioning:

This process step is critical in preparing the non-conductive surface to receive the graphite dispersion. The slightly alkaline chemistry contains a cationic polyelectrolyte with multiple positive charges, the highly charged polyelectrolyte provides a net positive charge on the non-conductive surface, aiding in the electrostatic attraction of the graphite particle [23].

Generally expressed as internal pressure or surface tension and it is measured in millinewtons per meter (mN/m). Water with about 70 mN/m has a relatively high surface tension, which is clearly indicated by the spherical shape of the drops. This is responsible for the poor washing and cleaning capacity of water. In order to improve these properties, the wetted surface must be increased considerably through an addition of wetting agents.

The conditioner contains a proprietary mixture of positively charged high molecular weight compounds which are characterized by one hydrophilic part (miscible with water) and one hydrophobic part (non-miscible with water) and having distinct distribution of electric charge (polarity). In water these substances show a tendency on one hand to dissolve and on the other hand to separate completely.

This double nature can only exist due to the fact that the conditioner molecules concentrate predominantly on the interface of the phases. In such away that hydrophilic part of the molecule remains in the solution and points “towards the in side” while the hydrophobic part is oriented “towards the out side” in the direction of the adjacent phases, however, it is in this region that the maximum internal pressure exists, which is now reduced by the introduction of the long stretched conditioner molecules between the water molecules [22].

On all interfaces between phases, the forces of attraction of the molecules of water can, as a result of change of the steric conditions, only act in a reduced way with effect that a water drop collapses and, by doing this considerably increases the wetted surface area and reduces its edge angle from α_1 to α_2 as shown in figure 2-2

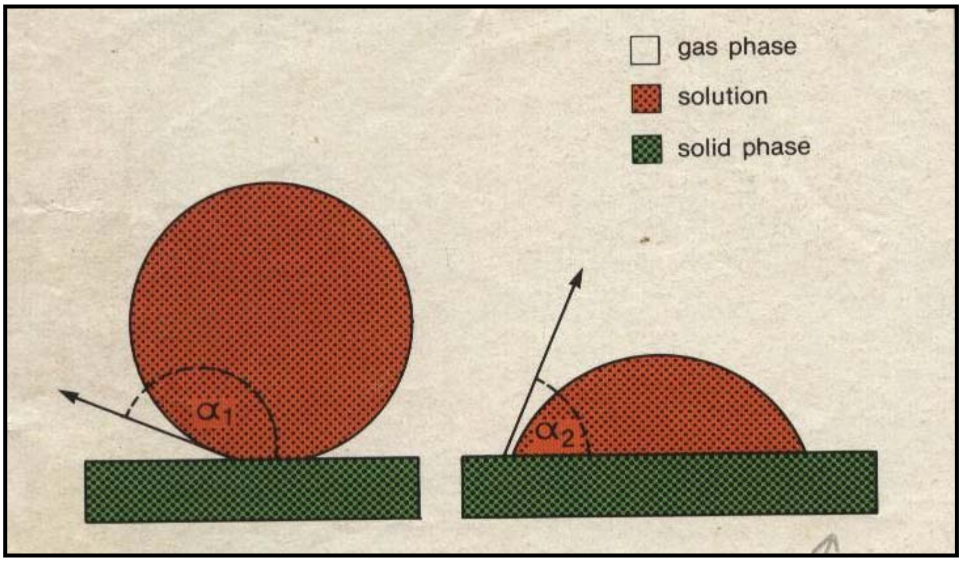


Figure 2-2 Cleaning and Conditioning mechanism[23]

One has to appreciate that the surfaces are completely covered with a monomolecular conditioner film as shown in figure 2-3.

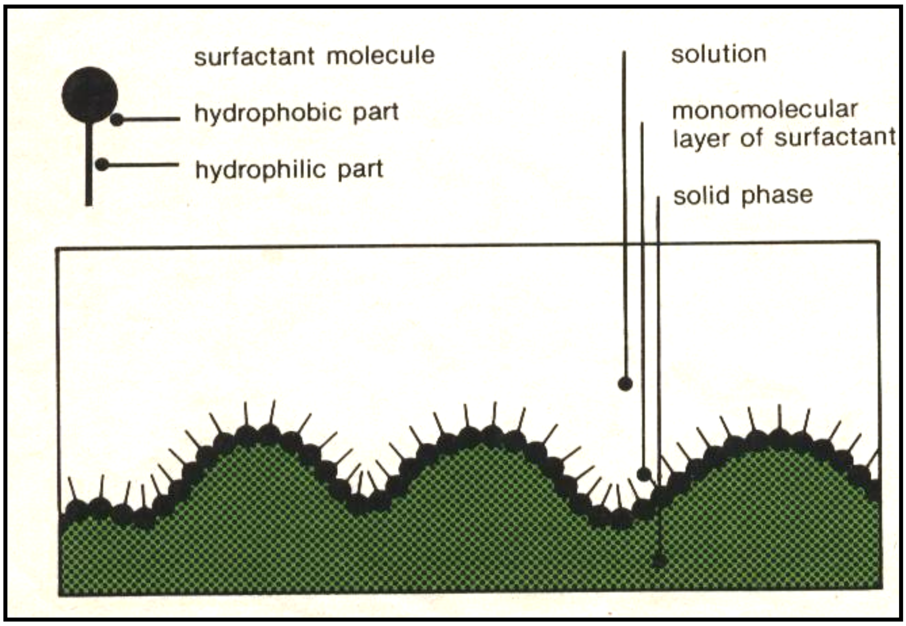


Figure 2-3 Mechanism of operation of surfactants[23]

In accordance with its nature the conditioner molecule clings with its hydrophobic part to the solid phase that will adsorb onto the surface this charge leaving it positively charged the conditioner is highly substantive in that it remains adsorbed onto the surface even after rinsing [10].

2.4.2 Graphite Coating

After cleaning and conditioning the non-conductive surface,a specialized dispersion of graphite is containing three critical ingredients, graphite particles, binding agent and aqueous dispersing medium which are suitable for subsequent metallization of plated the non-conductive surface [9,10].

2.4.2.1 Graphite

One component of the present conductive compositions is electrically conductive graphite, but, the graphite may be either a synthetic or a naturally occurring entity. For reasons of superior conductivity synthetic graphite is preferred. The graphite particle, by virtue of its crystalline structure, is highly conductive and has been demonstrated to enable the uniform electro deposition of copper from acid sulfate electrolytes [15].

It should be noted that a graphite system based on mean particle diameter as small as possible. Graphite may have a mean particle size within the range from about (0.5 to 50 microns) from the perspective of performance and ease of dispersion, particles from the smaller end of the size range are preferred when "average particle diameter” as employed refers to (the average by number) [21].

The average mean diameter may be determined through the use (Sieve Analysis) which refer to particles passing through an opening mesh screen is equivalent to diameter for particles.

It is also required that the graphite particles retain their crystal structure and are essentially free of crystal defect [16].

2.4.2.2 Binding Agent

Another component of some of the present compositions is dispersible binding agent for binding the graphite particles. The binding agent is believed to assist the dispersed graphite particles in adhering to the surface of the non-conductive (i.e., dielectric) substrate which is to be made conductive for electroplating. Binding agent can be selected from a variety of polymers, resins [24, 25], and other acrylate compounds selected in the present work are as follows :

1. Resin:- which includes Epoxy resin: and Polyester resin
2. Acrylate Adhesive

A practical upper limit to the amount of binding agents used is contemplated to be that amount which materially interferes with the conductivity of the resulting conductive coatings by diluting the conductive solids in the composition after it is deposited as a film [11].

2.4.2.3 Aqueous Dispersing Medium

Another component of the compositions of the graphite coating is an aqueous dispersing medium. The phrase, "aqueous dispersing medium," as used herein, includes any solvent that is from 80% water wherein the balance of the material is a water soluble composition.

Alternatively, the aqueous dispersing medium may be organic acids, such as formic acid and acetic acid. Aqueous dispersing medium, this action helps to prevent the graphite particles from being attracted to each other and forming an agglomerated species [14,15].

2.4.2.4 Mechanism of Deposition Graphite Coating

The mechanism that enables the graphite particle to bind to the dielectric surface is as follows: The nitrogen groups on the backbone of the cationic polyelectrolyte (contained in the cleaner/conditioner) coat the dielectric surfaces (non–conductive). The charge density of the cationic surfactant has a significant influence on the degree of adsorption and coverage of the graphite dispersion. It should be noted that charge density of different cationic surfactants vary. Therefore, it is critical that the optimum conditioning agent be selected as to not over- or under-condition the substrate. When the colloidal graphite solution comes in contact with a conditioned non-conductive surface the negatively charged colloidal particles are neutralized by the positively charged conditioner. This causes flocculation (weak aggregation). As particles collide with the surface, aggregates grow from one primary particle to which others are added. This continues until all of the charge is neutralized and even beyond this point. Once particles flocculate on the surface there is a hydrophobic interaction between these particles that holds them together [22]. The mechanism of surface reaction (epoxy-fiber glass) as example is shown in figure 2-4

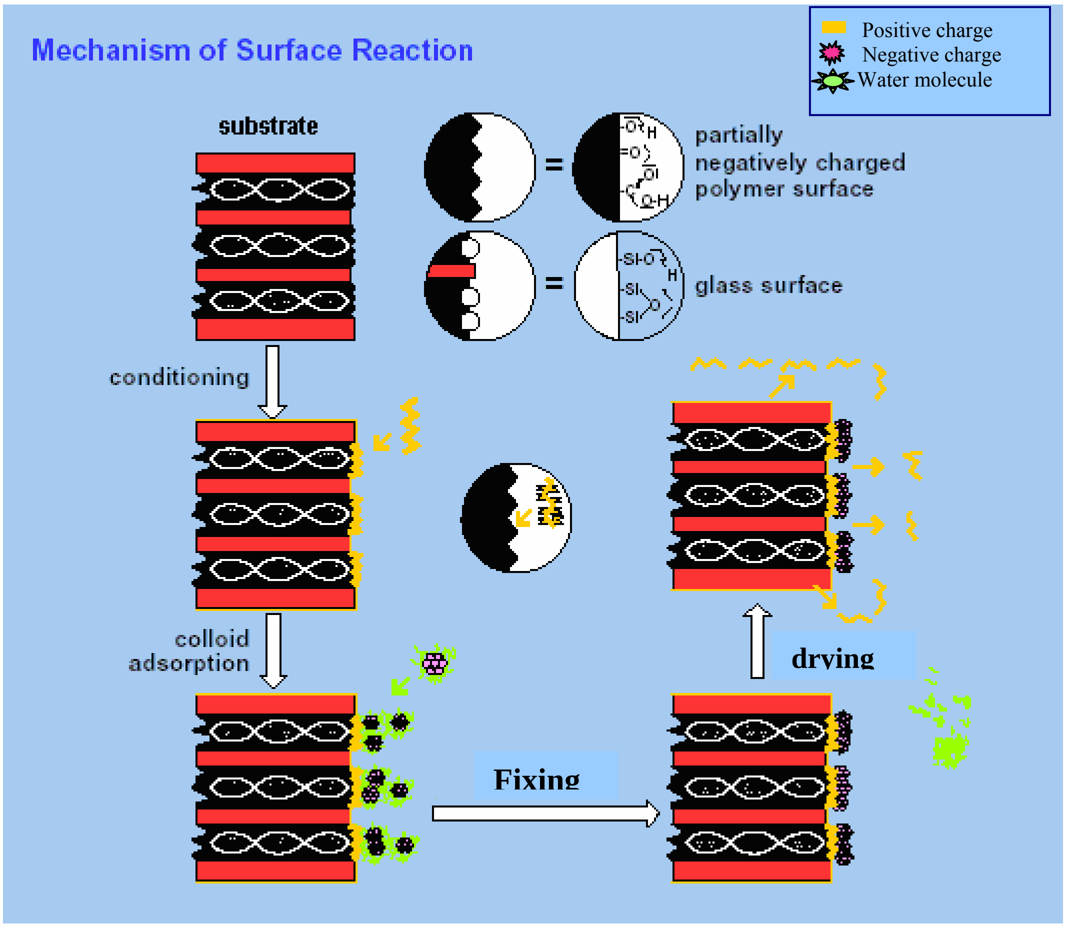


Figure 2-4 Mechanism of surface reaction [22]

2.4.3 Fixing

A very significant factor with respect to metallization of surface. This mildly acidic solution is applied to the non-conductive surface immediately after the graphite dispersion has coated the surface. Fixer ensures no excess material that would compromise interconnect integrity. Therefore, fixing solution benefits:

1. Removes excessive graphite composition deposits.
2. Cross links the first monolayer of graphite which is directly attached to the substrate can improve adhesion without interfering with microeching.
3. Smoothing the graphite coating on the non-conductive surfaces by eliminating lumps and by making the coating more uniform [12].

2.4.4 Drying

The graphite conductive colloid covered substrate is then subjected to a step where substantially all of the water in the applied dispersion is removed and a dried deposit containing graphite is left on the surface of the non-conductive be accomplished by conventional drying. Drying understood to more fully crosslink the graphite coating as well[15,16].

2.4.5 Acid Copper

Importance of high throwing power, high leveling acid copper electro deposition process takes on added significance the copper plating must be uniform and have optimum physical properties. Additionally, the quality of the copper deposit dependence in part on the performance of the metallization process. The character of copper deposit is influenced by the concentrations of copper salt and of free acid, the temperature, the cathode current density, and the nature and degree of agitation [26].

The deposit obtained without additives is generally dull, soft and somewhat coarse, it can be significantly altered by the use of additives, the additives can be effective in grain refinement, leveling and hardening and as a brightener.

Tables 2-2 and 2-3 list the composition and operating conditions for copper acid. It should be noted that there are two variations. The first is the standard formulation, and the second is formulation consisting of low metal and high acid to increase throwing power[20].

Table 2-2 Specifications for Acid-Copper[20]

Component	**Standard g/l**	**High throwing power**
Copper Sulfate ($CuSO_4.5H_2O$)	160-300	60-90
Copper Cu^{+2}	40-75	15-22.5
Sulfuric Acid (H_2SO_4)	52.5-135	187.5-225
Addition Agents	As Required	
Chloride Ion	20-80 ppm	

Table 2-3 Operating Conditions [20]

Variable	**Range**	**Optimum value**
Temperature	21-34 °C	25 °C
Agitation	Blower Air	
Cathodic current density range	1-5 A/dm^2	3 A/dm^2
Anodes	Copper (99.9%)	
nodic current density	0.5-2 A/dm^2	1.5 A/dm^2

2.5 Mathematical Analysis of Plating Uniformity

The development models testing plating uniformity. With respect to plated surfaces and through hole, the models attempted to predict what influence key variables had on plating uniformity. The variables included in these models are:

- Mass Transport
- Ohmic resistance
- Electrode reaction

Basically, one has to optimize the electrolytic copper process for plating on the surface and in the through hole. Studies indicated that ohmic resistance tended to dominate the plating process when, ohmic resistance (or voltage drop) can be explained by the following model:

$$E = \frac{i\,\tau^2}{2KL} \tag{2.8}$$

where E is the ohmic resistance, i is cathode current density, K is the solution resistance, L is the length of substrate and τ is the thickness of substrate.

As the model shows, the thickness of the substrate influences the difficulty of plating by squared term.

Plating uniformity is a continual challenge for through hole PWB manufacturing and is becoming more difficult with increasingly complex designs. It should be quite clear that plating uniformity is closely influenced by solution chemistry and solution agitation conditions [22].

2.6 Variables Affecting The Graphite Based Direct Metallization

There are variables influence in the characteristic graphite direct metallization system are:

- Mean particle sizes of graphite.
- Types of plastics.
- Types of binding agent.
- Copper concentration in acid copper bath.
- Current density in acid copper bath
- Solution temperature
- Agitation Speed
- Plating time

Each variable can be considered with regard to its general effect.

2.6.1 Mean Particle Sizes

The mean particle size is a critical parameter that affects the plating characteristics of substantially even plating and resistant to plating pull away. When the average particle sizes are more than about (0.5- 50) microns, a subsequent copper electroplated deposits will be pulled away from the non-conductive surface and becomes more probable in this range and non-uniform areas of plating (lumpiness or localized area) in the graphite coating[21].

2.6.2 Types of Plastic (non-conductive surface):-

Plated plastic components have properties of the base plastic as well as properties of the deposited metal. The type of plastic selected has a great influence on the performance of the plated plastic part [27]. However, plastic are divided into two distinct group:

Thermoplastic, the majority of plastics are thermoplastic, meaning that once the plastic is formed it can be heated and reformed over and over again, ABS and polystyrene were selected in the present work as thermoplastic for plating.

Thermoset plastic, other group of plastic, can not be remelted and remolded after it is cured, epoxy-fiber glass and phenolic were selected in the present work as thermoset plastic for plating [28].

Because of the different plastics, parameters of conditioner bath is different from epoxy- fiber glass and phenolic than ABS and polystyrene by the normal conditioner bath is adjusted by raising the temperature and increasing the time. When the conditioner process is critical for provides graphite deposition and any imperfections in this process are magnified by plating [29].

It is also the type of plastic affected on adhesion of the copper deposit on surfaces due to physical properties elasticity, thermal expansion and heat distortion temperature see Appendix (A)

2.6.3 Types of Binding Agent:

The binding agent is affecting on drying time according to the cure conditions for each type of binding agent using in graphite conductive colliod. Another influence is that each type of binding agent is designed to coat the graphite particles and effect on the particles in adhering to the dielectric surfaces [28].

After graphite coating, once the plastic surface is conductive ,it is plated as any metal it is beyond the same condition for acid copper bath as explain subsequent.

2.6.4 Bath Concentrations of Copper Sulfate in Acid Copper Plating:

Increasing the copper sulfate concentration will increase in the rate of deposition. A concentration of less than 60 g/l copper sulfate result in decreased cathode efficiency. But also excessive copper concentration impairs the metal distributing qualities [30,20].

2.6.5 Temperature:

Increasing the temperature of the working bath lead to break down the rate of deposition decrease. Too low a temperature will lower the efficiency of the bath, to maintain the proper operating temperature, the appropriate heating or cooling equipment should be installed [30].

2.6.6 Current Density :

Increasing the current density tends to increase the rate of deposition. But, the permitted current density should be between 1 and a maximum of 5 A/dm^2, and is dependent on the bath temperature and agitation. To obtain a good distribution of the copper layer [30].

2.6.7 Degree Agitation

Blower air should be used for acid copper. The degree of agitation will depend largely on the surface area, the agitation should be kept as uniform as possible. Agitation from and to the anodes is necessary to ensure a good exchange of electrolyte.

Since the agitation speed of articles is limited due to flow technology[30**]**

2.6.8 Copper Plating Time

The effect of increasing the copper plating time on the layer thickness is independent of the applied current density, the layer thickness, depending on the copper plating time, as shown in table 2.3

Table 2-3 Time plating for copper sulfate [3]

Thickness, μm	Current densities (A/ dm^2)							
	10 min	15 min	20 min	25 min	30 min	40 min	50 min	60 min
2.5	1.14	0.76	0.57	0.46	0.37	0.27	0.22	0.19
5.07	2.26	1.5	1.14	0.9	0.76	0.57	0.45	0.37
7.6	3.4	2.26	1.7	1.39	1.14	0.86	0.68	0.57
10.15	4.5	3.0	2.26	1.8	1.5	1.14	0.914	0.76
12.7	5.7	3.7	2.9	2.26	1.9	1.39	1.14	0.95
15.228	6.88	4.5	3.44	2.69	2.26	1.7	1.39	1.14
17.66	7.96	5.38	3.98	3.22	2.69	1.93	1.6	1.29

Chapter Three
Experimental Work

The present chapter illustrates the experimental work for studying the parameters which affect on deposition process and the laboratory design of plating system.

3.1 System Specification for Preparing the Surface of Plastic Prior to Electroplating:

a. Grinding machine for roughening surface type (prodit) by abrasive paper with diameter200 and no. of grinding (180).
b. Test sieve shaker type RV(Retch GmbH) with sieves for grain size analysis type (Retsch) of dimensions (200 mm dia. x 50 mm), ASTM II, and diameter 212, 150, 75, 36 microns.
c. Working baths: A bath was made of polyethylene with dimensions 22 x 15 x 15 cm.
d. Water bath: water bath with heater range (0-100) ^{o}C of type Memmert.
e. Magnetic stirrer type of (Harvard / LTE) with (0-10) r.p.m. main speed and magnetic bar
f. Laboratory beaker (Pyrex) as a bath for graphite deposition with volume (1) liter.

3.1.1 Preparing (non–conductive) Surface for Electroplating Procedure:

Preparing the substrate of plastic by following the steps as in Fig. 3-1 is to describe the simple sketch for directly plating plastic and the present system in this work as shown in Fig. 3-2.

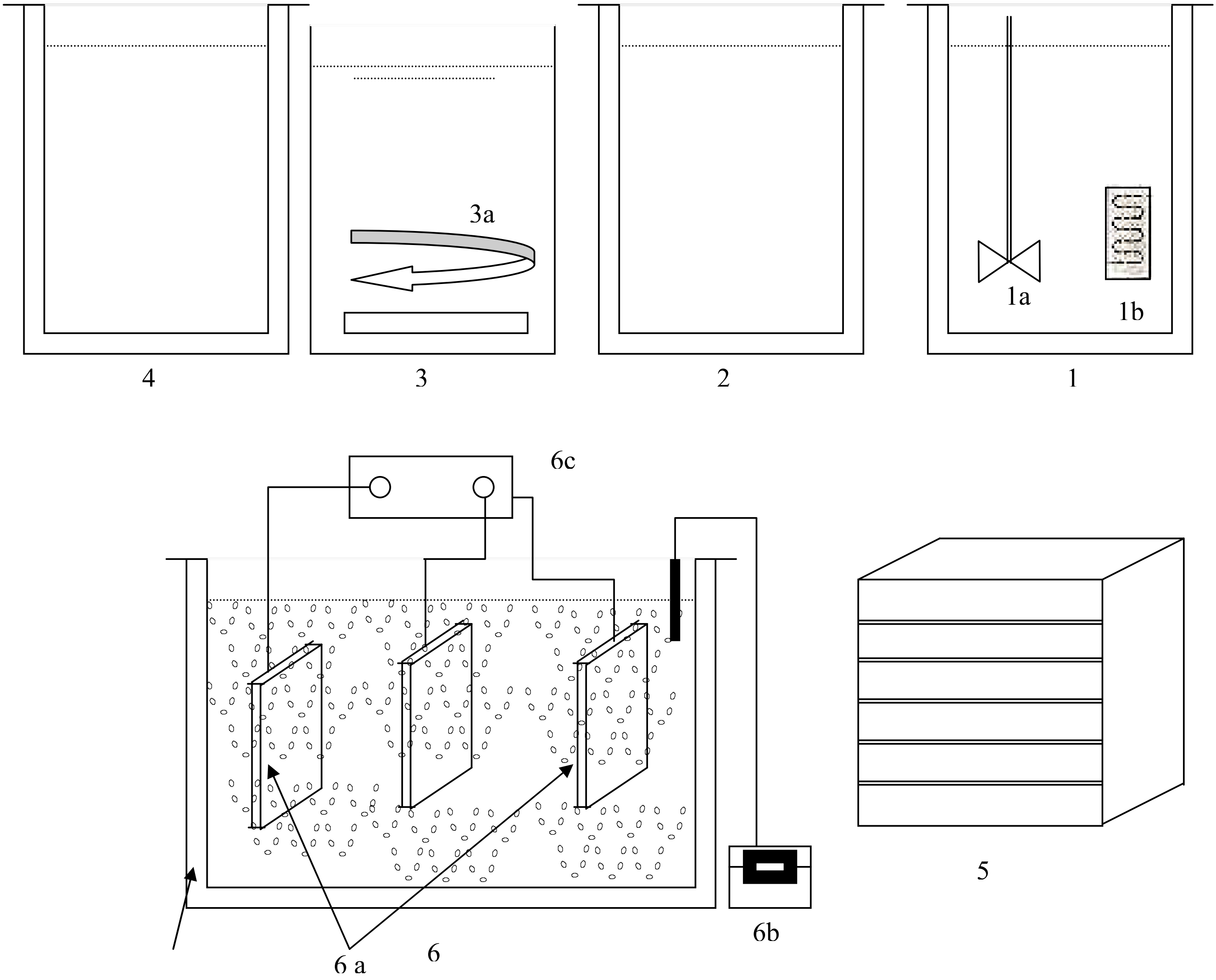


Figure 3.1 A simple sketch showing the details of the laboratory plating system and its identification as follows:

1. Cleaning / conditioning bath
    - 1a. Mixer
    - 1b.Heater
2. Rinsing (Distilled) water
3. Graphite coating bath
    - 3a. Magnetic stirrer
4. Fixing bath
5. Dryer
6. Electroplating cell
    - 6a. Copper anodes
    - 6b. Air aquarium pump
    - 6c. D.C. Power supply

Step 1: Cleaner / Conditioner

The first step of the process is cleaning step combined with conditioning, the substrate is thoroughly wetted and contaminants such as grease, oil, or dirt are removed from the substrate that is to receive plating.

Figure 3-2 Plating of Plastic System

Before the cleaning/conditioning step, simple roughening of surface substrate by grinding machine with abrasive paper with speed (2 r.p.m.), see Fig. 3-3.

Solution make – up:

For 1 liter working solution added

Sodium carbonate	10 g/l
Ethylene glycol	5 g/l
Sodium hydroxide	5 g/l
Mono ethanol amine	5 g/l

The chemical materials are annalar supplied from (BDH) company.

The (1) liter solution in the bath is well stirred. Bath temperature and immersion time are $(45\text{-}55)^{o}$C and (5-25) minutes according to the type of plastic.

Figure 3-3 Grinding machine

Step 2: Rinsing:

Rinsing steps are optionally added between various reagent baths to prolong the life of the subsequent reagent baths. The bath temperature and immersion time are room temperature and 1 minute, and the rinsing medium is normally distilled water.

Step 3: Graphite Conductive Colloid:

After cleaning/conditioning and rinsing, the substrate is subjected to contact with a graphite colloid, the graphite colloid is applied from a bath by immersion process on double – sided of substrate. Bath temperature and immersion time are room temperature and 6-10 minute.

Solution make – up:

Colloid graphite having:

Particle size of about (36 µm)	300 g/l
Type of binding agent	100 g/l
❑ Epoxy risen	
❑ Polyester resin	
❑ Cyanoacrylates	
Acetic acid(3%)	to complete 1 liter volume

The graphite supply from (LPKF Leaser & electronics AG company), acetic acid from (TETENAL – Photo Werk) Germany.

300 g of graphite having a particle size of about 36 µm, and 500 ml of acetic acid were mixed, and the mixture was stirred for approximately 15 minutes using magnetic stirrer with speed of 4 r. p. m. in beaker with (1)L volume ,then added 100 g according to the of binding agent type selected.

The mixture was stirred for approximately 25 minutes. The graphite colloid is ready for immersion of the plastic substrate.

The above preparation was repeated for different changes in graphite coating, different particles size, different binding agent and different types of plastics.

Step 4: Fixing

Sulphuric acid solution is applied to the substrate surface immediately after the graphite conductive colloid had coated the surface by immersing the substrate in the bath. The bath temperature and immersion time are room temperature and 60 second.

Solution make – up:

Sulfuric acid (98%)	15 ml
Distilled water	to complete 1 liter volume

Annalar sulfuric acid is supplied from Gainland Chemical Company.

15 ml of concentrated sulfuric acid were added to sufficient volume of distilled water to avoid splattering and then diluted to 1 liter. The diluted sulfuric acid solution is placed in a fixer bath.

Step 5: Drying

After the graphite coating is applied and fixed, the graphite coat is dried, thus depositing a dry graphite coat on the substrate.

Drying may be accomplished by simple air drier, typical drying conditions for(5-25) minutes according to the typical cure conditions for each type of binding agent using at 45°C.

3.1.2 System Specifications for Preparing the Electroplating Cell:

a. Working cathode:

The cathode was the substrate of plastic to be plated as a cathode in electroplating cell placed vertically with (3 x 3 x 0.4) cm for polystyrene and ABS ,for epoxy – fiber glass and phenolic (3 x 3 x 0.154) cm.

b. Working anodes:

The anode was a plate of pure metal (copper 99.8%), the dimensions of each anode (5 x 5 x 1) cm placed vertically in an opposite direction to the counter cathode. For handling in the bath the anodes were drilled at the upper edge center about 1cm and using copper bar for manipulating.

c. D.C Power supply:

A filtered D.C power supply which is equipped with current and voltage limiters offers better stability and control and can be used for applying galvanostatic boundary condition. It is type (Sodilec) with range (0-20 V) and (0-2 A).

d. Simple agitator:

For agitation equarium air pump was used .To make simple agitator, small holes drilled the plastic pipe in along the bath and connected with equarium air pump from one end. While another end was closed. The bubbles should float up around the substrate.

e. Anode positioning:

Two anodes were placed on two sides of the bath to keep anode at least 7.5 cm away from cathode (substrate). Their wires are joined together ready for the positive terminal from the power supply to be attached.

f. Solvent used:

Hydrochloric acid (HCl 3%) was used to clean anodes of copper before each run using a solution of HCl.

3.1.3 Step 6: Copper Electroplating:

Copper electroplating was conventional. The substrate was used as cathode and fixed by wire of copper through drilled hole in the substrate (out side the solution) by bar of copper, cathode was immersed between the two anodes in the electrolyte solution. Plating was continued for a time sufficient to form a deposit of desired thickness with the preferred current density.

Therefore, cathodic polarization was appled on electroplating cell to obtain preferred current density.

Solution make – up

The electrolyte is prepared from annalar materials of purity about (99.8%) for copper sulfate supplied from (Sojuz Chiem Export Company, Mosxww) sulphuric acid (98%) (Gainland Chemical Company) and HCl (32%) (BDH company).

The quantities required for preparing 2.5 L is:

200 g/l	sulfate copper ($CuSO_4 .5H_2O$)
50 g/l	sulfuric acid (H_2SO_4)
50 mg/l	(HCl)
	Brightener as
0.5 g/l	Thiouera
0.003 mg/l	Sodium salt, Benzen dislphonic acid

In about 1.25L of distilled water, slowly add (500) g copper sulfate per (2.5) L bath, stirring continuously until dissolved. Then carefully and stirring continuously, add the entire amount of sulphuric acid, the temperature of the electrolyte will rise to 50-60°C. After cooling down to operating temperature, add (125) mg of hydrochloric acid, chemically pure (ρ=1.19), as well as (1.25) g from thiouera and (0.0075) g of sodium salt, benzene disolphonic acid. The electrolyte is now ready for use. And analytical procedure for this bath in Appendix B. The substrate (itself) was the cathode for forming copper layer, see Fig. 3.4, a copper electroplating bath was operating under the conditions:

Plating solution temperature	25°C
Current density	$3A/dm^2$
Time immersion	60 minutes
Effecting slow air agitation	

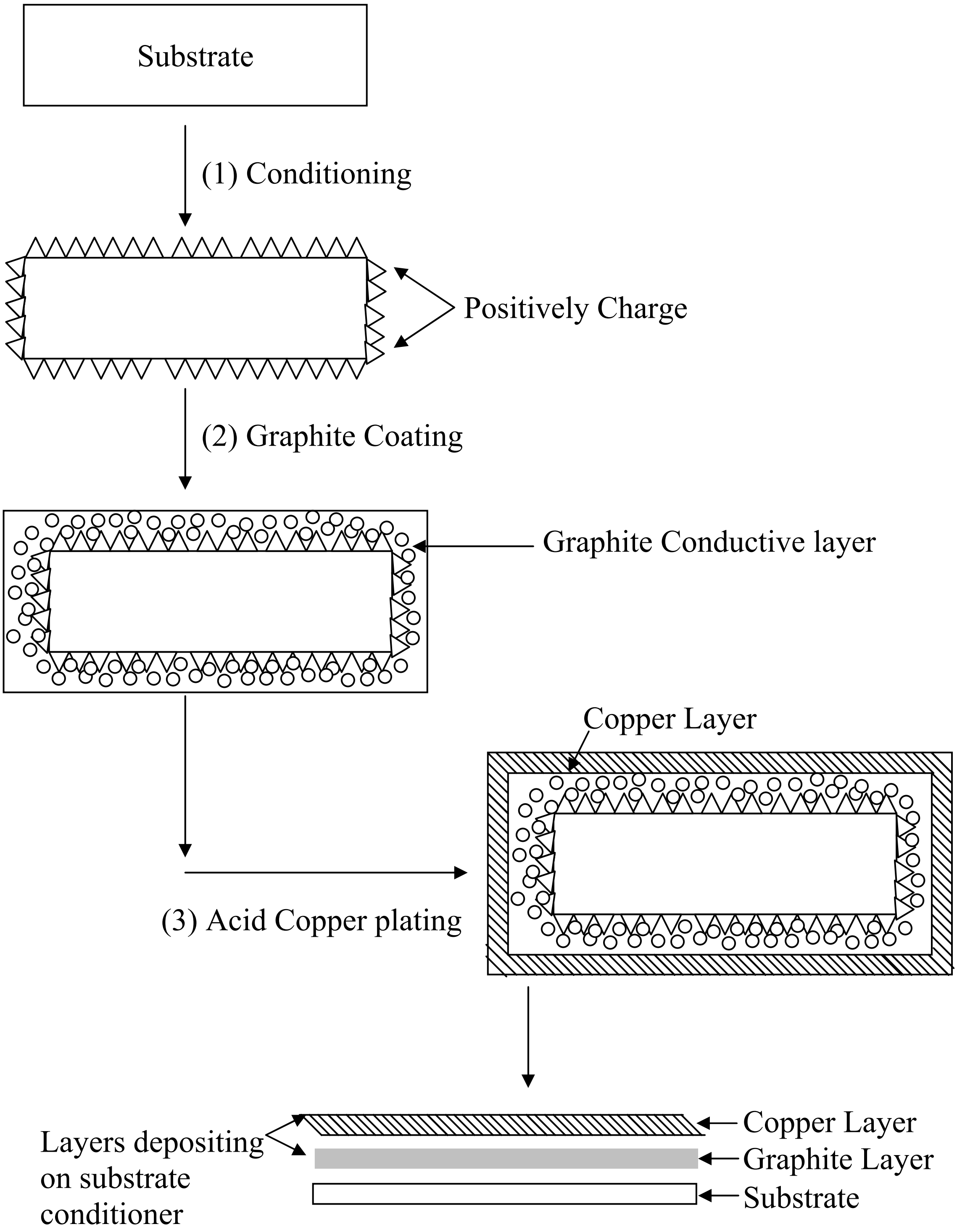


Figure 3-4 Layer depositing on the substrate of plastic by direct plating.

3.1.4 Cathodic Polarization Investigation Procedure: to obtain the current density for plating

After the solution (200 g/l of $CuSO_4.5H_2O$, 50 g/l H_2SO_4, and 50 mg/l HCl and brightener) preparation the electrolyte solution, before starting the experimental run. The fixing cathode in the copper acid bath was 8 cm above the bottom of the bath solution as shown in figure 3-5.

The electrical circuit was connected to the reference electrode Saturated calomel electrode (SCE) after checking all the electrical connections. The polarization electrical circuit was set to the(ON) position in order to draw the curve of any given condition, according to galvanostatic technique by making the voltage of the D.C. power supply constant at 6 V and changing the current by altering the resistance of the circuit. At each setting of the resistance two parameters were recorded (potential and cathodic current) by the voltmeter and the ammeter respectively, i.e. to measure the cathodic portion of the polarization curve (see figure 3-6). Two minutes at least were allowed in order to record the steady state values of the polarization process). After reaching the limiting current density, the run was ended by switching off the power supply and the system was then washed entirely using distilled water to make sure that there was no electrolyte left in the system.

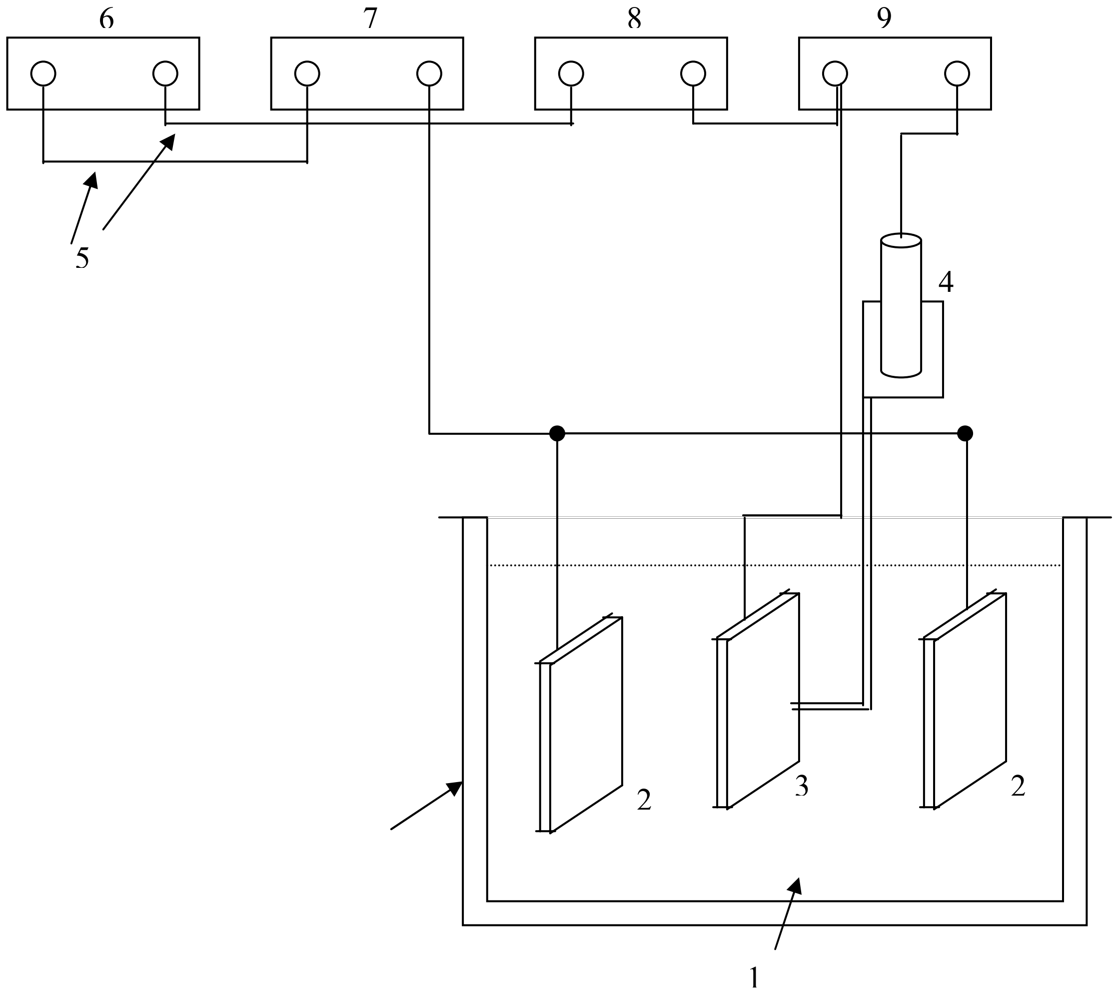


Figure 3-5 A simple sketch illustrating the details of the laboratory polarization system and its identification is given in table 3-1

Table 3-1 The item numbers with details as illustrated in figure 3-5

Item No.	Details
1	Plating Solution
2	Copper anode (5x5x1)cm
3	Cathode (3x3x0.4)cm
4	Saturated calomel electrode (SCE)
5	Connecting wires
6	D. C. power supply
7	Multi range Ammeter
8	Resistance Box
9	Multi range Voltmeter

Table 3-2 Cathodic polarization results

V(mV)	-1	-55	-91	-125	-193	-200	-225	-273	-300
I(mA/cm^2)	8.58	12.70	15.38	17.83	23.07	23.52	25.42	28.98	31.21
V(mV) cont.	-371	-420	-500	-585	-630	-760	-920	-1170	-1830
I(mA/cm^2)	38.5	43.70	50.1	59.42	71.34	79.15	97.54	125.9	210.0

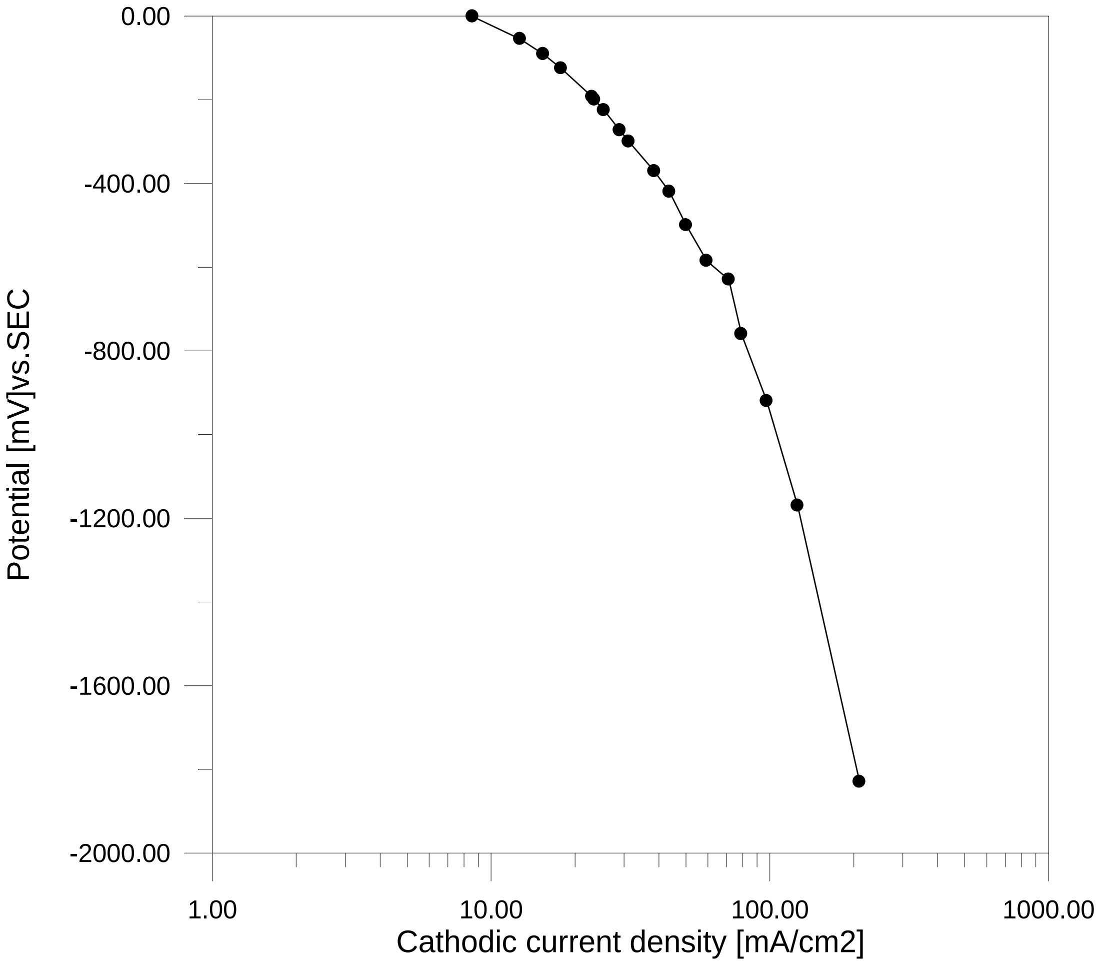


Figure 3-6 Cathodic Polarization Curve

After these steps are explained, the procedure of experimental work can be applied as shown in Fig. 3-7

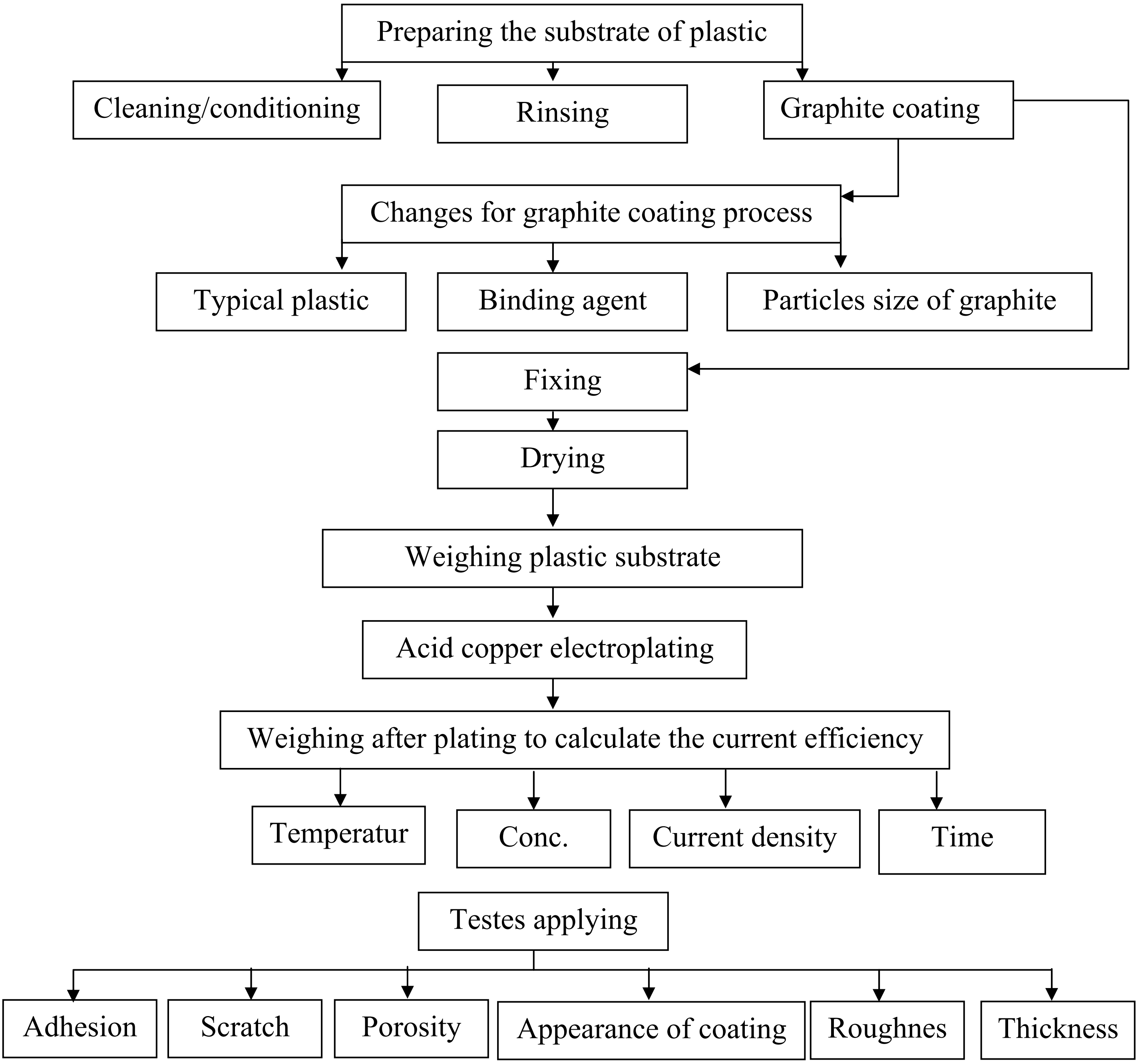


Figure 3-7 Diagram of experimental work steps

3.2 Experimental Procedure:

3.2.1 Different Graphite Particle Size for Plating Plastic Procedure:

Preparing the different average particle diameter determined through using sieves for grain size analysis (test sieve shaker) as follows:

1. Set the sieves in sieve shaker according to the average diameter of particles from large range to the smaller which is selected as 212, 150, 75, and 36 μm as in table 3-3. Sieve series are specified by “mesh” which is the number of openings per inch of screen. Make sure each sieve is clean before amount of graphite is put in it. See Fig. 3-8.

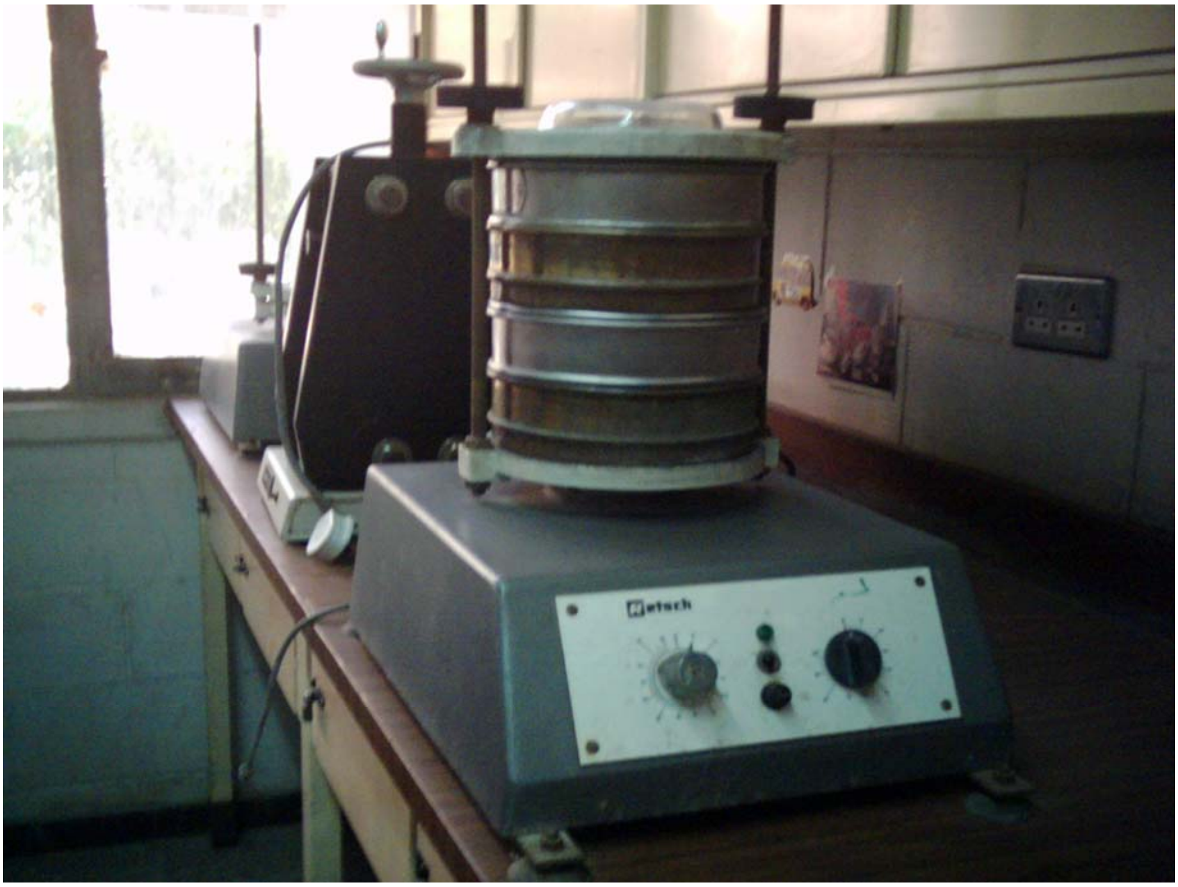


Figure 3-8 Sieve Shaker tester

2. Sieving the amount of graphite by using test sieve shaker with time at least (30 minute).
3. Removing the graphite particles from each sieve which represents the range of mean diameter particles of graphite and the final from the pan respectively as (212 ≤ 150) μm, (150 ≤ 75) μm, (75 ≤ 36) μm, (36 ≤ under).

Table 3-3 Sieve series

Mesh	in.	mm
48	0.00835	0.212
100	0.00591	0.150
200	0.00295	0.075
450	0.00142	0.036

After preparing different range diameter particles of graphite, apply graphite conductive colloid step.

The above procedure and specifications was repeated for different particles size (212, 150, 75) μm from step 1 to step 6.

3.2.2 Different Binding Agents Used for Graphite Conductive Colloidal in Plating Plastic Procedure:

In the present work, different binding agents are used, which are forming graphite coating step, as in the following:

1. Epoxy resin, supplied from Vantico group.
2. Polyester resin supplied from (SIRO Pol 7130-MM).
3. Cyanoacrylate, supplied from (JAPAN YAPISTIRCI), as shown in Table B-1 Appendix B. The above procedure and specifications were

repeated as the same steps except for the graphite coating in solution make up and in drying time as follows :

a. Graphite coating step: (using epoxy resin binder)

Solution make- up: after mixing of 300 g graphite particles size and 500 ml of acetic acid then added 60 g of bisphenol A-(epichlorhydrin) epoxy resin and 40 g of triethylene tetramine (hardener), and the mixture was stirred for 25 minutes, and in drying step needed about 25 minutes.

b. Graphite coating step: (using Polyester resin)

Solution make- up: after mixing of 300 g graphite particles size and acetic acid then, 80 g of unsaturated ester and 20 g of methyl ethyl keton (MEK) peroxide (hardener) the mixture was stirred for 25 minutes. And in drying step needed about 10 minutes.

c. Graphite coating step: (using cyanoacrylate resin)

Solution make – up: after mixing of graphite particle size and acetic acid, then added 100 g of cyanoacrylate and the mixture was stirred for25 minutes, and drying step needed about 5 minutes.

3.2.3 Different Plastic Types used for Plating Procedure:

Different plastic types are used such as:

1. Acryloniteral Butadene styrene(ABS) (thermoplastic).
2. Polystyrene (thermoplastic): two types of plastic supplied from (Basf, Germany Co.) which is symbol as (Terluran 958I), (Terluran 957I) and molded by (Anmar Industrial Co. for Plastic).
3. Epoxy – fiber glass (thermosetting).

4. Phenolic (thermosetting) suppliedm (LPKF laser & electronic AG, Germany Company)

The above procedure and specification were repeated from steps 1 to 6 by using substrate for each type of plastic as above with dimension (3x3x 0.4) cm for ABS, Polystyren and (3 x 3 x 0.145) cm for epoxy fiber glass and phenolic, for each type of binding agent and graphite particles size .

3.2.3.1 Measuring Graphite Deposition on Different Plastic Types with Different Parameter in Cleaning /Conditioning Bath :

After preparing the solution of the conditioner bath, the heater controller in bath was set to the required temperature (35 **^{o}C) ,** the substrate (different type of plastic) was immersed in the bath for 10 minutes and rinsing ,then substrate immersion in graphite conductive colloid. After drying process weighing the substrate and recording for each temperature (45, 55, 65, 75^{o}C).

The above procedure again was repeated for different times 5,10, 15, 20, and 25 minutes, at temperature 45 **^{o}C** (for ABS and polystyrene) and 65 ^{o}C (for epoxy-fiber glass and phenolic).

After stability all parameters as graphite particle size (36µm) and binding agent (epoxy resin) for graphite layer into plastic surface to measure the current efficiency in acid copper electroplating.

3.3 The Current Efficiency in Acid Copper Electroplating Bath Procedure:

The cathode was plastic substrate was (3x3x0.4) cm and the anode plate (copper) were (5 x 5 x 1) cm. in order to use it in the current efficiency experiments. Before each experimental run, the anodes immersed in (3% HCl) for two minutes, then washed with distilled water, dried with paper tissue, then left to dry for 12 hour in the disscater over silica gel. Weighing the cathode (substrate of plastic) was carried out using digital balance to 0.1 mg accuracy (analytical balance type AE260 Delta Range mattler) and Fig. 3-7 describes the subsequence of experimental work steps.

a. Measuring Cathode Current Efficiency with Concentration of Copper Sulfate ($CuSO_4 . 5H_2O$)

150 g/L of $CuSO_4$. $5H_2O$, 50 g/L of H_2SO_4 ,50 mg/L HCl and additive as brightener were added to the bath (see step 6 in section 3.3.1) to obtain acid copper bath solution. Before starting each run, the cathode (substrate of plastic) and anodes (electrode copper) were fixed in the bath at room temperature.

Then set the D.C. power supply until obtaining a total constant current of 0.54 A. The experimental run lasted 60 minutes, then the cathode was taken for washing with distilled water and finally allowed to dry about (10) minutes. Weighing the cathode and recorded.

The above procedure was repeated for different concentrations 200 and 250 g/L of $CuSO_4$. $5H_2O$.And in these concentrations also measuring the electrical conductivity for solution bath by conductive meter type CRB3(capcitor Analyeser and Resistance BRI-DGE) and apply the following relation : **$K = 1.52/ R$ at 25 ^{o}C**.

Where K is the electrolyte conductivity of solution resistance, R is the measured resistance for the solution.

b. Measuring Cathode Current Efficiency with Current Density :

200 g/Lof $CuSO_4.5H_2O$, 50 g/L H_2SO_4, and 50 mg/L HCl and additive as brightener (step 6) to obtain acid copper bath solution at room temperature (25°C).

The above procedure and specification were repeated for different current densities of 2 and 4 A/dm^2.

c. Measuring Cathode Current Efficiency with Temperature:

200 g/L of $CuSO_4.5H_2O$, 50 g/L H_2SO_4, and 50 mg/L HCl and additive as brightener (step 6) to obtain acid copper bath solution at current density 3 A/dm^2.

The above procedure and specification were repeated for temperatures of 25, 35, 45, and 55°C. Each run was repeated twice with a third run when reproducibility was in doubt.

d. Measuring Cathode Current Efficiency with Time:

200 g/L of $CuSO_4.5H_2O$, 50 g/L H_2SO_4, 50 mg/L HCl and additive as brightener (step 6) to obtain acid copper bath solution at current density 3 A/dm^2.

The above procedure and specification were repeated for different times 15, 30, 45 and 60 minutes. and in these times also measuring the thickness of copper electrodeposition within the different current densities 1,1.5, 2, 2.5 and 3 A/dm^2 .

3.4 Methods of Testing

To assess the reliability of plated plastic part and predict its possible behavior during service life under adverse conditions by a number of testing, these methods of testing including testing the adhesion of metals to plastic, measuring the coating thickness, scratch, porosity, appearance of coating and roughness of surface.

3.4.1 Adhesion Testing

Copper sulfate electroplating was conducted at temperature of 25 ^{o}C and a current density of 3 A/dm^2 for 60 min. And the plated substrate was peeled away from the plastic at constant rate (0.5 mm/min) using a tensile strength (product of Shimadzu Corp.) and ASTM B 533 to measure the peel strength see Fig. 3-9.

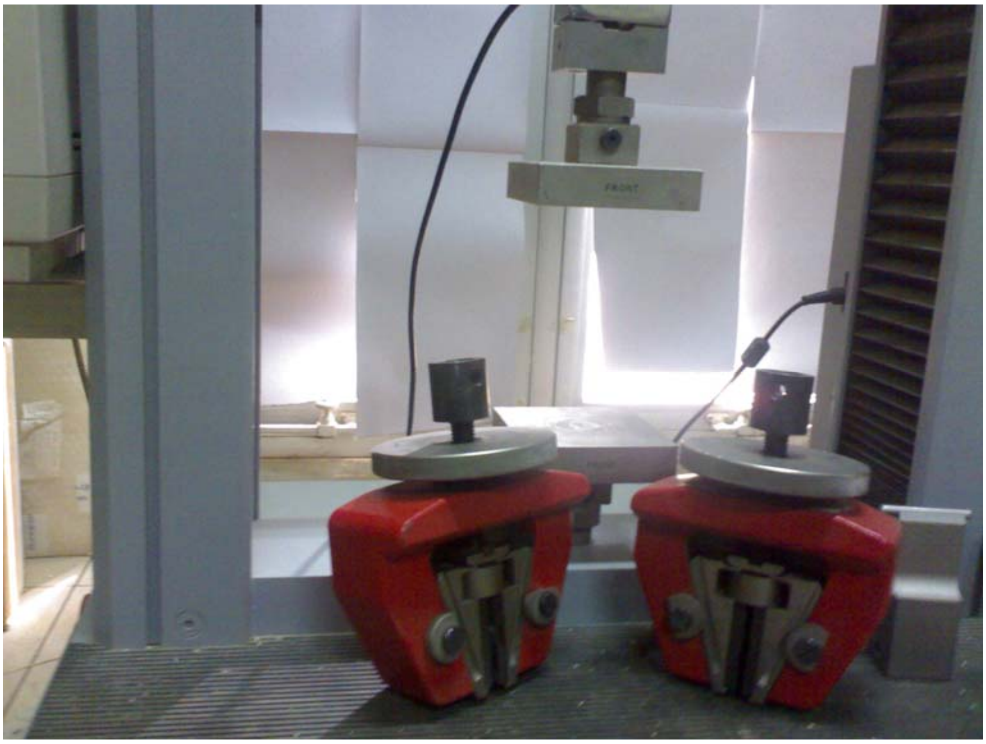


Figure 3.9 Tensile strength equipment

3.4.2Thickness Measuring

A method used for determining the thickness of electrodeposits on metals can be used on plated plastics. This method includes:-
Optical microscope [31].

Thickness measuring has been carried out using optical microscope type (Nikon Eclips ME 600 provided with digital camera, Japan ACT-1, version 2.62, copyright 2000) working with software (niuon DXM 120 aF).

The coated layer was analyzed using image analysis software (LuciA, version 4.81, copyright 1991-2003). In this test cut the substrate to give cuts of 10 mm in width, then reading is taken as average of measured values obtained at 10 points for each side of plating as shown in Fig 3-10 which explains the optical microscope used in the present work (Science and Technology Ministry).

Figure 3.10 Optical microscope

3.4.3 Scratch Resistance

A copper electroplating procedure was carried out at a current density of 3 A/dm^2 for 60 minutes, scratch resistance for the plated substrate by the following method: A test plane is clamped to a slide which slowly withdraws the panel while a needle scratched the surface. Tests are using a single specified load by increasing the load to determine the minimum load at which the coating is penetrated for substrate plating [32]. This scratch testers is (E17/ISO 12137-1, loop stylus version BS 3900) in center office for measuring and quality control as shown in Fig. 3-11, and Fig. 3-12 represent a needle scratch on the surface of substrate platted .

Figure 3-11 Scratch tester

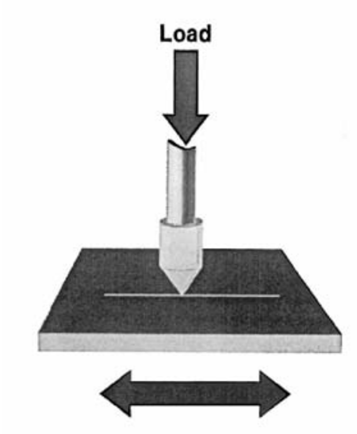


Figure 3-12 Needle of Scratch tester

3.4.4 Surface Roughness

Average roughness value is measured by (TALYSURF 4) which is supplied from (TAYLOR HOBSON company) with (styles) made of diamond with maximum moving distance of 11 mm [33], the horizontal magnification 4x→100x and the vertical magnification 500x→10^5x for different substrate as shown in Fig. 3-13 showing the surface roughness tester.

Figure 3-13 surface roughness tester

3.4.4 Percentage Porosity

Porosity is measured by mercury porosimeter, a product from (Rusk instrument company), which depends on ratio volume of porosity in the surface of substrate by saturated method to the total volume of substrate by mercury porosimeter[34] as shown in Fig. 3-14a and Fig. 3-14b.

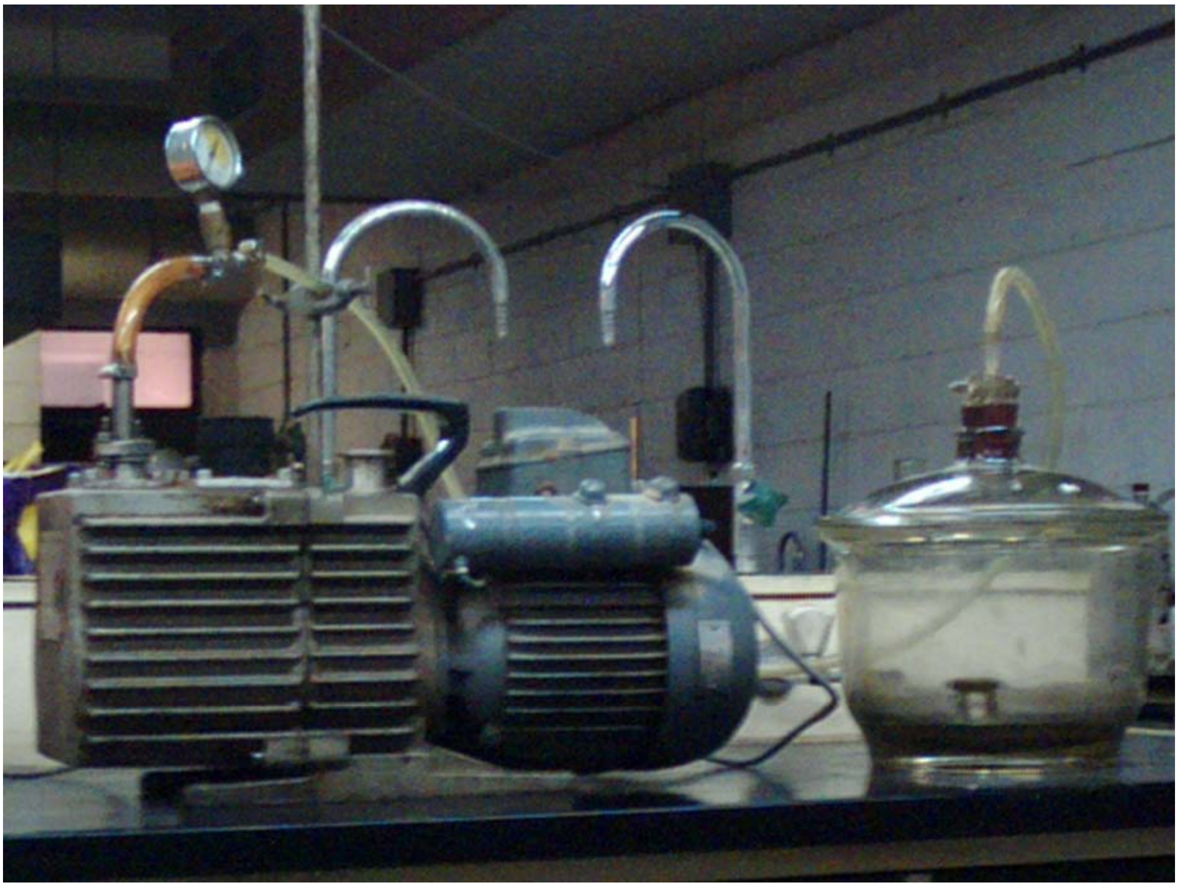


Figure 3-14 a Effective porosity by saturated method

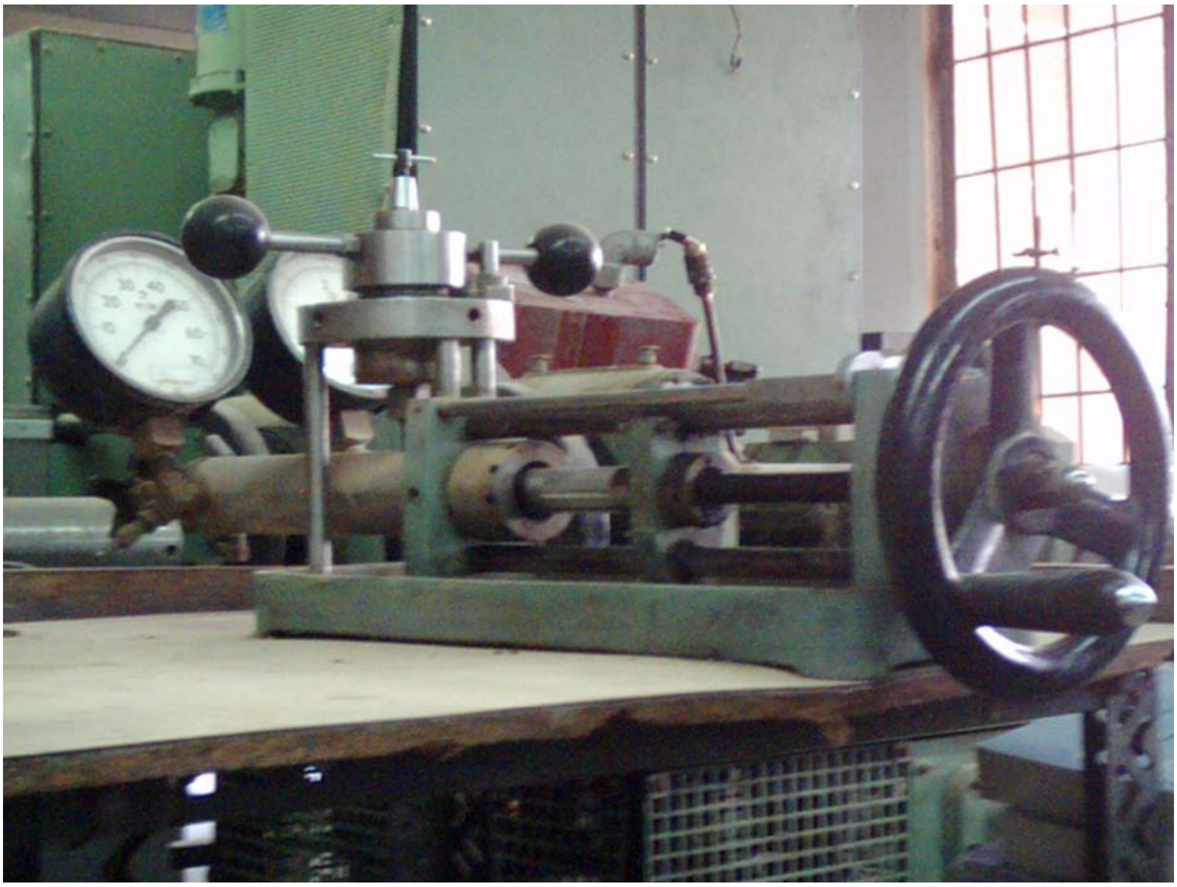


Figure 3-14 b Mercury porosmeter

Chapter Four

Results and Interpretation

4.1 Introduction

The present work has been mainly aimed to find the best results from experimental work on types of plastic by studying the effect of the particle size of graphite and different types of binding agents. The critical ingredients for preparing the conductive layer prior to electroplating bath have been also considered.

Also it is required to find a relationship between cathodic current efficiency with current density, time, temperature and $CuSO_4.5H_2O$ concentration in plating bath, as well as, tests for thickness, adhesion, roughness, porosity, scratch and appearance coating.

4.2 Parameters Studied

In the present work eight parameters have been studied as follows:
Graphite particle size, type of plastic, type of binding agent, concentration of cupper sulfate, current density, temperature, time, and plating uniformity.

4.3 Experimental Results:

4.3.1 Effect of Graphite Particles Size

The effect of particle size of graphite on plating time is shown in Table 4.1. It can be noticed that an increase in particle size will increase the plating time at current density $3A/dm^2$.

Table 4.1 Effect of particles size on plating time for ABS and epoxy resin

Mean diameter (μm)	**Plating time (min.)**
36	30
75	45
150	70
212	120

4.3.2 Effect of Binding Agent

The effect of binding agent type on drying time for graphite deposition is shown in Table 4.2 The increase in drying time for epoxy resin is more than polyester resin and cyanoacrylates.

Table 4.2 Effect of binding agents on drying time , particle size of 36µm ,substrate ABS

Type of binding agents	**Drying time (min)**
cyanoacrylates	5
Polyester resin	10
Epoxy resin	25

4.3.3 Effect of Plastic Types

The effect of plastic types on conditioner process in Table 4.3 for temperature and Table 4.4 for time in conditioner bath .The increase in temperature and time will lead to increase the amount of graphite depositing.

Table 4.3 Effect of plastic types and temperature on graphite deposition using epoxy resin as binding agent, particle size 36μm, and time 10 min.

Temperature ^oC / Type of plastic	Graphite deposition g/cm^2			
	ABS	Polystyren	Epoxy-fiber glass	Phenolic
35	0.0159	0.0112	0.00337	0.00138
45	0.0173	0.0119	0.00395	0.00144
55	0.0192	0.0131	0.00462	0.00149
65			0.00545	0.00167
75			0.00646	0.00177

Table 4.4 Effect of plastic types and time for epoxy resin as binding agent using and particle size 36μm at 55 ^oC (ABS, Polystyren) and 65 ^oC (epoxy-fiberglass and phenolic**)**

Time min. / Type of plastic	Graphite deposition g/cm^2			
	ABS	Polystyren	Epoxy-fiber glass	Phenolic
5	0.0141	0.0116	0.00283	0.00129
10	0.0217	0.0176	0.00452	0.00176
15	0.0226	0.018	0.0047	0.00180
20	0.0236	0.0184	0.00492	0.00184
25	0.0243	0.0185	0.00501	0.00187

4.3 Cathodic Current Efficiency

The best indication for electroplating is cathodic current efficiency, which is calculated from equations (2.1) and (2.2) (as shown in Appendix C) with equivalent weight 31.773 g for Cu.

4.4.1 Effect of Concentration

The effect of concentration of $CuSO_4.5H_2O$ on cathodic current efficiency is shown in table 4.5 for copper. It can be noticed that an increase in concentration of ($CuSO_4.5H_2O$) will lead to increase the cathodic current efficiency.

Table 4-5 Cathodic current efficiency, total current (I), experimental weight of deposit (Δw), and the theoretical weight of deposit (w_{th}) for different concentrations of $CuSO_4.5H_2O$ at time period of 60 min, T=25 °C, $A_{cath.}$=17.94 cm^2 for copper solution (substrate ABS)

Conc. of $CuSO_4.5H_2O$ (g/l)	Δw actual (g)	I (A)	w_{th} (g)	Efficiency %
150	0.583	0.54	0.640169	91.2
200	0.613	0.54	0.640169	95.8
250	0.627	0.54	0.640169	97.98

4.4.2 Temperature of Solution

Effect of solution temperature (copper) on cathodic current efficiency is shown in table 4.6 The increase in temperature will lead to break down and decreasing in the efficiency of the bath.

Table 4.6 Cathodic current efficiency, total current (I), experimental weight of deposit (Δw), and the theoretical weight of deposit (w_{th}) for different solution temperatures for copper deposition at time period of 60 min, $CuSO_4.5H_2O$ 200g/l, A_{cath}.=15.88 cm^2 for substrate epoxy – fiberglass

Temperature (^oC)	Δw actual (g)	I (A)	w_{th} (g)	Efficiency %
25	0.5576	0.48	0.574998	96.97
45	0.1540	0.48	0.574998	26.78
55	0.078	0.48	0.574998	13.56

4.4.3 Effect of Cathodic Current Density

The effect of cathodic current density for copper plating on cathodic current efficiency is shown in table 4.7. The increase in current density will lead to an increase in cathodic current efficiency.

Table 4.7 Cathodic current efficiency, experimental weight deposit (Δw), and the theoretical weight of deposit (w_{th}) for different cathodic current densities, $CuSO_4.5H_2O$ 200g/l at time period of 60 min, T=25 ^oC, A_{cath}.=17.94 cm^2 for copper solution (substrate ABS)

C.D A/dm^2	**Δw actual (g)**	**I (A)**	**w_{th} (g)**	**Efficiency %**
2	0.394	0.36	0.4268	92.3
3	0.614	0.54	0.640169	95.91
4	0.832	0.717	0.8500	97.88

4.4.3 Effect of Copper Plating Time

The effect of copper plating time on cathodic current efficiency is shown in table 4.8. The increase in plating time increased the cathodic current efficiency of system.

Table 4.8 Cathodic current efficiency, total current (I), experimental weight of deposit (Δw), and the theoretical weight of deposit (w_{th}) for different time periods of copper electroplated at T=25^{o}C, $CuSO_4.5H_2O$ 200g/l, A_{cath}. = 17.94 cm^2 for substrate ABS

Time (min)	Δw actual (g)	I (A)	w_{th} (g)	Efficiency %
15	0.04432	0.54	0.160042	27.696
30	0.21899	0.54	0.320084	68.419
45	0.43687	0.54	0.480169	90.991
60	0.6134	0.54	0.640169	95.818

4.5 Ohmic Resistance of Electrolyte Solution

The plating uniformity of the electrolytic copper deposit to the non-conductive surface is calculated from equation (2.8) as ohmic resistance for electrolyte copper plating (see Appendix C)

4.5.1 Effect of Concentration

The effect of copper concentration $CuSO_4.5H_2O$ on plating uniformity is shown in table 4.9. It can be noticed that an increase in concentration will lead to an increase in electrolyte conductivity which will lead to a decrease in ohmic resistance for electrolyte copper plating.

Table 4.9 Ohmic resistance for electrolyte copper plating, current density 3A/dm^2, length 2.7cm, thickness 0.4cm for different solution resistance K (substrate ABS)

Conc. Of $CuSO_4.5H_2O$ (g/l)	K (S/cm)	E (V)
150	0.038	0.02339
200	0.10133	0.008772
250	0.2362	0.003763

4.5.2 Effect of Thickness

The effect of substrate thickness on ohmic resistance is shown in table 4.10.It can be seen that the increase in thickness will lead to anincrease in ohmic resistance for electrolyte copper plating.

Table 4.10 Ohmic resistance for electrolyte copper plating, current density 3A/dm^2, length 2.7cm,K 0.10133*10^{-6}, length 2.7 cm for different thicknesses of substrate (ABS)

Thickness (cm)	E (V)
0.15	0.001300
0.2	0.002193
0.4	0.008772

4.6 Tests for Best Conditions

The results are obtained from tests were also assessed after the Best conditions for graphite deposition layer on plastic were depended on particle size, binding agent ,different plastic types and copper plating after applying thickness, adhesion, roughness, porosity, scratch and appearance of coating tests.

4.6.1 Plating Thickness

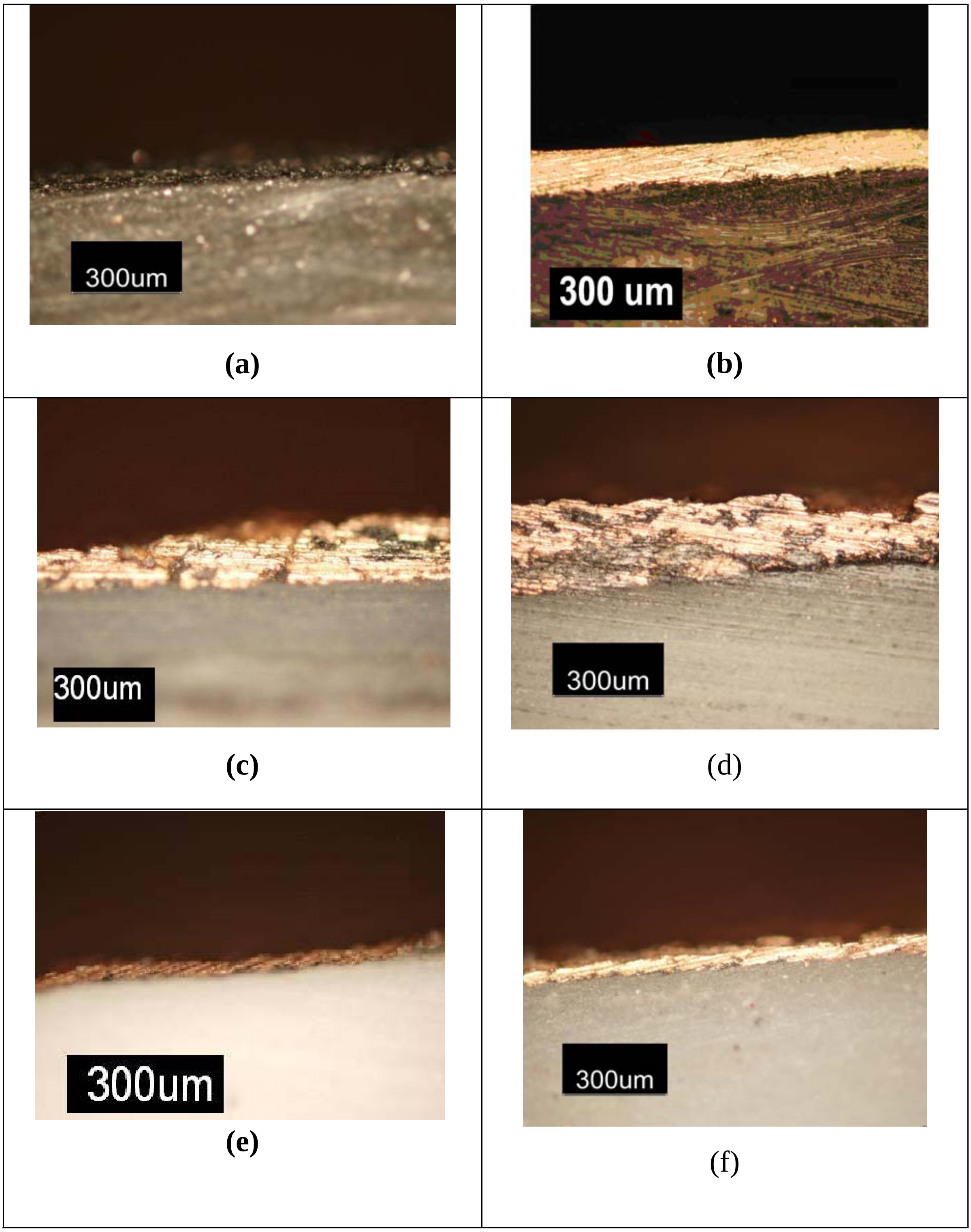
The results of plating thickness test are shown in Table 4.11 for the effect of particle size of graphite on plating thickness for different plastic types. Table 4.12 shows the effect of plating time on the layer thickness according the applied current density and as calculated from equation (2.7) see (Appendix C). An increase in the particle size of graphite more than 36 µm will lead to increase non- uniform plating thickness and increase in plating time will increase the plating thickness, **Fig. 4.1,** when viewed in cross – section by microscope at 500 times magnification for copper plating thickness.

Table 4.11 Effect of particles sizes on thickness of copper plating at 3 A/dm^2 and 60 min for epoxy resin

Particle size (µm) / Type of plastic	Plating thickness (µm)			
	ABS	Polystyrene	Epoxy-fiber glass	Phenolic
36	38.508	38.0165	34.160	32.031
75	76.706	66.52	60.45	56.054
150	151.268	145.064	119.12	115.116
212	217.839	210.761	200	190.221

Table 4.12 Layer thickness depending on copper plating time, ABS, 36μm, epoxy resin

Time (min.) / C. D A/dm^2	Thickness (μm)				Rate of plating (μm/min)
	15	30	45	60	
From eq. (2.7)	3.3	6.6	9.9	13.2	0.22
1	2.97	5.95	8.93	11.9	0.198
From eq. (2.7)	4.95	9.9	14.85	19.8	0.33
1.5	4.5	9.03	13.5	18.06	0.30
From eq. (2.7)	6.6	13.2	19.8	26.4	0.44
2	6.1	12.2	18.3	24.4	0.40
From eq. (2.7)	8.25	16.5	24.75	33	0.55
2.5	7.73	15.54	23.33	31.09	0.52
From eq. (2.7)	9.9	19.8	29.76	39.7	0.66
3	9.52	19.03	28.55	38.06	0.634



(a) **(b)**

(c) (d)

(e) (f)

Fig. 4.1 Thickness of copper deposit on plastic types-cross-sectional views (about 500x). (a) graphite deposition for 36 µm particle size (b) ABS surface for 36 µm; (c) ABS surface for particle size 150 µm;(d) ABS surface for 212 µm particle size; e) epoxy-fiber glass surface for 36 µm particle size (f) phenolic surface for 36 µm particle size

4.6.2 Adhesion of Plating

The results of adhesion of plating test are shown in Table 4.13 for the effect the particle size on peel strength and Table 4.14 for effect of the binding agent type on peel strength for different types of plastic. An increase in the particle size will lead to decrease the peel strength for copper plating, and peel strength increase for epoxy resin more than cyanoacrylates and polyester resin.

Table 4.13 Effect of particles size on peel strength for epoxy resin

Particle sizes (μm) / Type of plastic	Peel strength kg/cm			
	ABS	Polystyrene	Epoxy-fiber glass	Phenolic
36	2	1.8	1.5	1.3
75	1.2	0.9	0.75	0.7
150	0.75	0.5	0.4	0.35
212	0.35	0.25	0.2	0.15

Table 4.14 Effect of binding agent on peel strength

Binding agent type / Type of plastic	Peel strength (kg/cm)			
	ABS	Polystyren	Epoxy-fiber glass	Phenolic
Epoxy resin	2	1.8	1.5	1.3
cyanoacrylates	1.3	1	0.9	0.85
Polyester resin	1	0.85	0.7	0.55

4.6.3 Porosity

The results of porosity test are shown in Table 4.15 for the effect of the particle size on porosity for plastic types and Table 4.16 for effect of the plating thickness on porosity of plating. An increase in the particle size will lead to increase the porosity and an increase in the plating thickness will decrease the porosity.

Table 4.15 Effect of particle size on porosity.

Particle sizes (µm) / Type of plastic	Porosity %			
	ABS	Polystyrene	Epoxy-fiber glass	Phenolic
36	1.8	2.7	1.3	0.11
75	3.6	4.3	2.9	2.3
150	8.4	10.2	7.5	6.5
212	25.2	30.6	22.3	20.9

Table 4.16 Effect of plating thickness on porosity for ABS, epoxy resin, 36 µm and current density 3 A/dm^2

Time of plating (min.)	Thickness (µm)	Porosity %
15	9.52	20.85
30	19.03	12.11
45	28.55	5.97
60	38.06	1.8

4.6.4 Surface Roughness

The results of surface roughness test are shown in Table 4.17 for the effect of the particle size on surface roughness for plastic types and Table 4.18 for the effect of the plating thickness on surface roughness for copper plating. An increase in the particle size will lead to increase the surface roughness and an increase in the plating thickness will increase the surface roughness.

Table 4.17 Effect of particle size on surface roughness.

Particle sizes (µm) / Type of plastic	Roughness µm			
	ABS	Polystyrene	Epoxy-fiber glass	Phenolic
36	0.02	0.01	0.008	0.005
75	0.035	0.024	0.017	0.011
150	0.068	0.053	0.044	0.028
212	0.162	0.132	0.098	0.068

Table 4.18 Effect of plating thickness on surface roughness for ABS, epoxy resin and 36 µm and current density 3 A/dm^2

Time of plating (min.)	Thickness (µm)	Roughness (µm)
15	9.52	0.004
30	19.03	0.0074
45	28.55	0.0108
60	38.06	0.02

4.6.5 Scratch resistance

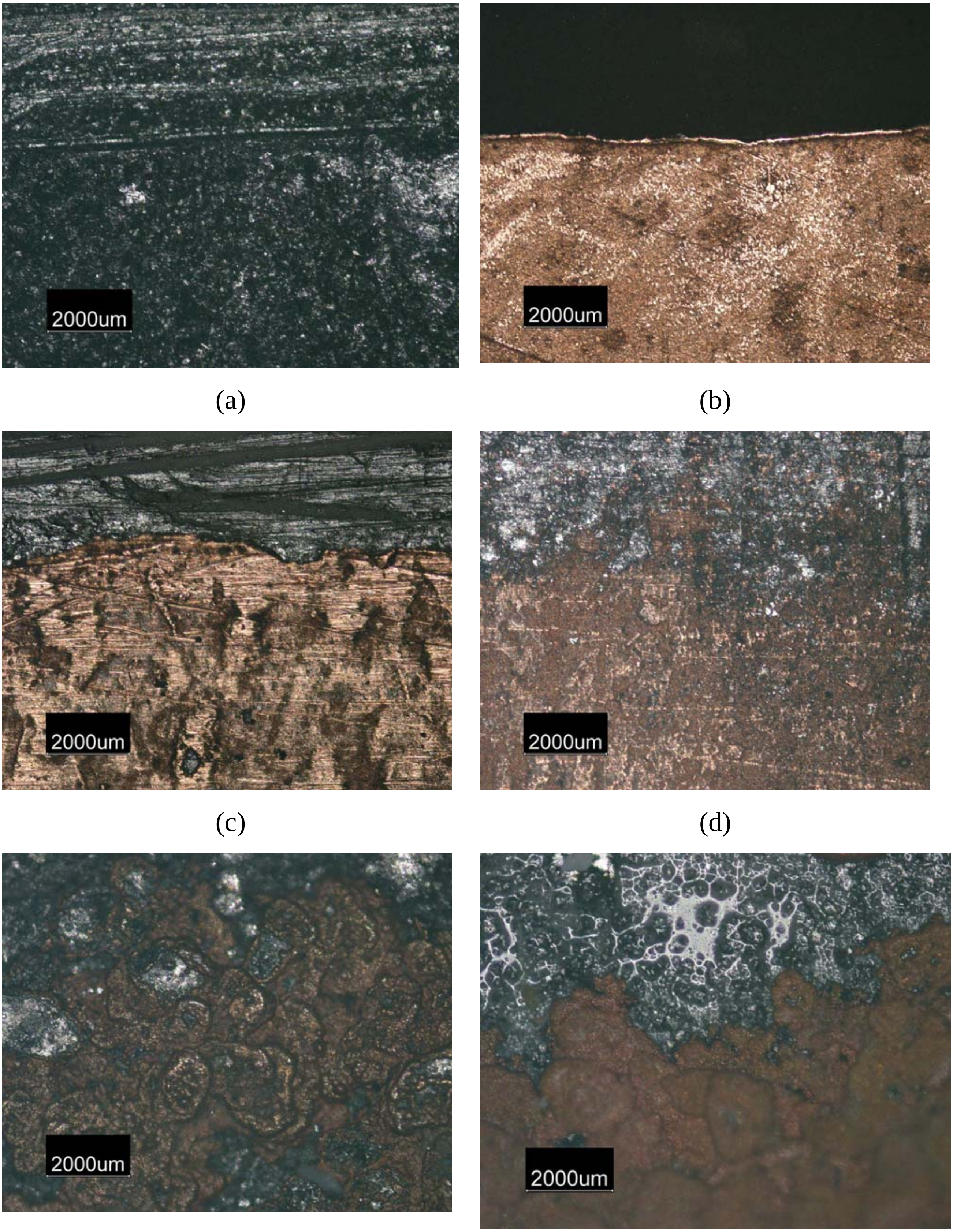
The results of surface scratch test are shown in Table 4.19 for the effect of the binding agent type on surface scratch for plastic types**.** An increase in the load applied in scratch test for epoxy resin is more than cyanoacrylates and polyester resin.

Table 4.19 Effect of binding agent in graphite colloid on scratch result.

Binding agent type / Type of plastic	Load (kg)			
	ABS	Polystyren	Epoxy-fiber glass	Phenolic
Epoxy resin	2	1.950	1.250	1.050
cyanoacrylates	1.5	1.350	1	0.920
Polyester resin	1	0.900	0.800	0.750

4.6.6 Appearance of Coating

The appearance of coating for copper plating is according to particle size of graphite. When the increase in the particle size is more than 36µm plating will cause copper plating appearance less desirable from non-uniform areas of plating, lumpiness or localized areas are visible under microscope as shown in **Figure 4.2**.



(a) (b)

(c) (d)

(e) **(f)**

Fig. 4.2 Appearance of coating on plastic (ABS) (a) 36 µm graphite (b) 36 µm (c) 75 µm (d) 150 µm(e) 212 µm, lumpiness and (f) 212 µm

Chapter Five

Discussion

5.1 Introduction

In this chapter the variables involved in the present work, i.e., particle size of graphite, type of binding agent, type of plastic, concentration of copper ion, current density, time, solution temperature, and ohmic resistance of acid copper solution will be explained, as well as their influence on the properties of direct plating on plastic.

The manner in which this chapter is presented is, therefore, similar to that used in Chapter four. When these sections deal with the effect of each variable on current efficiency, tests are applied on electroplated plastic substrate as thickness, adhesion, surface roughness, porosity, and scratch plating test, and it also shows relationship between cathodic current efficiency and concentration, temperature, time and current density.

5.2 Effect of Graphite Particle Size

5.2.1 Deposition Time

Figure 5.1 shows that the deposition time for copper plating increases with the increasing of the particle size. This could be attributed to the fact that increasing the average distance between particles, thereby making it more difficult for plating to proceed from one particle to another, therefore, the rate of deposition is very low or the time needed for copper electroplating is very long and this behavior was stated in Ref.[9].

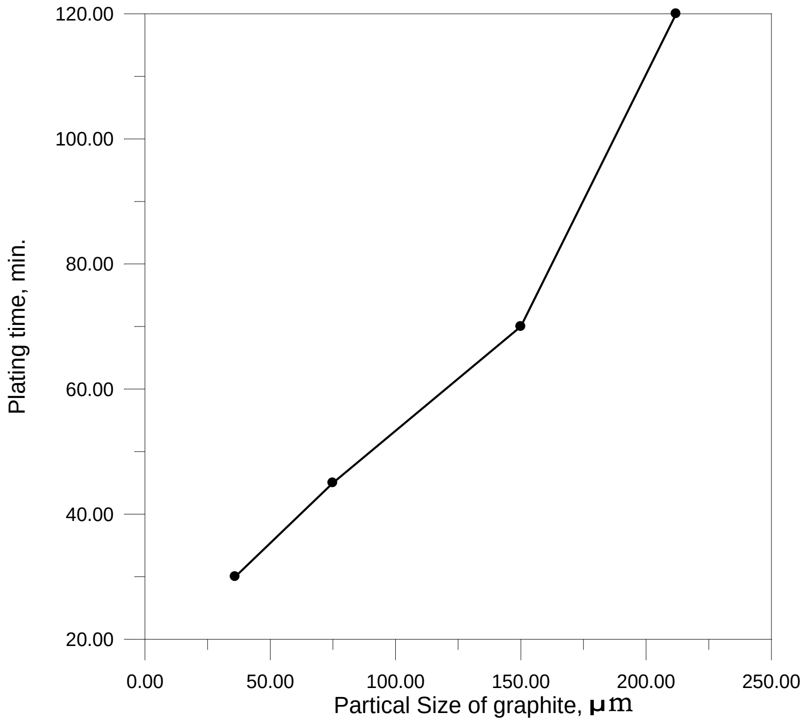


Figure 5.1 Plating time vs. particle size of graphite, T = 25°C, i = 3 A/dm^2

Using the best fit technique, the following is obtained:

For copper plating:

$$t = 5.957 + 0.8636\,d - 0.00623\,d^2 + 2.21776 \times 10^{-5}\,d^3 \qquad \ldots(5.1)$$

where t is time in minutes and d is the particle size in μm.

5.2.2 Plating Thickness

It can be seen from **Figure 5.2** that the thickness of copper plating for different plastic types, increases with the increasing of the particle size of graphite. This result is due to the non-uniformity in plating, i.e. lumpiness, where graphite is deposited first in non-uniform fashion followed by copper deposition and consequently the resultant will be mixed layers of graphite and copper. This phenomena was observed from Ref.[10]. It can be noticed that different plating thickness for same graphite particle size of different types of plastic as (ABS and polystyrene) versus (epoxy-fiberglass and phenolic) is due to the nature and composition for each type of plastics.

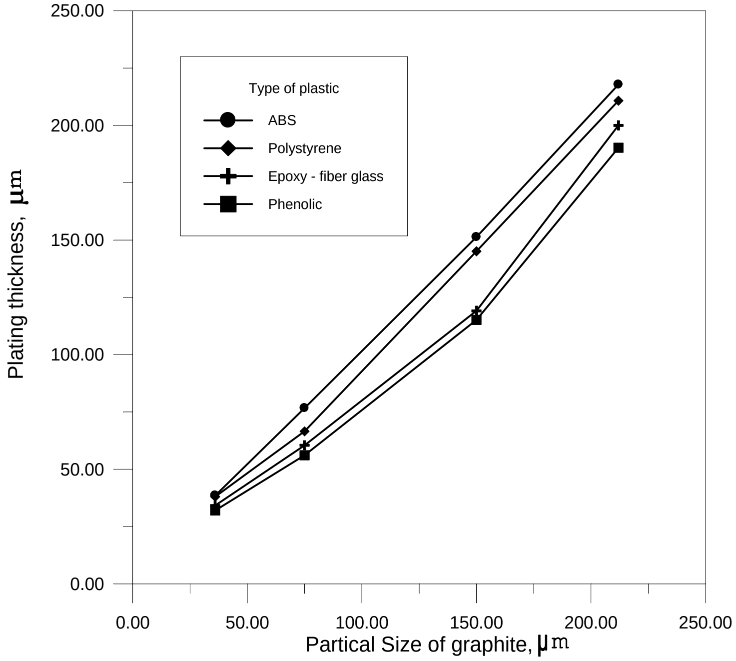


Figure 5.2 Plating thickness vs. particle size of graphite, t= 60min., C=200g/l conc. Of $CuSO_4.5H_2O$, current density 3 A/dm^2, for different plastic substrates

From **Figure 5.2** it can be seen that plating thickness increases with the increased particle size for ABS and polystyrene as (thermoplastic) and epoxy – fiberglass and phenolic as (thermosetting). The best fitting for these curves is given in table 5.1.

5.2.3 Plating Adhesion

Figure 5.3 shows that the peel strength decreases with the increasing of the particle size for different types of plastic. This result is due to non-uniform plating thickness on the substrate for particle size more than 36 μm which will lead to pullaway for copper deposition. This is in good agreement with the experimental observations from Refs.[14] and [15], i.e., for (ABS and polystyrene) more than (epoxy-fiberglass and phenolic) is due to nature of bound between metal and each plastic type.

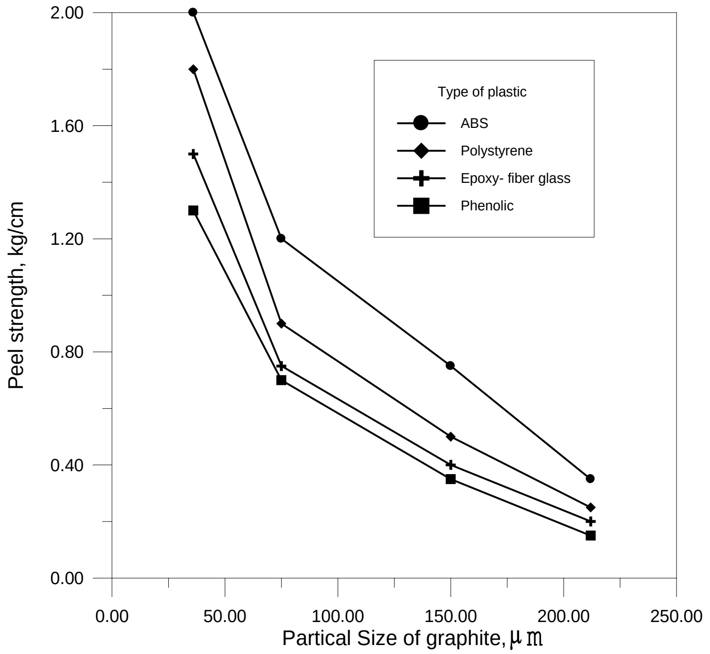


Figure 5.3 Peel strength vs. particle size of graphite, t= 60min., C=200g/l conc. Of $CuSO_4.5H_2O$, current density 3 A/dm^2, for different plastic substrates

The fitted equations for Fig. 5.3 are given in table 5.1 at the end of this chapter

5.2.4 Plating Porosity

It can be noticed from **Fig. 5.4** that porosity increases with increasing particle size of graphite for different types of plastic. This is due to the increase of the average distance between particles which will lead to the increase the small non-conducting areas on the substrate which are not bridged over during the early stage of deposition as stated as Ref.[11],acceptance level for porosity of plating shall not be more than 10% of plating area[34]. Taking into consideration that the initial surface before plating is unique in its roughness according to each type of plastic.

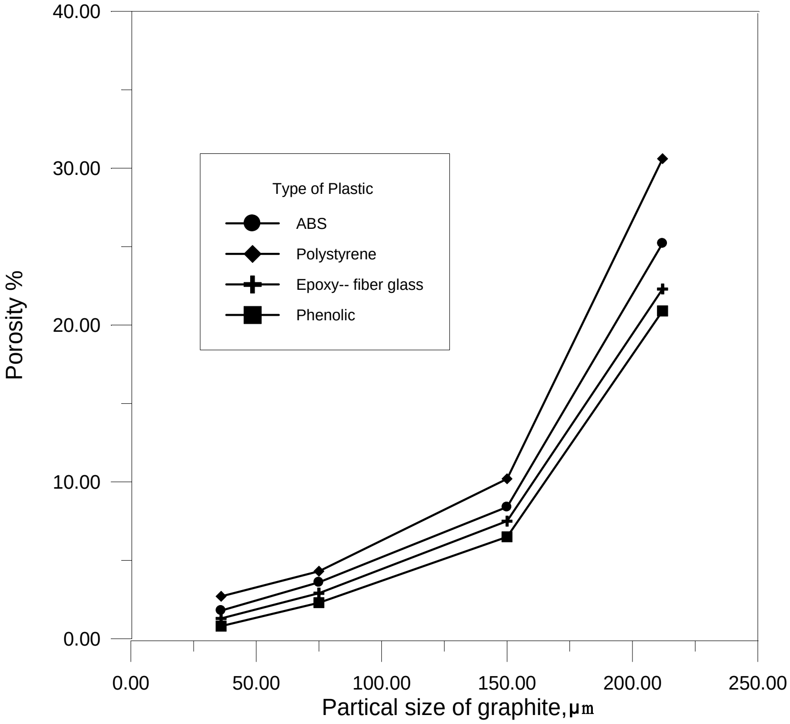


Figure 5.4 Porosity vs. particle size of graphite, t= 60min., C=200g/l conc. Of $CuSO_4.5H_2O$, current density 3 A/dm^2, for different plastic substrates

The fitted equations for Fig. 5.4 are given in table 5.1 at the end of this chapter

5.2.5 Surface Roughness

From **Figure 5.5** one can notice that the increase in the surface roughness with the increasing particle size of graphite. This is due to spacing of the irregularities of the surface as stated in Ref.[11]. Acceptance level for surface roughness shall be covered with smooth and bright copper coating with not more than(R_a=0.5μm)[33]. Different surface roughnesses for the same particle size of different types of plastic. This is perhaps by the effect of the original surface roughness of substrate, e.g., ABS and polystyrene surface have 0.041 and 0.027 μm, while epoxy-fiberglass and phenolic 0.019 and 0.011μm as surface roughness of substrate before applying any pretreatment process for plating.

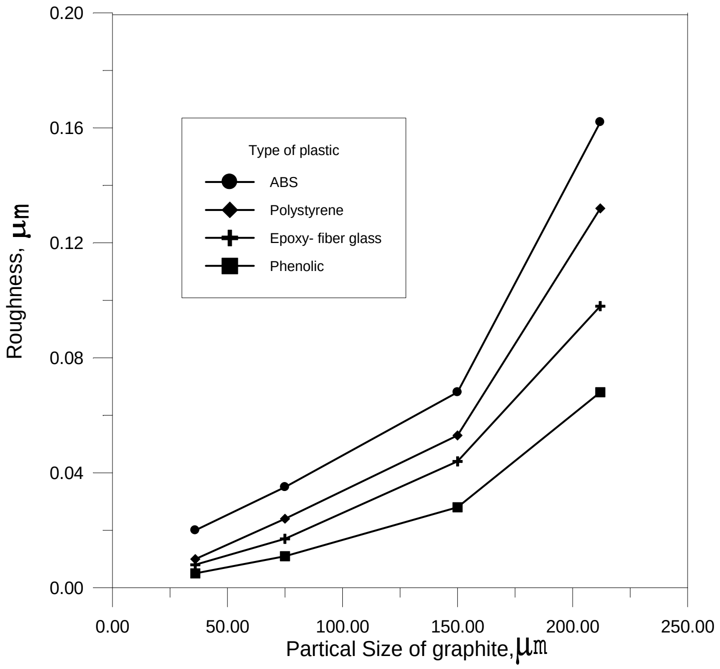


Figure 5.5 Roughness vs. particle size of graphite, t= 60min., c=200g/l conc. Of $CuSO_4.5H_2O$, current density 3 A/dm^2, for different substrates

The fitted equations for Fig. 5.5 are given in table 5.1 at the end of this chapter

5.3 Effect of Binding Agent

5.3.1 Drying Time

Table 4.2 shows that the drying time for epoxy resin is more than polyester resin and cyanoacrylates due to cure time for cross-linking occurrence. The properties of the cross-linked resins depend very greatly on the type of resin and is agreed with the Ref.[12].

5.3.2 Plating Adhesion

It has been seen from Table 4.14 that peel strength for epoxy resin is more than cyanoacrylate and polyester resin. This is because the mechanical properties for epoxy resin are dependent on the density of cross-links which are fixed at their mean position on plastic substrate and this is agreed with the works of Ref.[35].These are sufficient for graphite coating adhesion leading to good adhesion for copper plating. It is also the influence of plastic type on peel strength for the same resin type due to the nature of the polymer surface.

5.3.3 Scratch Resistance

It can be seen from Table 4.19 that the maximum load 2 kg is applied on epoxy resin as a binding agent on the deposited metal on the plastic substrate more than cyanoacrylates and polyester resin for using in graphite coating. This is due to the graphite coating cohesion is affected by attractive forces between atoms for epoxy resin more than another resin leading to greater resistance of copper plating against scratch as proved in Ref.[35]. And it is also affected by plastic type for the same resin type because of the different plastic properties such as rigidity and elastic deformation.

5.4 Effect of Plastic Type

5.4.1 Conditioner Temperature

Figure 5.6 shows that the amount of graphite deposition on substrate for different plastic types, increasing with the increasing of solution temperature of conditioner bath. This result is due to increase the wetting surface area by increasing the area size. It must be noticed that the behavior of epoxy-fiberglass as (thermosetting plastic) can be applied at temperature above 75^{o}C, while ABS and polystyrene as (thermoplastic) can not be applied at temperature above 55^{o}C The effective temperature is 55^{o}C for thermoplastic and 65 ^{o}C for thermosetting plastic as these values improve the peel strength at these temperatures. A similar effect of temperature was achieved by the work of [6].

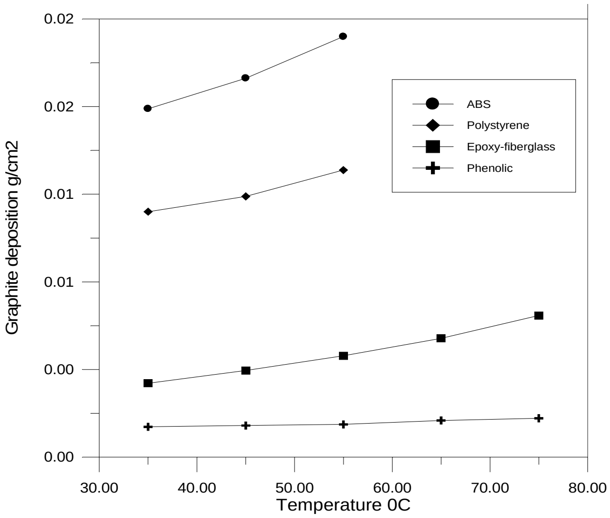


Figure 5.6 Graphite deposition vs. Temperature for 36 μm and epoxy resin for different plastic substrates

5.4.2 Conditioner Time

Figure 5.7 shows that the amount of graphite deposition on substrate increases with the increasing time for different plastic type, because the influence is to improve the wetting surface of plastic which will lead to increase the deposition graphite. It must be noticed that over conditioning, about 25 min., is less effective on substrate for different types of plastic comparative to effective time of 10 min. The fitted equations for Fig. 5.7 are given in table 5.1 at the end of this chapter

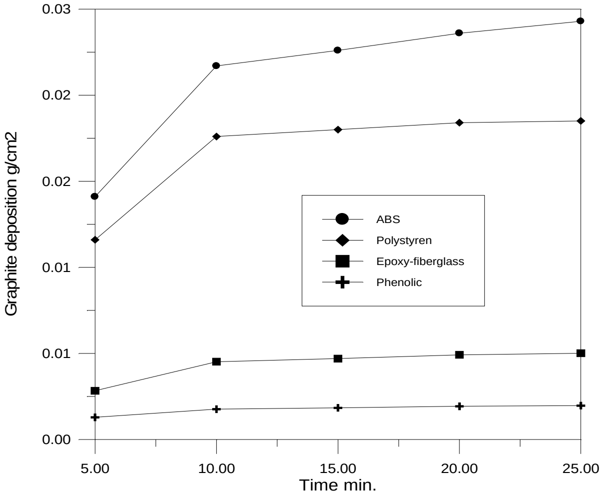


Figure 5.7 Graphite deposition vs. time for 36 μm and epoxy resin for different plastic substrates

5.5 Effect of Concentration of $CuSO_4.5H_2O$

5.5.1 Cathodic Current Efficiency

Figure 5.8 shows that the cathodic current efficiency, increases with increasing the concentration of copper sulfate ($CuSO_4.5H_2O$) in acid copper bath. This result is due to the increase of the deposition rate. But it can notice that concentration of copper may not increase more than 200 g/L, as this will lead to deposit of copper as rough, thick and very brittle deposits which agrees with Refs. [20] & [29].

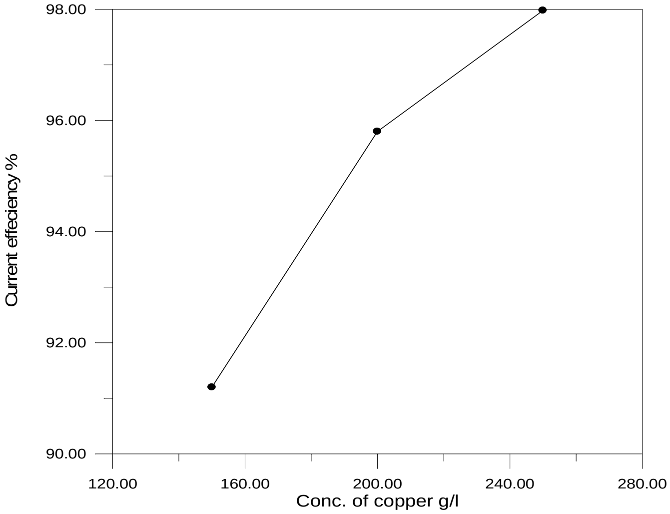


Figure 5.8 Cathodic current efficiency vs. concentration of $CuSO_4.5H_2O$, t= 60 min., current density 3 A/dm^2, temperature 25^0C for ABS plastic substrates

The curve in Fig. 5.8 may be fitted as follows:

$$\xi = 62.88 + 0.2614\,C - 0.000484\,C^2 \qquad \ldots(5.2)$$

where ξ is the cathodic current efficiency and C is the concentration of copper sulfate in g / L

5.5.2 Ohmic Resistance(or Voltage Drop)

It can be seen from **Figure 5.9** that an increase of concentration of $CuSO_4.5H_2O$ will lead to decrease in ohmic resistance (or voltage drop) for solution in acid copper bath. This is due to the increase in solution conductivity leading to low resistance levels which enable the rapid propagation of the electrodeposited copper in direct metallization as proved in Ref.[22].

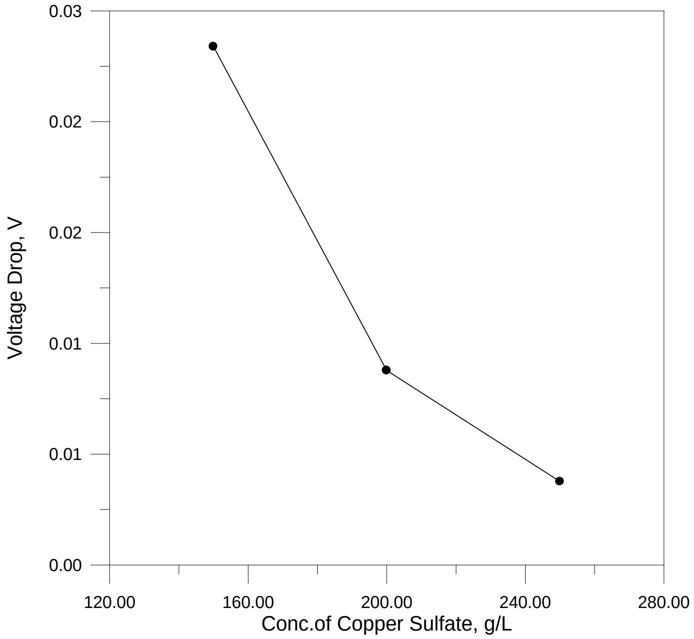


Figure 5.9 Ohmic resistance(or voltage drop) vs. concentration, current density 3A/dm^2

The ohmic resistance (or voltage drop) relation with concentration is fitted as follows:

$$E = 124898 - 964.99\,C + 1.9218\,C^2 \qquad \ldots(5.3)$$

where E is the ohmic resistance in Volts and C is the concentration of copper sulfate in g / L.

5.6 Effect of Temperature on Cathodic Current Efficiency

Figure 5.10 shows that the cathodic current efficiency, decreases with the increasing temperature of solution in acid copper bath. This is due to the rate of deposition which is decreased very quickly because the anode becomes coated with an insulating film as observed from Ref.[20].

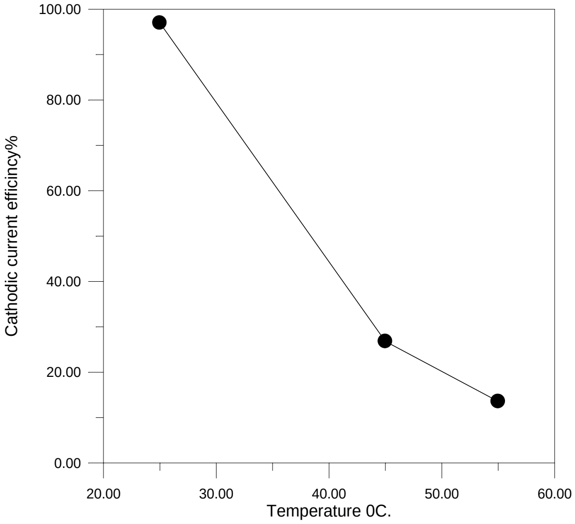


Figure 5.10 Cathodic current efficiency vs. temperature, t= 60min., C=200g/l conc. of $CuSO_4.5H_2O$, current density 3 A/dm^2, for epoxy-fiberglass substrate

Figure 5.10 is fitted as follows :

$$\xi = 266.738 - 8.613\,T + 0.0729\,T^2 \qquad \ldots(5.4)$$

where ξ is the cathodic current efficiency and T is the temperature in ^{o}C.

5.7 Effect of Cathodic Current Density

5.7.1 Cathodic Current Efficiency

It has been seen from **Figure 5.11** that cathodic current efficiency increases with the increasing of the cathodic current density. This is due to the increase of the deposition rate, but at higher current densities above 3 A/dm^2 the deposits from the acid copper bath are spongy and burning the substrate plated, as it was shown by the experimental work of [8].

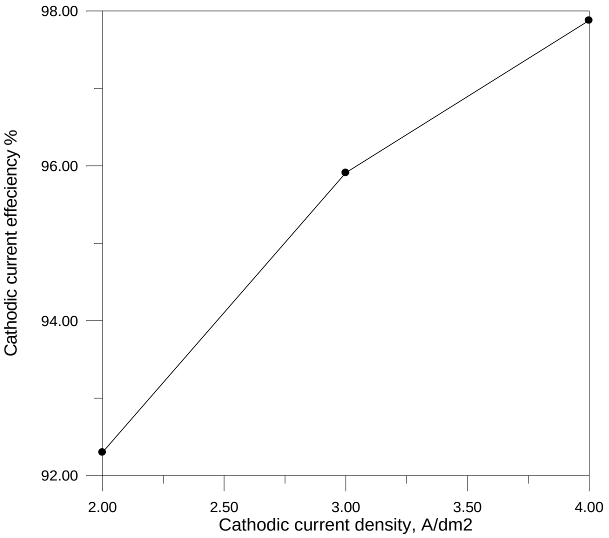


Figure 5.11 Cathodic current efficiency vs. cathodic current density, t= 60min., c=200g/l conc. Of $CuSO_4.5H_2O$, temperature 25°C, for epoxy-fiberglass substrate

Figure 5.11 is fitted as follows:

$$\xi = -109.56 + 118.38\, i - 16.63\, i^2 \quad \ldots(5.5)$$

where ξ is the cathodic current efficiency and i is the current density in A /dm^2.

5.7.2 Plating Thickness

Figure 5.12 shows that the plating thickness increases with the increasing of the current density for different times. This fact is due to the current density distribution leading to distribution of the metal deposit which is governed by mass transport to the cathode. When distribution of the metal deposit of crystal growth on the cathode surface occurs by way of growth layers, the thickness of these layers is strongly influenced by variations of current densities. These are in good agreement with Ref.[26]. It was also noticed from Table 4.12, the different thicknesses obtained from equation (2.7), because the cathodic current efficiency is actual, but equation (2.7) is based on 100% current efficiency.

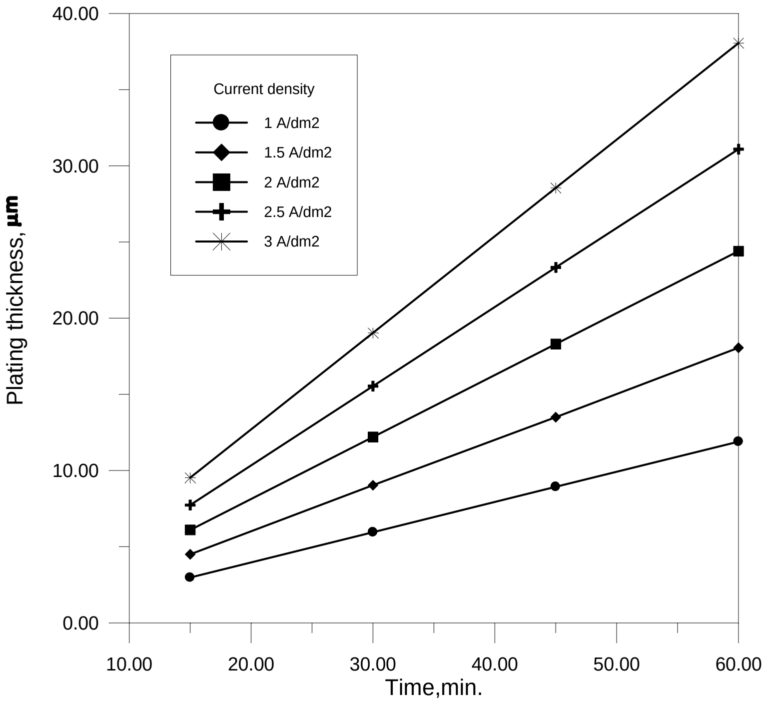


Figure 5-12 Plating thickness vs. plating time, C=200g/l conc. of $CuSO_4.5H_2O$, T= 25°C, for different current densities

The data presented in Fig. 5.12 may be fitted as follows :

$$\delta = -0.008 - 0.023987\ t - 0.002\ i + 0.217947\ t \times i \qquad \ldots(5.6)$$

where δ is the plating thickness in µm, t is the time in minutes, and i is the current density in A / dm^2.

5.8 Effect of Time

5.8.1 Cathodic Current Efficiency

Figure 5.13 shows that cathodic current efficiency increases with the increasing of the period time. This indicates that the longer time results in better or higher efficiency because further deposition is allowed to take place when time is increased.

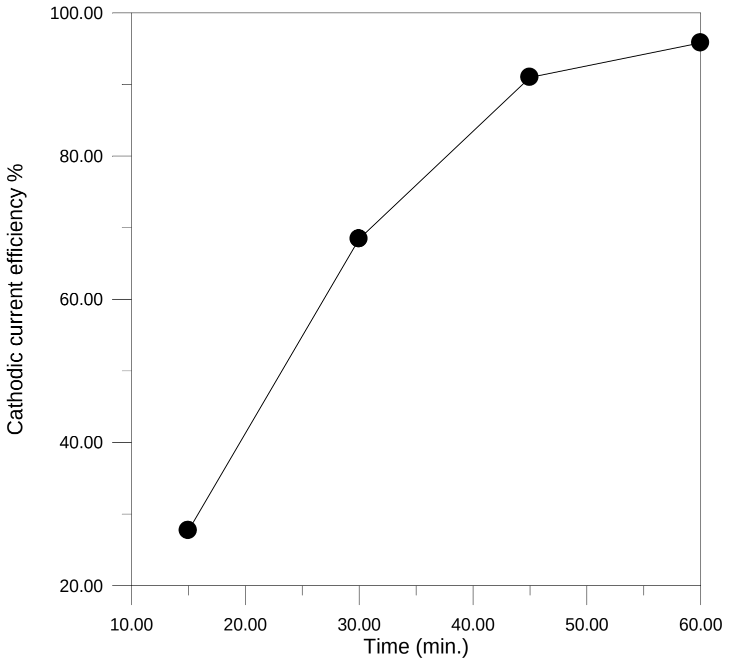


Figure 5.13 Cathodic current efficiency vs. time,C=200g/l conc. of $CuSO_4.5H_2O$, current density 3 A/dm^2, for epoxy-fiberglass substrate

The curve in Fig. 5.13 is fitted as follows :

$$\xi = -30.8735 + 4.50425\,t - 0.038988\,t^2 \qquad \ldots(5.7)$$

5.8.2 Plating Thickness

It is also shown from **Figure 5.12** that thickness increases with time because time is required to continue until the desired electrodeposit is built up with applying different current densities.

5.9 Effect of Plating Thickness

5.9.1 Porosity

It can be noticed from **Figure 5.14** that porosity decreases with the increasing of the plating thickness. This is due to the bridge pore-starts within the deposit and becomes bridged which leads to reduce porosity. The above observations are in good agreement with Ref.[36].

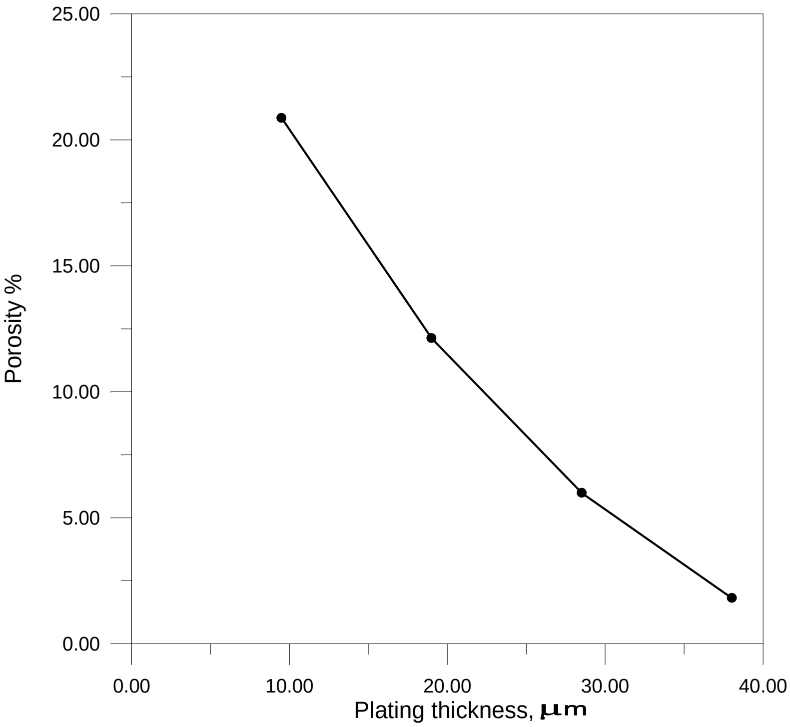


Figure 5.14 Porosity vs. plating thickness, C =200g/l conc. of $CuSO_4.5H_2O$, current density 3 A/dm^2, for ABS substrate

The curve in Fig. 5-14 is fitted as follows :

$$\phi = 31.7256 - 1.26598\,\delta + 0.012626\,\delta^2 \qquad \ldots(5.8)$$

where φ is the porosity% and δ is the thickness in μm.

5.9.2 Surface Roughness

Figure 5.15 shows that the increased surface roughness with the increasing of the plating thickness. Because the influence of the grain size and the direction as a function of thickness depends on micro throwing power of the solution, therefore, specific to the type of solution used, and also it is due to properties of the metal itself, as proved by the work of [37].

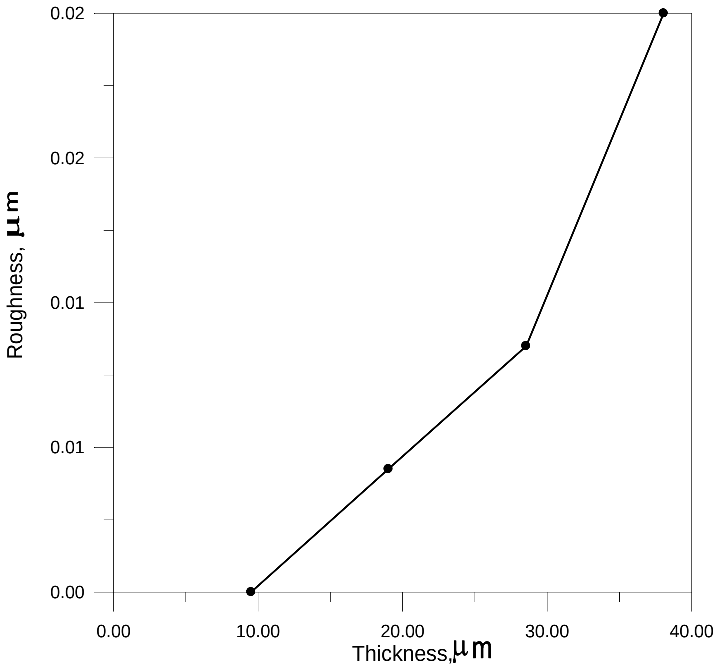


Figure 5.15 Roughness vs. plating thickness, C = 200g/l conc. of $CuSO_4.5H_2O$, current density 3 A/dm^2, for ABS substrate

The curve in Fig. 5.15 is fitted as follows:

$$R_a = -0.00522 + 0.001478\,\delta + 6.421 \times 10^{-5}\,\delta^2 \qquad \ldots(5.9)$$

where R_a is roughness in μm and δ is the thickness in μm.

5.10 Effect of Thickness of Plastic Film on Ohmic Resistance (or Voltage drop)

Figure 5.16 shows that the ohmic resistance (or voltage drop) increases with the increasing of plastic film thickness which is due to increasing the thickness of the substrate make the current distribution less uniform. This behavior is very important to achieve a uniform plating distribution across the surface (specially for plating through hole in printed circuit board or complex design).

By the optimum electrolytic copper is chosen according to these conditions needed to achieve ohmic resistance limited plating necessary for surface uniformity as stated in Ref.[38].

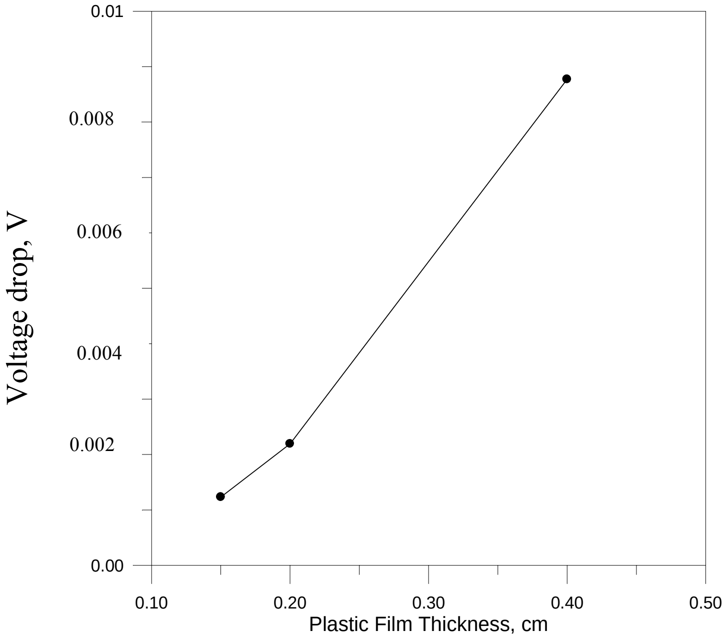


Fig. 5.16 Ohmic resistance(or voltage drop) vs. thickness of substrate, C=200g/l conc. of $CuSO_4.5H_2O$, current density 3 A/dm^2

The curve in Fig. 5.15 is fitted as follows:

$$E = -1.61626 + 12.1159\,\tau + 54804.8\,\tau^2 \qquad \ldots(5.10)$$

where E is the ohmic resistance (or voltage drop) in Volts and τ is the thickness in cm.

Table 5.1 Fitted equations of figures 5.2 – 5.7

Figure	Equation	Plastic type
5-2	$\delta = 5.4213 + 0.911505\,d$	ABS
	$\delta = 8.3531 + 0.74132\,d$	Polystyrene
	$\delta = 24.02 + 0.22899\,d + 0.002814\,d^2$	Epoxy-fiberglass
	$\delta = 20.3386 + 0.260346\,d + 0.00254\,d^2$	Phenolic
5-3	$\sigma_S = 2.55463 - 0.019144\,d$	ABS
	$\sigma_S = 2.46 - 0.023\,d$	Polystyrene
	$\sigma_S = 2.063 - 0.01949\,d$	Epoxy-fiberglass
	$\sigma_S = 1.77 - 0.015911\,d$	Phenolic
5-4	$\phi = 6.03118 - 0.13193\,d + 0.00104\,d^2$	ABS
	$\phi = 8.1628 - 0.1733\,d + 0.0013\,d^2$	Polystyrene
	$\phi = 4.81438 - 0.111255\,d + 0.0009\,d^2$	Epoxy-fiberglass
	$\phi = 3.28719 - 0.0965\,d + 0.000838\,d^2$	Phenolic
5-5	$R_a = 0.03723 - 0.000543\,d + 5.288 \times 10^{-6} d^2$	ABS
	$R_a = 0.0229 - 0.0004\,d + 4.3 \times 10^{-6} d^2$	Polystyrene
	$R_a = 0.01323 - 0.000203\,d + 2.825 \times 10^{-6} d^2$	Epoxy-fiberglass
	$R_a = 0.01094 - 0.000203\,d + 2.213 \times 10^{-6} d^2$	Phenolic
5-6	$G = 0.01493 - 6 \times 10^{-5} T + 2.5 \times 10^{-6} T^2$	ABS
	$G = 0.01268 - 0.00013\,T - 2.5 \times 10^{-6} T^2$	Polystyrene
	$G = 0.0026 - 3.3428 \times 10^{-6} T + 7.2857 \times 10^{-7} T^2$	Epoxy-fiberglass
	$G = 0.001418 - 6.399 \times 10^{-6} T + 1.5 \times 10^{-7} T^2$	Phenolic

Table 5.1 cont.

5-7	$G = 0.00772 + 0.00162\,t - 3.9142 \times 10^{-5} t^2$	ABS
	$G = 0.00654 + 0.0013\,t - 3.37 \times 10^{-5} t^2$	Polystyrene
	$G = 0.001388 + 0.000366\,t - 9.028 \times 10^{-6} t^2$	Epoxy-fiberglass
	$G = 0.0009 + 0.0001\,t - 2.514 \times 10^{-6} t^2$	Phenolic

Where:

δ = plating thickness in (μm)

R_a =surface roughness in (μm)

σ_s= peel strength in (kg / cm)

φ = porosity %

G = the weight of graphite deposit in(g)

t = the time in (min)

d= graphite particle size in (μm)

T = temperature in °C

Chapter Six

Conclusions and Recommendations for Future Work

6.1 Introduction

The present work has been mainly aimed to electroplate different types of plastics and choosing the best particles size of graphite and binding agents for graphite layer deposited onto the plastic substrate, also to study the influence of variables on cathodic current efficiency on copper plating, such as concentration of copper, bath temperature, electroplating time, and current density.

6.2 Conclusions

1. The best main mean diameter of graphite particles size is equal or smaller than 36 μm and epoxy resin as binding agent for graphite conductive colloid.
2. The ability of plating for different plastic types ABS, polystyrene, epoxy-fiberglass and phenolic.
3. Cathodic current efficiency increases with the increased cathodic current density, plating time and concentration of $CuSO_4.5H_2O$. But it decreases with the increased bath temperature.
4. Plating uniformity is achieved as ohmic resistance for electrolyte decreases with increasing the concentration but increasing with the increasing the thickness of substrate.
5. The best sample obtained is 38.06 μm copper electroplating thickness, peel strength (σ_s=2 kg / cm), roughness surface (R_a= 0.02 μm), porosity (Φ=1.8%), scratch (2kg) for 36μm graphite particle size and epoxy

resin as binding agent at plating time 60 min, cathodic current density 3A / dm^2, 25^{o}C bath temperature, 200 g/L concentration of $CuSO_4.5H_2O$ in acid copper plating .

6.3 Recommendations for Future Work

The following suggestions are to be considered or to be examined in great deal for future work:

1. Using graphite particles of smaller size in order to improve the graphite conductive layer.
2. Depositing graphite on top of the carbon black layer and study the advantage from the two layers deposition.
3. Plating more types of plastics from thermoplastic and thermosetting, to study accurate behavior for each plastic type.
4. Plating number of layers of metals over copper plating, such as nickel – chrome plating.
5. Studying in more details the influence of variables to assess the efficiency of the plating.

Appendix A

Indirect Method for Plating and Properties of Plastic

A.1 Electroless line Steps

Figure A-1 describes the step – by – step process of electroless copper plating line: -

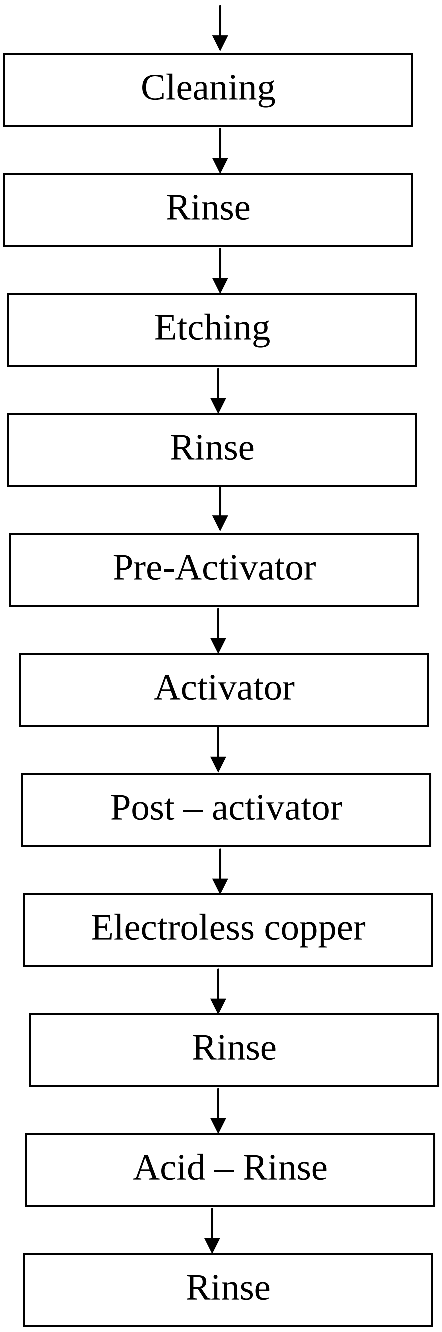


Figure A-1 Step–by– step process of electroless copper description [6]

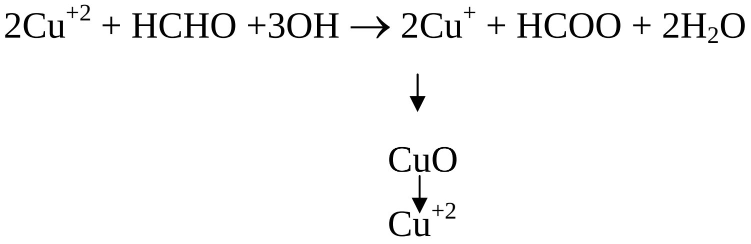
1. Cleaning:- clean is generally for preparing plastics for plating . However, it is very important that release handling problems, such as finger prints, and other dirt present on the surface.
2. Rinse: - spray rinse or counter flow with soft water.
3. Etching: - The purpose of etching is to provide some inter locking roughness on the surface.
4. Rinse:- spray rinse or counter flow with soft water.
5. Pre-Activator: - use hydrochloric acid dip reagent grade acid, 33 percent by volume.
6. Activator: - several proprietary solutions are referred to as activators. palladium system use palladium catalyst non-conductive surface with Stannic tin forms a protective colloid around metallic palladium. Briefly stated, it is the function of this solution to implant, on a non-conductive surface, a precious site that will initiate the desired reaction of plating by chemical reduction.
7. Post activator: - Also available as proprietaries are post activator solutions. The function of the solution is to solubilize the protective colloid and expose the precious metal sites for subsequent electroless plating.
8. Electroless copper: - At this point the surfaces to be metallized with copper are ready for the electroless bath.
9. Rinse: - Spray rinse or counter flow rinse.
10. Acid rinse: - Sulfuric acid (2 to 5 percent) by volume . The function of the acid is to neutralize the residual alkaline film from electroless copper.
11. Rinse: - Spray rinse or counter flow rinse.

A.2 Mechanism of Electroless Copper Solution

The electroless copper solution consists of the following elements:-

1. Copper sulfate – source for copper.
2. Formaldehyde – reducing agent.
3. Caustic – basic medium.
4. Chelating agent (amines , EDTA, as trat rates) governs the plating rate and has a marked influence on the properties of the deposit and the bath stability.

As shown in the chemical reaction below, with the presence of palladium as a catalyst and under a strongly basic medium, electrons are obtained from the reducing agent, formaldehyde, to reduce the cupric ions to metallic copper (6).



$$2Cu^{+2} + HCHO + 3OH \rightarrow 2Cu^{+} + HCOO + 2H_2O$$

$$\downarrow$$

$$CuO$$

$$\downarrow$$

$$Cu^{+2}$$

However, the reduction proceeds through a couprous state. An excess of cuprous oxide formation will cause the reduction reaction to proceed out of control [20].

Table A-1 Comparison of the Specific Gravity of some Common

Metal	**Sp. Gravity**	**Polymer**	**Sp. Gravity**
Magnesium	1.74	Polyurethane (foams)	0.03 upward
Beryllium	1.83	Polypropylene	0.902-0.906
Aluminum	2.70	polyethylene	0.93 – 0.965
Titanium	4.5	Polystyrene	1.04 – 1.065

Metals and Plastics[3]

Table A-1 *(Cont.)*

Vanadium	6.0	ABS	1.01 – 1.15
Chromium	7.1	Polyamide	1.09 – 1.15
Zinc	7.1	Polyester	1.01 – 1.46
Tin	7.29	Cellulose acetate butyrate	1.15 – 1.22
Iron	7.87	Acrylics (Methyl methacrylate)	1.17 – 1.20
Cobalt	8.6	Epoxies	1.11 – 1.40
Cadmium	8.64	Polyvinyl chloride	1.15 – 1.35
Nickel	8.9	Polycarbonate	1.2
Copper	8.93	Cellulose acetate	1.23 – 1.34
Silver	10.5	Phenol – formaldehyde	1.25 – 1.30
Lead	11.37	Diallyl phthalate	1.3 – 1.4
Palladium	11.40	Polyacetal	1.41 – 1.425
Gold	19.32	Melamine – formaldehyde	1.48
Platinum	21.50	Polyvinylidene fluoride	1.76 – 1.77
		FEP	2.12 – 2.17
		PCTFE	2.1 – 2.2
		PTFE	2.13 – 2.22

Table A-2 Comparison of the Mechanical Properties of Some Unplated and Plated Plastics[3]

Polymer	**Tensile Strength * lb/in^2**			**Impact Strength*(Notched Izod ft-lb/in)**			**Flexural Strength * lb/in^2**		
	Unplated	**Plated****	**% Incr.**	**Unplated**	**Plated****	**% Incr.**	**Unplated**	**Plated****	**% Incr.**
Phenolic (unfilled)	**9,525**	**10,500**	**10.2**	**0.33**	**0.40**	**21.2**	**14,000**	**16,775**	**19.8**
Urea – formaldehyde	**7,500**	**8,775**	**17.0**	**0.28**	**0.33**	**21.4**	**12,000**	**13,500**	**12.5**
Melamine – formaldehyde	**6,500**	**7,250**	**11.5**	**0.24**	**0.31**	**29.2**	**9,500**	**10,750**	**13.1**
Polyvinyl chloride	**6,775**	**8,650**	**27.7**						
Polystyrene	**4,775**	**6,225**	**30.4**	**0.30**	**0.36**	**20.0**	**12,750**	**14,750**	**15.9**
Polymethyl methacrylate	**10,250**	**11,750**	**14.7**	**0.35**	**0.41**	**17.1**	**10,000**	**12,000**	**20.0**
Cellulose acetate	**5,775**	**6,725**	**16.4**	**2.40**	**2.95**	**22.9**	**6,500**	**7,765**	**17.9**

*Values given are average of three test specimens, **Polymers plated with 0.0003 in. (7.6 μ) copper and 0.0005 in. (12.7 μ) cadmium[6].

Table A-3 Comparison of the Heat Distortion Temperature of some Unplated and Plated Plastics[3]

Polymer	**Heat Distortion Temperature ^{o}C***		
	Unplated	**Plated****	**% Increase**
Phenolic (unfilled)	127	254	100
Urea – formaldehyde	127	160	33.9
Melamine – formaldehyde	132	210	59.1
Polyvinyl chloride	77	107	39.0
Polystyrene	77	113	46.8
Polymethyl methacrylate	68	121	78.0
Cellulose acetate	71	96	35.2

* Temperature values given are average of three test specimens (Source – Electrochemical Society[3].,**Samples electroplated with 0.0003 in. copper approximately and 0.0005 in. cadmium.[3].

Table A-4 Coast of Basic Materials – Metals and Plastics[3]

Polymer	**Cost per in^3**		**Polymer**	**Cost per in^3**	
	Pence	**cents**		**Pence**	**cents**
Magnesium	1.7	2.0	Polyethylene	0.6	0.7
Aluminum	1.8	2.1	Polystyrene	0.5-1.0	0.6 –1.2
Zinc	3.3	3.7	Polypropylene	1.0	1.2
Stainless steel	11.3	13.3	ABS	1.3	1.53
Copper	16.4	19.3	Polyamide	3.3 –3.4	3.9 –5.1
Nickel	22.1	26.1	Polycarbonate	3.8	4.5
Silver	63.1	74.0	PTFE	30-51	35.3 –60

Table A-5 Comparison of the Water Absorption Properties of Some Unplated and Plated Plastics

Polymer	**% Water Absorption, 24 hr immersion***		
	Unplated	**Plated****	**% Decrease**
Phenolic (unfilled)	0.21	0.04	80.9
Urea – formaldehyde	1.6	0.05	96.9
Melamine – formaldehyde	0.14	0.02	86.7
Polyvinyl chloride	0.42	0.11	73.9
Polystyrene	0.01	0.00	100.0
Polymethyl methacrylate	0.35	0.03	91.4
Cellulose acetate	3.1	0.09	97.1

A.3 Typical Properties of Acrylonitrile Butadiene Styrene (ABS)

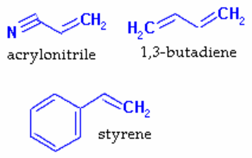


Figure A-2 Structure of ABS[25]

Table A-6 Typical Mechanical and Physical Properties of ABS Resins[34]

Property	**Unfilled**	**ASTM Test Method**
Tensile strength, *lb/in*^{2}		D638
23^{o}C	5,500 – 8,800	
71^{o}C	3,200	
-40^{o}C	9,500	
Compressive strength, *lb/in*^{2}	4,500 – 7,000	D695
Flexural strength, *lb/in*^{2}	7,000 – 13,000	D790
Impact strength, *ft-lb/in*		D256
*½*½ in notched bar (Izod)*		
23^{o}C	1.1 – 4.3	
-40^{o}C	0.5 – 1.4	
Tensile modulus, *lb/in*^{2}	200,000 – 400,000	D638
Flexural modulus, *lb/in*^{2}	240,000 – 450,000	D790
Elongation, %	5 – 40	D638
Hardness *(Rockwell)*	R80 – 120	D785
Abrasion resistance, *mgm, 10^2 cycles, 1 kg load, CS-17 wheel*	18.8	
Deformation under load, % 2000 lb/in^2, 24 hr, 50^{o}C	0.53	D1044

Typical Physical Properties of ABS[34]

Property	**Unfilled**	**ASTM Test Method**
Specific gravity	1.02 – 1.2	D792
Water absorption, % 1/8 in thick, 24 hr, 23^{o}C	0.2 – 0.4	D570
Clarity	Translucent to opaque	

Table A-7 Chemical Resistance of ABS* [34]

Solution	**Immersion Time (days)**	**Remarks**
Inorganic acids:		
Chromic acid, 6%	**	Brownish edges
Hydrochloric acid, 10%	14	No visible effect
conc		dark grey discolouration
Nitric acid, 10 %		Yellowish discolouration
		Partially disintegrated
Phosphoric acid, conc.		No visible effect
Sulphuric acid, 30% conc		No visible effect, carbonized and disintegrated
Organic acids:		
Acidic acid, 12%		No visible effect
, 99%	7	Softened
Bases:		
Ammonium hydroxide, 10%	14	No visible effect
Potassium hydroxide, 40%***	28	No visible effect
Organic solvents:		
Benzaldehyde	18	Dissolved
Carbon tetrachloride	7	Softened and swelled
Chloroform	18	Dissolved
Diethyl ether		Softened
Ethyl alcohol	14	No visible effect
triethanolamine	18	No visible effect

* room temperature ** 1 year *** 66°C

Table A-8 Typical Electrical Properties of ABS[34]

Property	**Value**	**ASTM Test Method**
Dielectric constant		D150
60 Hz	2.7-5.0	
1 kHz	2.68 – 4.5	
1 M Hz	2.45 – 3.8	
Dielectric factor		D150
60 Hz	0.004 – 0.03	
1 kHz	0.002 – 0.01	
1 M Hz	0.006 – 0.02	
Dielectric strength, ***volt/mi1***, short time, 1/8 in thick	400 – 500	D149
Dielectric strength, ***volt/mi1***, step by step, 1/8 in thick	350 – 500	D149
Volume receptivity***, ohm-cm***	10^{14}	D257
Surface resistivity***, ohm/sq***	$>10^{14}$	
Arc resistance***, sec***	71 – 87	D495

A-4 Typical Properties of Polystyrene:

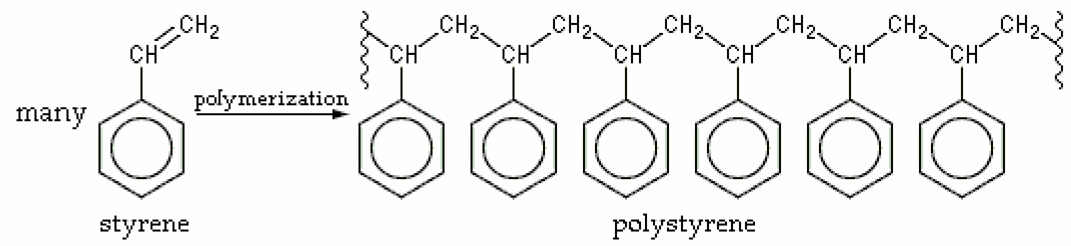


Figure A-3 Structure of polystyrene[25]

Table A-9 Typical Mechanical Properties of Polystyrene[34]

Property	**General Purpose**	**Heat Resistance**	**Impact Resistance**	**Styrene Acrylo- nitrile**	**ASTM Test Method**
Tensile strength, *lb/in²*	**4,300 – 8,500**	**5,000 – 8,000**	**2,500 – 5,000**	**6,000 – 11,000**	**D638**
Compressive strength, *lb/in²*	**11,000 – 16,000**	**11,000 – 16,000**	**4,000 – 9,000**	**14,000 – 17,000**	**D695**
Flexural strength, *lb/in²*	**8,000 – 17,000**	**8,700 – 14,000**	**5,000 – 11,000**	**14,000 – 19,000**	**D790**
Impact strength, *ft-lb/in* *½*½ in notched bar (Izod)*	**0.2 – 0.6**	**0.3 – 0.6**	**1.0 – 8.0**	**0.3 – 0.8**	**D256**
Tensigle modulus, lb/in²	**300,000 – 550,000**	**400,000 – 600,000**	**200,000 – 450,000**	**400,000 – 560,000**	**D638**
Elongation, %	**0.8 – 2.0**	**1.0 – 2.5**	**1.2 – 4.5**	**1.5 – 3.5**	**D638**
Hardness *(Rockwell)*	**M65 – 80**	**M65 – 80**	**M25 – 60**	**M80 – 90**	**D785**

Table A-10 Typical Physical Properties of Polystyrene [35]

Property	General Purpose	Heat Resistance	Impact Resistance	Styrene Acrylo- nitrile	ASTM Test Method
Specific gravity	1.04 – 1.09	1.04	0.98 – 1.10	1.07 – 1.10	D792
Water absorption, % 1/2 in thick, 24 hr	0.02 – 0.01	0.05	0.05 – 0.6	0.2 – 0.3	D570
Refractive index	1.595	1.57	–	1.56 – 1.57	D542
Light transmission	88 – 92	88 – 90	–	80 – 88	

Table A-11 Chemical Resistance of Polystyrene **[34]**

Solution	**Remarks**
Inorganic acids:	
– Hydrochloric acid, conc.	Satisfactory
– Hydrochloric acid, dil.	Satisfactory
– Nitric acid, 15 %	Unsatisfactory
– Sulphuric acid, conc.	Satisfactory
Organic acids:	
– Acidic acid, 15%	Satisfactory
– Acidic acid, glacial	Unsatisfactory
– Formic acid, 90%	Satisfactory
Bases:	
– Sodium Hydroxide, 20%	Satisfactory
– Ammonium hydroxide	Satisfactory
Organic solvents:	
– Acetone	Unsatisfactory
– Benzene	Soluble
– Carbon tetrachloride	Soluble
– Chloroform	Soluble
– Trichloroethylene	Soluble
– Formaldehyde	Unsatisfactory

* 20°C

A.5 Typical Properties of Epoxy-Fiber glass:

Table A-12 Typical Electrical Properties of Epoxy Resins [34]

Property	**Unfilled**	**Silica filled**	**ASTM Test Method**
Dielectric constant			
60 Hz	3.5 – 5.0	3.2 – 4.5	D150
1 kHz	3.5 – 4.5	3.2 – 4.0	
1 M Hz	3.3 – 4.0	3.0 – 3.8	
Dielectric factor			
60 Hz	0.002 – 0.010	0.008 – 0.03	D150
1 kHz	0.002 – 0.02	0.008 – 0.03	
1 M Hz	0.03 – 0.05	0.02 – 0.04	
Dielectric strength, *volt/mi1,* short time, in thick	400 – 500	400 – 550	D149
Dielectric strength, *volt/mi1,* step by step, in thick	380		D149
Volume receptivity, *ohm-cm* *23^{o}C, 50% RH*	$10^{12} – 10^{13}$	$10^{13} – 10^{16}$	D257
Arc resistance, *sec*	45 – 120	150 – 300	D495

Table A-13 Typical Mechanical Properties of Epoxy-fiberglass[34]

Property	**Unfilled**	**Silica filled**	**ASTM Test Method**
Tensile strength, *lb/in*^{2}	4,000 – 13,000	7,000 – 13,000	D638
Compressive strength, *lb/in*^{2}	9,000 – 23,000	12,000 – 32,000	D695
Flexural strength, *lb/in*^{2}	13,000 – 21,000	5,000 – 19,000	D790
Impact strength, *ft-lb/in* *½*1/2 in notched bar (Izod)*	0.2 – 1.0	0.3 – 0.45	D256
Tensile modulus, *lb/in*^{2}	350,000		D638
Elongation, %	1 – 7	1.5 –2.0	D638
Hardness *(Rockwell)*	M80 – M 110	M85 – M120	D785

Table A-14 Typical Thermal Properties of Epoxy –fiberglass[34]

Property	**Unfilled**	**Silica filled**	**ASTM Test Method**
Specific heat, $cal/^{o}C/gm$	0.25	0.20 – 0.27	
Thermal expansion, $10^{-5}/^{o}C$	3.0 – 7.0	2.0 – 4.0	D696
Thermal conductivity, $10^{-4}cal/sec/cm/^{o}C$	4 – 5	10 – 20	C177
Resistance to heat, ^{o}C	121 – 232	121 – 232	
Heat distortion temp. ^{o}C $264lb/in^{2}$	49 – 323	89 – 232	D648

A.6 Typical Properties of Phenolic:

Table A-15 Typical Mechanical Properties of Phenolic Resins[24]

Property	**Unfilled**	**ASTM Test Method**
Tensile strength, lb/in^2	7500	D638
Flexural strength, lb/in^2	12000	D790
Impact strength, $ft\text{-}lb/in^2$	0.8	D256
Elongation, %	1 – 7	D638
Hardness *(Rockwell)*	125	D638

Table A-16 Typical Thermal Properties of Phenolic Resins[24]

Property	**Unfilled**	**ASTM Test Method**
Thermal expansion, $10^{-5}/^{o}C$	1.2-1.7	D696
Thermal conductivity, $Btu.h/ft^2.in\ F^o$	1.7	C177
Heat distortion temp. $F^o/264,\ lb/in^2$	300	D648
Flammability, *in/min*	Slow	

Appendix B

Analytical Procedure for Acid Copper Electroplating

The analysis of acid copper bath by a number of conventional techniques according to the following procedure [34]:

B.1 Determination of Copper Content

The following reagents are required:

1. Murexide indicator (Mix 0.2 g with 100 g of sodium chloride. And Store .
2. 0.2 N EDTA di sodium salt (23-37) g/l.
3. Ammonium buffer. Dissolve 68 g of ammonium chloride in 300 ml of distilled water. Add 570 ml of 29 percent ammonium hydroxide and dilute the mixture to 1 litter.

B.1.2 Procedure

1. Pipette of 2ml of solution into 600 ml flask
2. Add 5ml of ammonium buffer and dilute to 450 ml, with water. The solution should be clear at this point, if it is not, add ammonium buffer until it is.
3. Add 0.2 to 0.4 g of murexide indicator
4. Titrate with 0.2 N EDTA to blue-violet end point.

B1.3 Calculatio*n*

1ml 0.2 N EDTA= 0.0063579 g Cu

1ml 0.2 N EDTA × 3.18= g/l Cu

B.2 Determination of Sulfuric Acid Cntent

The following reagents are required:

1. 0.1 percent methyl orange. Dissolve 0.1 g of the salt in 100 ml of water.
2. 1 N sodium hydroxide (40 g/l)

B.2.1 Procedure:

1. Pipette 5 ml of solution into a 250 ml Erlenmeyer flask.
2. Add 150 ml of distilled water and 10 drops of methyl orange indicator.
3. Titrate with 1 N sodium hydroxide to a pal-green end point.

B.2.2 Calculation:

1 ml NaOH = 0.049 H_2SO_4

ml 1 N NaOH×9.8= g/l H_2SO_4

The titration process is applying on solution for each 10 days of laboratory work.

- For copper content:

$14.2 \times 3.18 = 45$ g/L Cu

when the copper content for bath solution contain (200 g/l) $CuSO_4.5H_2O$ is 50.89 g/Lcopper

- For sulfuric acid:

$4.9 \times 9.8 = 48.02$ g/L H_2SO_4

when the sulfuric acid for bath solution contain 50 g/L H_2SO_4.

B.3 Replenishment

Add 50 mls from acid copper solution to the bath to obtaine the original concentration. But the solution is discard from the bath when the copper content reach to 30 – 35 g/ and new preparation solution using for plating.

Table B-1 binding agents types

Binding agent type	Comment	**Typical curve condition (min)23^{o}C**	**Features**	**Flexibility toughness**	**Chemical resistance**	**Appear ance with hard**	**Mixed with hard.**	**Typical peel strength N/m**	**Engin-ering thermo -plastic (PS, ABS, PPS)**	**Engineer-ing thermosett-ing (EF, Ph, Phf)**
Epoxy resin Aw 136H /XB5067	Bisphenol A-(eipchl-orhydrin	72	Liquid viscous	Rigid	Excellent	White / gray	100:40	4	*	*
Aw 136H /Hyaal Germany	Triethylene tetramine R hardener									
Polyester resin	Unsaturated ester	Minutes to hours	Liquid viscous	Flexible	Excellent	Transparency /Transparency	100:20	3	*	*
7130 MM	Methyl ethyle keton(MEK) peroxide									
Cyno acrylate			Low viscosity liquid	Rigid	Excellent	Transparency	With out hardener	3.5	*	*

* acceptable

Appendix C

Sample of calculations

C.1 Calculations of cathodic current efficiency for copper:

By using equation:

$$E = \frac{w}{w_{th.}} * 100\% \qquad \ldots(2.1)$$

where (w) is the experimental weight of the deposit and (w_{th}) is the theoretical weight of the deposit. The theoretical weight of metal deposit can be calculated as follows:

$$W_{th} = \frac{.Q.}{F} \times Z \qquad \ldots(2.2)$$

Where (Q = I x t) is the amount of electricity passed through the cell and expressed in ampere second and F= Faraday 's constant is 96485 and Z is the equivalent weight of copper 31.773 [21].

for Acid copper bath:

Total current I=0.54 A, time =60 min, Temperature =25°C, 200 g/L $CuSO_4.5H_2O$ and equivalent weight of copper is 31.773.

For copper plating / ABS plastic	
W_{C1} (cathode weight before electroplating) (g)	**W_{C2} (cathode weight after electroplating) (g)**
5.0219	5.6353

$W= W_{C2} - W_{C1}$

W =5.6353 – 5.0219

W =0.6134 g

$Q = 0.54 \times 60 \times 60$

Q=1944 A . Sec. (Coulomb)

$W_{th} = \frac{.Q.}{F} \times Z$

$W_{th} = \frac{1944}{96485} \times 31.773$

$W_{th} = 0.640169\,\mathrm{g}$

Eff.%= (0.6134/0.640169)*100

Eff %= 95.9% cathodic current efficiency for copper at temp. 25°C, 200g/L $CuSO_4.5H_2O$ and 50 g/l H_2SO_4.

C.2 Calculations of thickness for copper plating;

Using the following equation

$$\delta = \frac{Z.i..t.\xi}{F\,\rho} \qquad \ldots(2.7)$$

Where Z is the equivalent weight of copper, F is faraday's constant, i is current density, ξ cathodic current efficiency, t time, ρ is density of copper (8.96×10^3 kg/m^3)[21].

For Example:

Z = 31.773, F = 96485, t = (15, 30, 45, 60) min., i = 1 A/dm^2, for cathodic current efficiency is 100% ξ, ρ = 896 kg/m^3

$\delta = 31.773 \times 0.01 \times 15 \times 60 \times 1/896 \times 96485$

$\delta = 3.3 \times 10^{-6}$

δ= 3.3 µm.

C.3 Calculations of solution resistance (k);

By applying the following relation:

K = 1.52/ R at 25 °C

Where K is solution conductivity(s/cm), R is resistance measuring by conductive meter (Ω) 1.52 is cell constant, For Example:

R= 15 Ω, K = 1.52/ 15 = 0.10133 µs/cm for copper concentration 200 g/L then applying equation (2.8) as following:

$$E = \frac{i\,\tau^2}{2\,K\,L} \qquad \ldots(2.8)$$

Where E, ohmic resistance (or voltage drop) (V), i 3A/dcm^2 current density, τ thickness 0.4 cm, L length 2.7 cm

$E = 0.03\times(0.4)\ 2\ /\ 2\times\ 0.10133\text{x}10^{-6}\times\ 2.7$

$E= 0.008772\times10^{6}$ V

*** A_{cath}= 2[(L×W) + (L×h)] + (w ×h)**

when:
L = length of substrate (cm)
w= width of substrate (cm)
h = thickness of substrate (cm)

الخلاصة

الغاية الأساسية من هده الدراسة طلاء أنواع من الدائن المطاوع حراريا (ABS والبولي ستايرين) والدائن المتصلب حراريا (ايبوكسي – فابير كلاس والفينولك) ولدِراسَة أفضل حجم حبيبة الكرافيت ونوع الرابط المستخدم للحصول على افضل طبقة كرافيت مترسبة على سطح البلاستيكِ هذه العمليةِ يُمْكِنُ أنْ تَجْعلَ طَلاء النحاسِ كهربائيا محتملِ بدون استخدام طبقة وسطية موصله من النحاس عن طريق طلاء النحاس غيرالكهربائي باستخدام عملياتِ الترسيب النحاس الكهربائي المباشر.

َوهناك سببان لاستعمال طبقة النحاس على المكون ألدائني لأنه يَبْدو لامع جداً بسبب الاستواء وخواص اللمعان . بالإضافة إلى ذلك، الطبقة النحاسية ناعمةُ ومرنةُ جداً ويُمْكِنُ أنْ تتناسب مع متطلباتُ التمدد الحراري المختلف بين المعدنِ والدائن .

واهتمت الدراسة الحالية بمتغيرات أساسية هي حجم حبيبة الكرافيت، نوع الرابط المستخدم على انواع البلاستك ، تركيز كبريتات النحاس ، كثافة التيار، درجة حرارة المحلول ووقت الطلاء لهما تأثيران رئيسيانُ:

1. تأثير مباشر عن طريق أجراء الفحوصات ، كفحص سُمك الطلاء,الالتصاق ,المسامية , الخشونة وفحص خدش على سطح البلاستيك المطلي.
2. تأثير مباشر على كفاءة التيار لأربعة عوامل رئيسية والتي تؤثر على عمليات الطلاء وهي درجات الحرارة ,وقت عملية الطلاء ,كثافة التيار الكاثودي , وتركيز كبريتات النحاس في طلاء النحاس الكهربائي.

حيث تزداد كفاءة التيار الكاثودي بزيادة تركيز كبريتات النحاس و كثافة التيار الكاثودي ووقت عملية الطلاء في طلاء النحاس .

ودلت النتائج بأن صغر حجم حبيبة كرافيت والايبوكسي كعامل رابط هو الأكثر مناسبا في العملية لإنجاز سمك منتظم لطلاء , التصاق جيد، سطح ناعم،أقل مسامية وأعلى حمل مسلط في مقاومة الخدش والتي قد تتعرض لها مثل هذه السطوح عند استخدامها عمليا في الصناعة أو الديكور، والتي تقود الى الحصول على أفضل نموذج لمطلي بالنحاس لسمك (δ =38µm) والذي إجهاد الشد له (σ_s=2kg/cm) وخشونة السطح له (R_a=0.02µm)والمسامية (Φ=1.8%) ومقاومة الخدش له (2kg) تحت ظروف تشغيلية هي 3 أمبير/ دسم^2 كثافة التيارالكاثودية المسلطة ,ودرجة الحرارة هي25◦ م, في محلول طلاء يتكون من 200 غرام / لتر كبريتات النحاس و 50غرام /لتر حامض الكبريتيك.

شكر و تقدير

أود أن أعبر عن خالص شكري وتقديري وامتناني العميق للمشرف الاستاد الدكتور قاسم جبار محمد سليمان لما بذله من جهد كبير وإرشادات سديدة وقيمة طوال فترة أعداد الرسالة أود ايضا أن اشكر موظفي قسم الهندسة الكيمياوية لإبدائهم المساعدة اللازمة إثناء فترة البحث•

وأتقدم بالشكر والامتنان الى من لازمني طوال فترة البحث وخلال أصعب الظروف الى اعز من في الوجود إلى أمي وجميع أفراد عائلتي فلهم جزيل الشكر التقدير .

أخلاص عبد الرحمن سلمان

الطلاء الكهروكيميائي للمواد البلاستيكية

رسالة

مقدمة الى كلية الهندسة في جامعة النهرين وهي جزء من
متطلبات نيل درجة ماجستير علوم في الهندسة الكيمياوية

من قبل

أخلاص عبد الرحمن سلمان

بكلوريوس علوم في الهندسة الكيمياوية 1998

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