

# 1. Introduction

## 1.1. Electroplating:

Electroplating is the process of coating a metal object with another metal, using electrical current passed through a chemical solution, this process produces a thin, metallic coating on the surface of the metal object. The main purposes of electroplating are to improve the appearance of the material and provide protection against corrosion.

Since metal is being taken from the solution it must be replenished. This is done by hanging pieces of the metal to be replenished in the solution. The chunks of metal are called anodes and the positive electrical lead is attached to these chunks of metal. They dissolve in the solution as metal is taken away by plating. At this point we have metal being removed from the anode and deposited on the cathode. Cathodes are the parts being plated.

The anode and cathode in the electroplating cell are both connected to an external supply of direct current a battery or, more commonly, a rectifier. The anode is connected to the positive terminal of the supply, and the cathode (article to be plated) is connected to the negative terminal. When the external power supply is switched on, the metal at the anode is oxidized from the zero valence state to form cations with a positive charge. These cations associate with the anions in the solution. The cations are reduced at the cathode to deposit in the metallic, zero valence state. For example, in an acid solution, copper is oxidized at the anode to  $\text{Cu}^{+2}$  by losing two electrons. The  $\text{Cu}^{+2}$  associates with the anion  $\text{SO}_4^{-2}$  in the solution to form copper sulfate. At the cathode, the  $\text{Cu}^{+2}$  is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode.<sup>(1)</sup>

**Faraday's Law of Electrolysis** - "The mass of a substance altered at an electrode during **electrolysis** is directly proportional to the quantity of electricity transferred at that electrode. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb."(Q)

## **1.2. History :**

It is widely held but unconfirmed that the Parthian battery may have been the first system used for electroplating.

Modern electrochemistry was invented by Italian chemist Luigi V. Brugnatelli in 1805. Brugnatelli used the voltaic pile, his colleague Alessandro Volta's invention of five years earlier, to facilitate the first electrodeposition. Brugnatelli's inventions were suppressed by the French Academy of Sciences and did not become used in general industry for the following thirty years.

By 1839, scientists in Britain and Russia had independently devised metal deposition processes similar to Brugnatelli's for the copper electroplating of printing press plates.

Boris Jacobi in Russia not only rediscovered galvanoplastics, but developed electrotyping and galvanoplastic sculpture. Galvanoplastics quickly came into fashion in Russia, with such people as inventor Peter Bagration, scientist Heinrich Lenz and science fiction author Vladimir Odoyevsky all contributing to further development of the technology. Among the most notorious cases of electroplating usage in mid-19th century Russia were gigantic galvanoplastic sculptures of St. Isaac's Cathedral in Saint Petersburg and gold-electroplated dome of the Cathedral of Christ the Saviour in Moscow, the tallest Orthodox church in the world.

Soon after, John Wright of Birmingham, England discovered that potassium cyanide was a suitable electrolyte for gold and silver electroplating. Wright's associates, George Elkington and Henry Elkington were awarded the first patents

for electroplating in 1840. These two then founded the electroplating industry in Birmingham from where it spread around the world.

The Norddeutsche Affinerie in Hamburg was the first modern electroplating plant starting its production in 1876.

As the science of electrochemistry grew, its relationship to the electroplating process became understood and other types of non-decorative metal electroplating processes were developed. Commercial electroplating of nickel, brass, tin, and zinc were developed by the 1850s. Electroplating baths and equipment based on the patents of the Elkingtons were scaled up to accommodate the plating of numerous large scale objects and for specific manufacturing and engineering applications. The plating industry received a big boost from the advent of the development of electric generators in the late 19th century. With the higher currents, available metal machine components, hardware, and automotive parts requiring corrosion protection and enhanced wear properties, along with better appearance, could be processed in bulk.

The two World Wars and the growing aviation industry gave impetus to further developments and refinements including such processes as hard chromium plating, bronze alloy plating, sulfamate nickel plating, along with numerous other plating processes. Plating equipment evolved from manually operated tar-lined wooden tanks to automated equipment, capable of processing thousands of kilograms per hour of parts.

One of the American physicist Richard Feynman's first projects was to develop technology for electroplating metal onto plastic. Feynman developed the original idea of his friend into a successful invention, allowing his employer (and friend) to keep commercial promises he had made but could not have fulfilled otherwise.<sup>(1)</sup>

### 1.3. Electroplating Chemicals (EPi):

EPi developed a single additive cyanide copper electroplating process in 1954 using the now famous **E-Brite 23-11** brightener and a single additive nickel plating process in 1961.

EPi was first in the electroplating industry to develop a production-proven, non-cyanide, non-pyrophosphate, alkaline copper electro plating process, the **E-Brite 30/30** process in 1991. It is an excellent strike bath on steel, stainless steel, brass, copper, zincated aluminum, die cast zinc and white metals. It makes an outstanding heat treat stop-off plate as well as a decorative copper plate.

The **E-Brite 200** acid copper plating process is the best leveling acid copper available and is unsurpassed in brightness, ductility and resistance to treeing and burning. It has excellent buff ability – the easiest to buff acid copper on the mark

EPi offers a variety of electroplating chemical processes for metal finishers. When it comes to electroplating and chemical plating, EPi is a leader in the industry. EPi's electroplating chemicals are of extremely high quality. Zinc plating, nickel plating, and copper plating chemicals are just a few of the many metal plating solutions EPi has to offer.

**Electroplating process:**

Electroplating is the process of using an electrical current to coat an electrically conductive object with a thin layer of metal. If you are interested in learning more about the electroplating process; check out the section on the Electrochemistry Encyclopedia.

With a proven electroplating track record, EPI has proven their ability to deliver product as promised<sup>(2)</sup>.

#### **1.4. Instructions:**

**1.4.1.** Cut off the end of a charger or power source that would be plugged into an electrical appliance. This will ruin the charger, so use one that you no longer need. Most importantly, it must be use DC current, which will be written on the back of the charger plug. You should now have a plastic box that plugs into the wall with a bare wire coming from it. Do not plug this into the wall, as it could produce electric shock at this point.

**1.4.2.** Strip the wires emerging from your power supply. There should be two wires held together in one strip, since this is DC. Peel the two wires apart and then strip them individually using wire strippers. Leave about an inch of exposed wire on each of the two halves.

**1.4.3.** Affix one alligator clip to the end of each exposed wire. Use pliers to tighten the alligator clips onto each wire.

**1.4.4.** Fill the glass container with a solution of copper sulfate and water. Copper sulfate can be found at any hardware store and often comes in the form of weed or grass killer. The solution should be composed of 1 tablespoon copper sulfate and

enough water to submerge three-fourths of the item to be coated and the copper sheet.

**1.4.5.** Use the multimeter to check the charge of each alligator clip. Attach one of the alligator clips to the multimeter, then plug your charger into the wall. If you get a positive reading, then that alligator clip is the positive charge and other one is the negative. Unplug the charger and label the two alligator clips positive and negative.

**1.4.6.** Stand up the copper sheet and your key (or other item) in the solution and attach the alligator clips to each one. You want enough of each piece to be exposed that it will be easy to clip on the alligator clips without getting any of the solution on the clips themselves. Attach the positively charged alligator clip to the copper sheet, and attach the negatively charged alligator clip to the key.

**1.4.7.** Plug in the power supply and watch it go. After about 10 minutes, there should be a thick build-up of copper on the key. Unplug the power supply once the entire object has been coated.

**1.4.8.** Sand down the jagged copper. When you pull out the key the copper coating will be jagged and uneven. The copper affixed to the key will be brittle where it is rough, making it simple to sand down the copper until a smooth coat is reached<sup>(3)</sup>.

## **1.5. The Purpose of Electroplating:**

Electroplating is the depositing of metal coatings to conductive surfaces by chemical processes that are driven by electric current. In an electrochemical cell, an object to be coated and a bar of coating metal serve as opposite electrodes in a chemical solution through which electric current is passed.

## **1.6. Electroplate of Plastic:**

Electroplating is the deposition of metal ions from solution onto an electrically charged surface. The surface must therefore be conductive. Plastic is not conductive, so direct electroplating of plastic is not practicable. Instead, the process is performed in steps, covering the plastic in an adhesive conductor, like metallic paint, before performing genuine electroplating. <sup>(4)</sup>

This invention relates to a process for copper plating and, more particularly, to a process for plating copper on a copper substrate which comprises etching, activating, electroless and electrolytic plating and heating or baking. The plated products formed exhibit improved copper to copper adhesion over products prepared by the prior art methods. In another aspect,

' this invention relates to a process for plating on copper-clad plastic substrates, as, for example, in the manufacture of printed circuit boards.

A number of electroless metal deposition processes exist for the plating of a metal coating on conductive, non-conductive or semi-conductive substrates. Typical prior art methods consist in cleaning of the substrate surface, treating the surface by immersion in a bath containing stannous chloride or another stannous salt, catalyzing the surface to provide catalytic nucleating centers on the surface of the substrate by immersion in a salt of a metal catalytic to the deposition of the desired metal coating such as palladium chloride, the metal ions being reduced to catalytic metal nuclei by the stannous ions previously adsorbed on the substrate surface or by contact with a reducing agent incorporated in the electroless metal deposition bath

and finally plating on the surface the desired metal such as copper, nickel or cobalt, by treating the catalyzed surface with an electroless solution comprising a salt of the metal and a reducing agent. Other processes in the art, such as the one-stage activation of surfaces for the reception of an electroless metal coating, exist. In such a process the surface after proper cleaning is activated by treatment with, for example, (a) an acidic aqueous solution containing 0.1 to 5.0 grams per liter of palladium ions as palladium chloride and an excess of the stoichiometric amount of stannous ions based on the amount of palladium ions present as set forth in British Pat. No. 942,850 or (b) a tin-palladium hydrosol such as that disclosed in copending DOttavio application Ser. No. 654,307, filed June 28, 1967, now US. Pat. No. 3,532,518.

In plating copper electrolessly on a copper substrate all of the processes proposed by the prior art have suffered from several disadvantages, the most serious being that the adhesion between the electrolessly plated copper and the copper substrate surface has been inconsistent and often very poor. For example, the electrolessly plated copper could easily be stripped off merely by the application of a pressure sensitive adhesive coated cellophane tape. This problem has been especially troublesome in the preparation of printed circuit boards.

In preparing printed circuit boards, the plastic substrate is commonly a copper-clad plastic laminate which may have a copper foil laminated to one or both of its surfaces. Generally, both surfaces of the plastic substrate are utilized on the printed circuit board and connections are provided between the two surfaces by means of holes through the laminate at appropriate locations, the walls of such through holes being made conductive with an electroless coating. However, in the course of electrolessly plating the through holes, electroless copper is also deposited,



unavoidably, on the pre-existing copper foil of the substrate. Then, since called two-stage process of activation was so poor, in order to achieve an adherent coating on the copper foil surface during the subsequent electrolytic plating step the surface of the copper foil was mechanically abraded before electroplating to remove all traces of the electroless deposit. Not only did this add additional operations which were costly and time consuming but frequently the laminates were ruined by such processing steps. Another major problem encountered because of the poor adhesion of the electroless coating to the copper cladding was that the poor bond caused difficulties at the boundary line between the electroless coating in the through holes walls and the copper foil at hole edges. Frequently, it was necessary to remove the electroless coating at the edge of the metal foil and unless this was done a poor connection often resulted. Removal of the electroless coating from the foil edge by machining and other appropriate methods not only increased the expense but frequently resulted in a high ratio of rejected laminates.

Some improvement in copper-to-copper adhesion was achieved with the introduction of the so-called one stage activation systems which employ, for example, a colloidal suspension of palladium or an activating agent of the type set forth in British Pat. No. 942,850 which comprises an acidic aqueous solution of palladium ions as palladium chloride and an excess of a stoichiometric amount of stannous ions based on the amount of palladium ions present. The improvement in the copper-to copper bond in such an electroless metal plating operation was achieved only when all the steps preceding metallization are stringently controlled. Despite the limited improvement made with certain refined processes in the art for electrolessly plating copper on a copper substrate or surface such as the one-stage activation process just described, prior to the process of the applicants, the art was not aware of any electroless process which gave adequate copper-to-copper

adhesion consistently and reliably. For this reason in manufacturing circuit boards commercially the step of sanding or buffing the copper-clad surface of the plastic laminate after the electroless plating step in order to remove completely the thin film thus laid down is still retained by some manufacturers.

It is a primary object of this invention to provide an electroless plating process for plating copper on a copper surface which will give an adequate bond between the deposited copper and the initial copper-clad surface. A second object of the invention is to provide a process for the manufacture of printed circuit boards in which the electroless copper plated on the copper clad surface will have a bond so strong that it will not need to be removed prior to the electrolytic plating step.

**ELECTROLESS PLATING PROCESS** In the first step in the electroless copper plating process of this invention the copper surface must be cleaned to remove any surface grime. Any of the commonly used metal cleaning processes known in the art can be employed to clean the surface of the copper sheet. Oils and greases on the copper sheet may be readily removed by immersion in an organic solvent vapor and trichloroethylene vapor degreasing is a common method employed. After the degreasing operation which are often designed to clean the copper by inclusion of complexing agents. Usually the copper surface is immersed in a cleaning solution maintained in a heated condition and with agitation of the work piece. A typical alkaline cleaner composition useful in cleaning copper surfaces is as follows:

Sodium isopropyl naphthalenesulfonate 3 g./L. Sodium sulfate 1 g./L. Sodium tripolyphosphate 14 g./L. Sodium metasilicate 5 g./L. Tetrasodium pyrophosphate 27 g./L.

Preferably, the cleaning operation is performed at a temperature of about 160-180F. and the copper sheet is permitted to remain in the bath for a period of about

three to about 30 minutes. Other suitable alkaline cleaning compositions such as conventional soaps and detergents may also be used although care should be employed in selecting the particular cleaning agent to be sure that the specimen to be treated is not attacked by the cleaner.

**ETCHING** Next, the copper surface is immersed, dipped or otherwise contacted with a copper etching solution to remove superficial oxides from the copper surface. Any of the commonly employed copper etchants may be utilized in the process of this invention. Typically suitable etchants include aqueous solutions of ammoniacal chlorite, ammonium persulfate, cupric chloride, etc. The etching treatment for removal of the copper oxide should be conducted at a temperature of about 85 to about 180F. for about 1 to about minutes. The

treatment time and temperature must be carefully selected particularly where the copper surface may be attacked excessively resulting in the removal not only of the oxide material but also a substantial amount of the copper substrate itself. Cupric chloride may leave a residue on the surface of the copper which can be readily removed by immersion in a dilute hydrochloric acid solution. **CATALYZATION**

The copper surface, after being rinsed and immersed in a mild acid bath is subjected to the catalyzation or activation step using any of the two-step or one-step activation procedures known in the art. In the two-step procedure the copper surface is first immersed in a solution of stannous chloride in hydrochloric acid at a temperature of from 70 to about 150F. for 1 to 10 minutes, following which it is dipped into a hydrochloric acid solution of palladium chloride at a temperature of from about 85 to about 175F. for 1 to 20 minutes or more, a well-known procedure as described in the art and as set forth in British Pat. Nos. 918,220 and 942,850. Activation or catalysis may also be effected by any of the one-step procedures such

as by employing an acid tin-palladium hydrosol. Such hydrosols can be prepared as disclosed in the aforesaid U.S. Pat. No. 3,532,518 by:

- a. first dissolving, for example, 2g. of palladium chloride in hydrochloric acid;
  - b. adding to the solution of step (a) 4g. of anhydrous stannous chloride, and agitating the resulting solution to dissolve the stannous salt therein completely;
  - c. separately dissolving in hydrochloric acid a mixture of 96g. of anhydrous stannous chloride and 14g. of sodium stannate and d. admixing the solution prepared in step (c) with that prepared in step (b) while effecting thorough agitation. In preparing the hydrosol, the amount of palladium chloride added must be sufficient to provide the equivalent of from about 0.05 to 5.0 grams of palladium per liter of hydrosol and the amount of sodium stannate and stannous chloride sufficient to provide the equivalent per liter of hydrosol of from about 0.35 to 35.0 grams of sodium stannate and from about 2;40 to 240 grams of stannous chloride. If desired, the one-stage activation solution described in British Pat. No. 942,860 consisting of an acidic aqueous solution of palladium ions as palladium chloride and an excess of stannous ions, can be employed.
- ELECTROLESS METAL PLATING** Following the activation or catalyzing step it is usually desirable to treat the copper surface with an accelerating solution which can be, for example, a dilute solution of a suitable acid such as 10 percent by volume solution of hydrochloric acid or an alkali metal hydroxide, such as a 5 percent by volume solution of sodium hydroxide. Preferably, the copper surface is immersed for about 0.1 to 5 minutes in the accelerating solution bath at room temperature. After rinsing, the copper surface is then plated in a copper electroless metal plating bath at a temperature of about to 150F. and for a period of about 5 to about 10 minutes. Any of the commercially available electroless copper baths are

suitable for use in this process. Typical compositions of such baths are set forth in U.S. Pat. Nos. 2,874,072; 3,075,855; and 3,095,309. The metal deposit laid down in the electroless plating step is very thin being of the order of from about 1 to about 30 millionths of an inch in thickness. The purpose of such a metal coating is merely to provide an initial conductive surface on which copper or other metals can be electrodeposited in order to produce a metal coating of any desired thickness.

The composition of a typical electroless copper plating bath useful in the process of this invention is given below:

CuSO<sub>4</sub> 5 H<sub>2</sub>O 8 g./L. KNaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> 4 H<sub>2</sub>O 9 g./L. HCHO (3771) 10 ml./L. pH (NaOH = 12.7)

ELECTROPLATING The copper substrate with the electroless copper on it, after rinsing, can be electroplated in a suitable electroplating bath to build up a sufficient thickness of metal to meet any of the mechanical requirements of the plated copper substrate. For example, the copper substrate with the electroless copper coating thereon can be plated in a conventional copper electroplating bath such as a copper pyrophosphate bath at 125-139°F. for about 40 minutes at 25 amperes per square foot resulting in a copper deposit approximately one mil in thickness. Higher current densities in plating can of course give thicker deposits as desired. Other standard electroplating baths such as the following bath may be employed:

CuSO<sub>4</sub> 5 H<sub>2</sub>O 188 g./L. H<sub>2</sub>SO<sub>4</sub> concentrated (66Be) 61.5 cc./L. Thiourea 0.001 g./L.

Wetting agent 25 ppm.

Surprisingly, it has been found that when the copper substrate with the electroless and electrolytic metal coating deposited thereon is heated or baked at a temperature of about 150 to about 450F. for about 10 mins. to about 2 hours or more at one or more points in a development of the completely plated product the bond strength between the initial copper surface and the electroless and electrolytic copper coating subsequently laid down thereon is tremendously improved. Preferably, the baking operation is conducted at a temperature of about 250 to about 420F. and from 0.4 to about 1 hour. The heating or baking operation can be carried out at one or more points in the process cycle, e.g., following the electroless plating step and/or after the electrolytic plating step, if employed. Usually the heating or baking step is conducted after application of the initial thin conductor metal layer in the electroless plating process and the subsequent electrolytic copper strike. While it is not necessary to heat or bake after the electroless plating step and after the electrolytic plating step, it is always required that the copper substrate be heated at least once following the electroless plating operation in order to obtain the surprisingly high adhesion results of this invention. While the mechanism by which the high adhesion values obtained is not fully understood, it is believed that baking permits the fine copper particles of the very thin electroless coating to grow, adhere and/or diffuse into the surface of the copper foil. When the process of this invention is employed in the electroless plating of copper on a copper surface, bond strengths or peel strengths of at least about 8 and as high as about pounds per inch or more are consistently obtained. The heating or baking step described is, moreover, essential to produce this improved result.

**MANUFACTURE OF PRINTED CIRCUIT BOARDS** In the process of this invention, circuit boards have.

conductor circuits on both sides and electrical interconnections (i.e., through hole connections) between certain areas of the opposite faces. The starting copper clad plastic laminate is punched to provide the through holes, after which the copper-clad faces of the laminate are cleaned, subjected to light etching or pickling followed by catalyzation and then by electroless deposition of copper over the entire exposed surface including the non-conductive walls of the through holes in the plastic substrate as well as the copper-clad faces of the substrate. In the next step a circuit pattern is applied using an organic or polymeric masking resist. The operator is afforded a choice of several methods in the selection and application of the resist coating, all of which are known and conventional in the art. Under one method the circuit design may be outlined by a chemical resist applied by squeegeeing it through an appropriate silk screen designed to produce coverage of the non-circuit areas of the board while leaving the circuit areas themselves free of resist material. Under the alternate resist application procedure, a positive or negative photoresist composition is applied to the entire surface of the board and this is exposed to a light source through a suitable film of the desired circuit areas (i.e. circuit areas) are electroplated with copper metal to the desired thickness and then covered with a metallic resist, such as a 60-40 tin-lead alloy, usually applied electrolessly or by electroplating. The organic resist is then stripped using a suitable solvent, leaving the non-circuit areas exposed and these are removed in a suitable acid or alkali etchant solution, such as an alkaline ammonical chlorite solution of the type described in US. Pat. No. 3,466,208, or in chromic acid or ferric chloride. An important feature of this invention is that the circuit board is heated or baked at a temperature of about 150 to about 450F. for about 10 min. to about 2 hours to promote effective bonding between the copper surface of the copper-clad board and the conductor metal formed in the electroless and

electrolytic plating operations. Such heating or baking operations can be carried out at any one or more points, such as following the electroless plating step, after application of the organic resist, after the copper electroplating step, after application of the metallic resist, etc., or after completion of the circuit board. The completed circuit boards exhibit high adhesion values or peel strength between the electrolessly plated copper coating and the initial copper-clad surface of the board.

Those skilled in the art will readily recognize that water rinsing, if required, may be employed between any of the steps of the various processes set forth herein.

The following examples illustrate various embodiments of this invention and are to be considered not limitative:

EXAMPLE 1 A sheet of copper having a thickness of about 0.0042 inch is first cleaned by dipping it in a cleaning bath at a temperature of about 180F. for about five minutes. The alkaline cleaner employed has the following composition:

Then the copper sheet is etched by immersing it in a 25 per-cent solution of ammonium persulfate for 1 minute at 70 F. After a thorough water rinse, the cleaned copper sheet is immersed in a bath containing hydrochloric acid (10 percent by volume) for a period of about 3 minutes at a temperature of about 70 F. to remove any residues which may be present. In the next operation, the copper sheet is activated using the conventional two-step activation process by first immersing the copper sheet in an acid stannous chloride bath containing 15g./L. of SnCl and 10 ml./L. of concentrated HCl following which it is contacted with an acid solution of palladium chloride containing about 1.66 grams of palladium chloride per liter and about 10 ml./l. of concentrated HCl at a temperature of about 80 for about 20 minutes. Following the activation process, the copper surface after



a thorough rinsing, is immersed in copper electroless plating bath for sufficient time to build up a copper coating of the desired thickness. The composition of the electroless plating bath is as follows:

CuSO<sub>4</sub> · 5 H<sub>2</sub>O 8 g./L. KNaC<sub>2</sub>H<sub>3</sub>O<sub>4</sub> · H<sub>2</sub>O 90 g./L. I-ICHO (37%) 10 ml./L. pH (NaOH) 12.6

Prior to the electroless plating step, the copper sheet optionally can be dipped in an accelerating solution comprising, for example, a percent hydrochloric acid solution, for 1 minute at room temperature. Following the electroless plating step, the sheet, after rinsing, is baked at a temperature of about 300F. for about 25 minutes. The copper sheet is then plated electrolytically in an acid copper bath containing about 200 g./l. of copper sulfate and 25 ml./l. of sulfuric acid for a period of about 45 minutes at 25 amperes per square foot and at a temperature of about 130F. resulting in a copper deposit approximately 0.001 inch in thickness. The peel strength of the copper coating plated on the initial copper surface is measured and found to be in excess of pounds per inch.

EXAMPLE II In the following example, which does not represent the process of this invention, the effect of omitting the heating or baking step is illustrated.

In this example a copper sheet having a thickness of about 0.002 inch was first cleaned by immersion in a mild alkaline cleaner at 170F. for 5 minutes after which it was thoroughly rinsed in clean water. Following etching of the sheet in a cupric chloridehydrochloric acid bath for 2 minutes at 75F. and after rinsing, it is immersed in a solution of 10 percent by volume hydrochloric acid to remove any residues from the etching step and again rinsed. In the activation step the copper sheet is dipped into a solution of an acid tinpalladium hydrosol having the

equivalent of 0.2 g. of palladium, 10 g. of sodium stannate and 12.6 g. of stannous chloride per liter of hydrosol. In this one-stage activation process, the copper sheet is immersed in the bath for 5 minutes, at room temperature. In the next step, the copper sheet is immersed in an accelerating solution containing 8 percent fluoboric acid for 2 minutes at room temperature and then rinsed. Copper is then deposited electrolessly on the copper sheet by immersing it for 10 minutes at 75F in the following bath:

CuSO<sub>4</sub> · 5 H<sub>2</sub>O 10 g./L. Na<sub>2</sub>CO<sub>3</sub> · 10 H<sub>2</sub>O 40 g./L. NaOH 10 g./L. Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2 H<sub>2</sub>O 12 g./L. Thiourea ppm. Formaldehyde (37%) cc./L Tetrasodium salt of ethylenediaminetetraacetic acid 2 g./L.

Following deposition of 1 mil, electrolytic copper from a copper sulfate-sulfuric acid bath it was found that the Cu/Cu bond was poor and the electrolytic/electroless deposits lifted off easily from the copper cladding.

EXAMPLE III This example illustrates the preparation of a printed circuit board by the process of this invention.

A copper-clad board with through holes already punched in it is cleaned of any surface grime by dipping next step the circuit board is dipped in a 10 percent by volume solution of hydrochloric acid at a temperature of about 70F for about 5 minutes, following which it is thoroughly water rinsed. After being activated in a one-step activation operation by immersing the board in an acid tin-palladium hydrosol such as that disclosed in HS. Pat. No. 3,532,518 the board is given a thorough water rinse. The board is then immersed in a 5 percent solution of sodium hydroxide for 1 minute at about 80F. and, after rinsing, is plated by immersion in an electroless metal plating bath of the following Water to make one liter The

electroless plating operation is suitably carried out at room temperature for about 10 minutes following which the copper-clad circuit board is rinsed thoroughly. The result of the electroless metal deposition step is that a very thin continuous layer of the order of about 20 millionths of an inch is deposited over the entire surface of the circuit board as well as the wall surfaces of any through holes present. In the next step a circuit pattern is applied to the circuit board surface using an organic polymeric masking resist to define the pattern of the desired circuit. The unmasked conductor areas (i.e. circuit areas) are then electroplated with copper utilizing a plating bath of the following composition:

CuSO<sub>4</sub> 5 H<sub>2</sub>O g./L. H<sub>2</sub>SO<sub>4</sub> concentrated (66Be) 50 cc./L. Thiourea 0.01 g./L. Wetting agent 25 ppm

board is subjected to a stripping action by treating it with a suitable organic solvent, for example, methyl ethyl ketone. In this operation the organic resist is stripped leaving the non-circuit areas of copper exposed and in the final step these non-circuit areas are removed by etching in an aqueous alkaline ammoniacal chlorite solution. The finished board is then rinsed, dried What is claimed is:

1. A process for electroless copper deposition on a copper substrate providing improved adhesion between the electrolessly plated metal and the substrate which comprises:

a. chemically etching the substrate with an etchant solution capable of removing superficial oxides from the surface,

b. catalyzing the substrate surface,

c. electrolessly depositing a copper coating on the catalyzed surface,

d. electroplating said electrolessly plated surface to build up a deposit of plated copper of suitable thickness and e. heating the plated substrate at a temperature of from about 150 to about 450F. for about minutes to about 2 hours after at least one of said plating steps.

2. The process of claim 1 wherein the plated substrate is heated to a temperature of from about 150 to about 450F. for about 10 minutes to about 2 hours after each of said plating steps.

3. A process for preparing printed circuit boards with improved adhesion between the plated copper and the copper metal of the laminated copper-polymerized resin substrate composition which comprises a. chemically etching the copper metal of the laminated copper-polymerized resin substrate composition. chemically stripping copper from the non-circuit areas in an etchant solution capable of dissolving the said copper,

i. and heating the plated circuit board at least once subsequent to the electroless plating step at a temperature ranging from about to about 450F. for about 10 minutes to about 2 hours.

4. The process of claim 3 wherein the board is heated after both the electroless and electroplating steps.

5. The process of claim 3 wherein the metallic resist is a 60/40 tin-lead alloy applied by electroless deposition from a solution.<sup>(5)</sup>

## **1.7. Use of Plastics:**

Since the end of the Second World War the use of plastics has increased remarkably due to a systematic exploitation of their principal advantages, i.e. lightness, flexibility and toughness, ease of fabrication of complex components, and excellent surface quality as fabricated. This has led, in a very wide range of applications, to the replacement of metals with plastics as materials of construction.

## **1.8. Advantage of Metals in the Automotive Industry:**

One property of metal articles that cannot be matched by plastics is the inherent ability to be polished to a bright, reflective metallic finish. This proved to be a disadvantage when, in the early 1960s, the motor industry was looking to replace metal with plastics for the manufacture of exterior and interior bright trim. At that time, trim components were normally finished in bright electroplated nickel/chromium generally known, both then and now, as chrome plating, which provided the required high quality lustrous finish. If plastics were to be used as a replacement, some method was therefore required of providing a similar surface appearance.

## **1.9. Alternatives to Chrome Plating:**

A number of alternative ways of providing this type of finish were investigated. However, it was soon established that only electroplated nickel/chromium would give the necessary quality that was related not only to aesthetic appeal but also to other properties of this particular coating system - good resistance to corrosion,

good resistance to abrasion, and ease of cleaning. The surface coatings industry was faced with the problem of producing this durable, attractive metallic coating on plastics components, thereby combining the advantageous properties of the substrate with those of the coating system.

### **1.10.Substrate Etching:**

Early processes, using conductive paint or chemically reduced silver on surfaces roughened either mechanically or by solvent attack, did not provide adequate adhesion. In the mid 1960s, etching solutions based on chromic acid were developed which could successfully be used with acrylonitrile butadiene styrene (ABS) copolymer. Use of these solutions resulted in selective removal of the butadiene phase from the resin to give a micro-etched surface providing bonding to the subsequent conductive layer.

### **1.11.Electroless Plating:**

This development came at a time when great improvements were also being made in the technology of electroless nickel and electroless copper deposition. These advances in electroless plating combined with the development of the etching technique gave rise to a system that provided a highly conductive coating exhibiting satisfactory adhesion to the plastics surface.

### **1.12.The Plating Process:**

Current plating-on-plastics processes still employ the basic technology developed at that time, although inevitably many refinements and improvements have been.

The basic steps are as follows:

- Etch in chromic acid based solution to promote adhesion
- Neutralise excess chromic acid
- Activate the plastics surface with a solution containing tin and palladium salts. This deposits nuclei of palladium metal on the plastics that catalyse nickel or copper growth from the subsequent electroless processes.
- Coat the surface with either nickel or copper (nickel is now generally the preferred commercial process) from an electroless plating solution.

Once the plastics component has been coated with this electrically conductive and adherent surface layer it can subsequently be electroplated using conventional technology.

The electrodeposited coating system used on plastics substrates always consists of an initial thick copper layer. This has been found to be necessary to compensate for the difference in thermal expansion between the metal coating and the plastics substrate.

In the early days copper was normally followed by a relatively thin bright nickel layer with conventional chromium topcoat. At that time it was considered that only thin nickel deposits were required since the plastics substrate would not be subject to corrosion in the way that metals are. However, it was subsequently shown that the thickness of nickel required on plastics substrates is similar to that necessary on metallic ones to prevent corrosion of the thick copper undercoat.

### **1.13. Resins For Electroplating:**

Although a wide range of plastics resins can be electroplated the market has always been dominated by acrylonitrile butadiene styrene (ABS). This has been estimated to account for 90% of the material currently used in this application worldwide. Polypropylene has been used, mainly for applications where its low water absorption is important, but has generally proved more difficult than ABS to electroplate reliably and its consumption has not grown significantly.

The plastics industry has recently introduced a range of new materials consisting of blends of ABS with polycarbonate.

Typically these contain 40-60% ABS with 60-40% polycarbonate, although a wider range of compositions can be used depending on the application. These blends not only have a higher inherent mechanical strength than unmodified ABS, but also show superior ductility in the as-plated condition. This is a most important property, particularly for the automotive industry, since it can provide a degree of recovery from impact. This may allow use of plated plastics for vehicle bumper bars. Other resins used for plating include nylon, modified polyesters, polysulphones, polyimides and polyetherimides, although the quantities are small compared to ABS. Particular interest is currently being shown in resins which are capable of being heated to higher temperatures than ABS in the as-plated state, such as rubber modified maleic anhydride copolymers. These would allow coloured, abrasion resistant lacquer finishes which require high curing temperatures to be applied on top of bright nickel as an alternative to chromium, thereby increasing the appearance options.



## **1.14.Applications of Electroplated Plastics:**

### **The Automotive Industry**

The initial motivation for the development of processes for electroplating on to plastics came from the automotive industry and this market sector has consistently been by far the largest user of the product.

Once a successful process had been developed it rapidly became accepted by the industry, and by the early 1970s large areas of nickel/chromium plated plastics trim were appearing on vehicles. A whole range of components were produced in plated plastics, including radiator grilles, window trim, name badges, front/rear lamp units, mirror housings, interior trim, and auxiliary lamp units. This trend was particularly evident with vehicles manufactured in North America, where bright trim has always been more popular than in Europe.

The use of plated plastics in the car industry reached a peak in the late 1970s and early 1980s. After that time the use of all types of bright trim declined as the design of cars changed in order to achieve a more aerodynamic profile to improve fuel consumption. This was particularly evident with European cars where nickel/chromium exterior trim was almost completely eliminated except on luxury models.

This eventually produced a generation of cars that were very similar in appearance. So by the early 1990s designers were seeking ways of creating a degree of visual individuality and of restoring marque identity. It is perhaps ironic that one of the most effective ways in which this has been achieved has been by restoring bright trim, albeit within the constraints of good aerodynamic shape. This has been used

particularly in high profile areas of the vehicle such as the radiator grille.

This resurgence of application in the motor industry has produced a remarkable expansion of the plating on plastics industry over the last three to four years. It is estimated that in Europe as a whole the industry has grown by 50% since 1993, whilst in the UK in particular the increase has been even more dramatic, producing a doubling of capacity over that period.

### **Domestic Fittings**

After the automotive market, the next most important application for plated plastics is for domestic fittings where the hygienic qualities of the finish and ease with which it can be kept clean are important factors. Items commonly produced in plated plastics include bath and wash basin taps, sink wastes, shower fittings, bathroom accessories, and kitchen accessories.

Other significant uses include knobs and buttons for the electronics and white goods industry. In France in particular the production of high quality perfume bottle caps in very large numbers represents a very important sector of the market. A new application appearing recently in the UK is for bar fittings and drinks dispenser units.

### **Summary**

The plating-on-plastics industry in both the European and North American markets has been expanding, primarily due to a resurgence of interest in this finish in the automotive industry. Other mainstream applications of the process have retained a firm hold on their market sector and a number of significant new uses have

appeared.

Reflecting the current optimism in the industry, recent symposia devoted to decorative electroplating of plastics have attracted enthusiastic support. The recent high rate of growth of plating on plastics is predicted to continue due to an ongoing commitment by the automotive industry and assisted by further promotional activity.

### **1.15.Uses of Electroplating deposition(EPD):**

This process is industrially used for applying coatings to metal fabricated products. It has been widely used to coat automobile bodies and parts, tractors and heavy equipment, electrical switch gear, appliances, metal furniture, beverage containers, fasteners, and many other industrial products.

EPD processes are often applied for the fabrication of supported titanium dioxide ( $\text{TiO}_2$ ) photocatalysts for water purification applications, using precursor powders which can be immobilised using EPD methods onto various support materials. Thick films produced this way allow cheaper and more rapid synthesis relative to sol-gel thin-films, along with higher levels of photocatalyst surface area.

In the fabrication of Solid Oxide Fuel Cells EPD techniques are widely employed for the fabrication of porous  $\text{ZrO}_2$  anodes from powder precursors onto conductive substrates.

EPD processed have a number of advantages which have made such methods widely used<sup>[6]</sup>

1. The process applies coatings which generally have a very uniform coating thickness without porosity.
2. Complex fabricated objects can easily be coated, both inside cavities as well as on the outside surfaces.
3. Relatively high speed of coating.
4. Relatively high purity.
5. Applicability to wide range of materials (metals, ceramics, polymers, etc.)
6. Easy control of the coating composition.
7. The process is normally automated and requires less human labor than other coating processes.
8. Highly efficient utilization of the coating materials result in lower costs relative to other processes.
9. The aqueous process which is commonly used has less risk of fire relative to the solvent-borne coatings that they have replaced.
10. Modern electrophoretic paint products are significantly more environmentally friendly than many other painting technologies.

Thick, complex ceramic pieces have been made in several research laboratories. Furthermore, EPD has been used to produce customized microstructures, such as functional gradients and laminates, through suspension control during processing.<sup>[6]</sup>

The major advantages that are normally touted for the anodic process are:

1. Lower costs compared to cathodic process.
2. Simpler and less complex control requirements.
3. Fewer problems with inhibition of cure of subsequent top coating layers.
4. Less sensitivity to variations in substrate quality.

The substrate is not subjected to highly alkaline conditions, which may dissolve phosphate and other conversion coatings.

5. Certain metals, such as zinc, may become imbrittled from the hydrogen gas which is evolved at the cathode. The anodic process avoids this effect since oxygen is being generated at the anode.

The major advantages that are normally touted for the cathodic processes are:

1. Higher levels of corrosion protection are possible. (While many people believe that cathodic technologies have higher corrosion protection capability, other experts argue that this probably has more to do with the coating polymer and crosslinking chemistry rather than on which electrode the film is deposited.)
2. Higher throwpower can be designed into the product. (While this may be true with the currently commercially available technologies today, high throwpower anodic systems are known and have been used commercially in the past.)
3. Oxidation only occurs at the anode, and thus staining and other problems which may result from the oxidation of the electrode substrate itself is avoided in the cathodic process.

A significant and real difference which is not often mentioned is the fact that acid catalyzed crosslinking technologies are more appropriate to the anodic process. Such crosslinkers are widely used in all types of coating applications. These include such popular and relatively inexpensive crosslinkers such as melamine-formaldehyde, phenol-formaldehyde, urea-formaldehyde, and acrylamide-formaldehyde crosslinkers.

Melamine-formaldehyde type crosslinkers in particular are widely used in anodic electrocoatings. These types of crosslinkers are relatively inexpensive and provide a wide range of cure and performance characteristics which allow the coating designer to tailor the product for the desired end use. Coatings formulated with this type of crosslinker can have acceptable UV light resistance. Many of them are relatively low viscosity materials and can act as a reactive plasticizer, replacing some of the organic solvent that otherwise might be necessary. The amount of free formaldehyde, as well as formaldehyde which may be released during the baking process is of concern as these are considered to be hazardous air pollutants.

The deposited film in cathodic systems is quite alkaline, and acid catalyzed crosslinking technologies have not been preferred in cathodic products in general, although there have been some exceptions. The most common type of cross linking chemistry in use today with cathodic products are based on urethane and urea chemistries.

The aromatic polyurethane and urea type cross linker is one of the significant reasons why many cathodic electrocoats show high levels of protection against corrosion. Of course it is not the only reason, but if one compares electro coating compositions with aromatic urethane cross linkers to analogous systems containing aliphatic urethane cross linkers, consistently systems with aromatic urethane cross linkers perform significantly better. However, coatings containing aromatic urethane cross linkers generally do not perform well in terms of UV light resistance. If the resulting coating contains aromatic urea cross links, the UV resistance will be considerably worse than if only urethane crosslink's can occur. A disadvantage of aromatic urethanes is that they can also cause yellowing of the coating itself as well as cause yellowing in subsequent topcoat layers. A significant

undesired side reaction which occurs during the baking process produces aromatic polyamines. Urethane cross linkers based on toluene diisocyanate (TDI) can be expected to produce toluene diamine as a side reaction, whereas those based on Methylene diphenyldiisocyanate produce diaminodiphenylmethane and higher order aromatic polyamines. The undesired aromatic polyamines can inhibit the cure of subsequent acid catalyzed topcoat layers, and can cause delamination of the subsequent topcoat layers after exposure to sunlight. Although the industry has never acknowledged this problem, many of these undesired aromatic polyamines are known or suspected carcinogens.

#### **1.16.Products to suit multiple needs:**

Besides the two major categories of anodic and cathodic, EPD products can also be described by the base polymer chemistry which is utilized. There are several polymer types that have been used commercially. Many of the earlier anodic types were based on maleinized oils of various types, tall oil and linseed oil being two of the more common. Today, epoxy and the acrylic types predominate. The description and the generally touted advantages are as follows:

1. Epoxy: Although aliphatic epoxy materials have been used, the majority of EPD epoxy types are based on aromatic epoxy polymers, most commonly based on polymerization of diglycidal ethers of bis phenol A. The polymer backbone may be modified with other types of chemistries to achieve the desired performance characteristics. Generally, this type of chemistry is used in primer applications where the coating will receive a topcoat, particularly if the coated

object needs to withstand sunlight. This chemistry generally does not have good resistance to UV light. However, this chemistry is often used where high corrosion resistance is required.

2. Acrylic: These polymers are based on free radical initiated polymers containing monomers based on acrylic acid and methacrylic acid and their many esters which are available. Such polymers often also include styrene as a monomer. Generally, this type of chemistry is utilized when UV resistance is desirable. These polymers also have the advantage of allowing a wider color palette since the polymer is less prone to yellowing when compared to epoxies.

### **1.17. Non-aqueous electrophoretic deposition:**

In certain applications, such as the deposition of ceramic materials, voltages above 3-4V cannot be applied in aqueous EPD if it is necessary to avoid the electrolysis of water. However, higher application voltages may be desirable in order to achieve higher coating thicknesses or to increase the rate of deposition. In such applications, organic solvents are used instead of water as the liquid medium. The organic solvents used are generally polar solvents such as alcohols and ketones. Ethanol, acetone, and methyl ethyl ketone are examples of solvents which have been reported as suitable candidates for use in electrophoretic deposition.<sup>(5)</sup>

### **1.18. Products to suit multiple needs:**

The metal frame of a vehicle has an extremely complex shape which makes it virtually impossible to coat many areas with conventional spray-applied paint. In order to achieve maximum corrosion resistance, the first coating layer in vehicle production is therefore applied via electro deposition.



This process is the most automatic, controllable, and efficient method for applying a corrosion inhibiting primer to a metallic work piece. The metal body is electrically charged and immersed in a bath containing oppositely charged paint particles which are attracted to the metal surface, neutralized, and then baked into a coherent, tough film. Current practice favors making the vehicle body the cathode in this process (this minimizes corrosion for steel). Coatings used in this process are called cathodic electro coats.

Electro coats are used in the automotive, agricultural, construction, heavy duty truck, sports and recreation, consumer products, heating and cooling, and military sectors.

Exalt Coating Systems is the second largest electro coat producer in the world, supplying electro coat to all major OEM manufacturers. It offers a full line of state-of-the-art technologies in addition to a full range of service and support resources.

We have a wide array of OEM qualified electro coat products to meet customers' specific needs. These products are formulated to provide superior performance over a variety of substrates including hot rolled steel, cold rolled steel, galvanized steel, aluminum, and magnesium. We offer all types of electro coats including lead- and tin-free, low volatile organic compound (VOC) systems, HAPS-free systems and special properties like improved edge protection, low bake, improved throwing power or weather durability<sup>(6)</sup>.

#### **1.19. Advantages of electro deposition are:**

- **Cost Efficiency.** After the initial capital investment, the electro

deposition process can significantly reduce operating expenses compared to conventional spray processes. These savings usually will result in "payback" of the investment during the initial two to three years of operation

- **Automatic application.** The electro deposition process is fully automated. In most instances a single system operator is the only direct labour required
- **Control.** With proper attention to bath chemistry, operating parameters and facility maintenance, an electro deposition process is capable of providing the highest first-run capability of any coating process at very high line speeds.
- **Efficiency.** The electro deposition process provides the highest material transfer efficiency obtainable by any coating process. Using closed-loop ultra-filter rinsing, material utilisation and recovery approaches 100%.

**Environmental safety.** Electro deposition coatings are water-based and contain as little as 1-3% volatile organic solvent. They are lead- and chrome-free. An electro deposition system goes a long way toward making an automotive assembly plant a good neighbour in terms of solvent emissions<sup>(6)</sup>.

## **2. Experiment's**

### **2.1. Materials:**

**All chemicals used on this research of Analytical grade type.**

- Copper(II) sulphate salt.
- Buffer solution, PH=4, PH=7, PH=10.
- Electrode of copper (anode).
- Electrode of plastic (cathode).
- Distilled water.

### **2.2. Equipments and apparatus :**

- Low voltage power supply.
- Sensitive balance.
- Conical flask (100ml).
- Connecting wires.
- Spatula.
- Funnel.

### **2.3. Method:**

#### **2.3.1. Method of Preparation the electrolytic solution of copper(II) sulphate :**

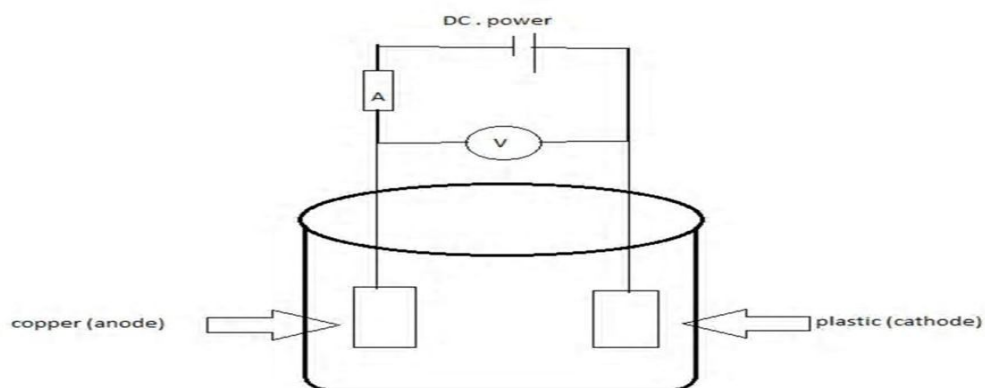
was weighted into a conical flask to prepared the concentration following:(0.05M),(0.1M),(0.2M),(0.3M) from copper sulphate , after that we added distilled water to the lapel.

#### **2.3.2. Electroplating method:-**

The plastic substrate were cut to  $2 \times 2 \text{ cm}^2$  . and was washed by distilled water, left to dry, then was washed by sodium

hydroxide solution to remove the oils, after that was weighted. , after that installation process was carried out by pickling the plastic about (5) minutes in chromic acid , then removed the plastic and left it about (30) minutes , after that Overwhelmed plastic in palladium chloride solution and shell off and was left about one hour , the sensitization was completed by installed small piece from silver in piece of plastic , then was inserted inside the electrolytic cell which containcopper sulphate solution after that the power supply was opened.

**The electroplating cell was shown digramiccly in Fig (2.1 )below**



After the preparation of the electrolytic cell systematic process were carried out to study the different operating condition (pH ,concentration, current value) were studied .

### 3. Results

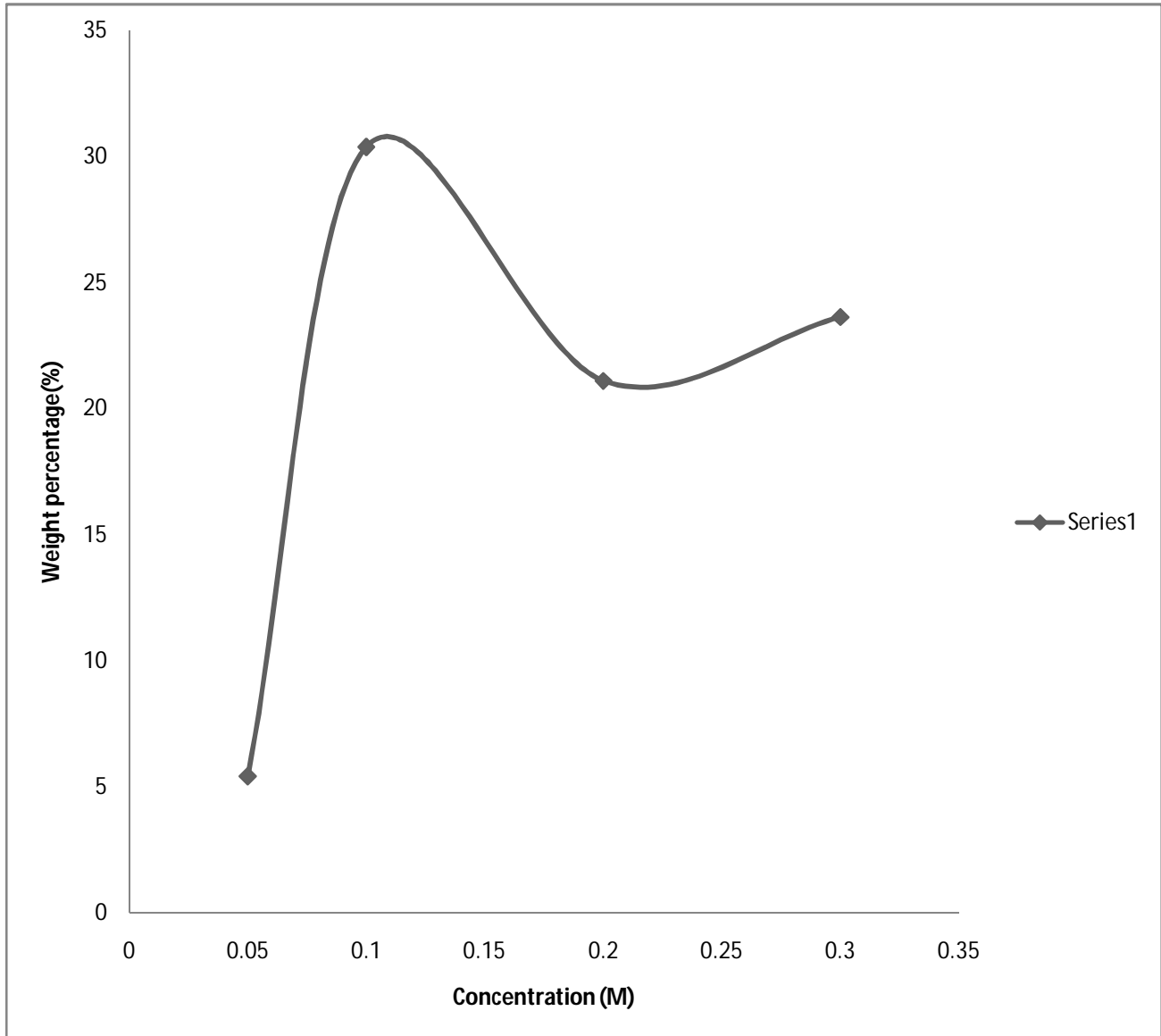
Table (3.1) show the relationship between concentration of electrolytic solution ( $\text{CuSO}_4$ ) and weight percentage(%) of the deposited (Cu):-

Concentration (M)	Weight percentage % (g)
0.05	5.42
0.1	30.39
0.2	21,11
0.3	23.64

The constant operating condition:

- ✓ The temperature =  $25^0$  C.
- ✓ pH = 7.
- ✓ Current value = 0.38

Fig(3.1) show the calibration curve between the concentration of electrolytic solution( $\text{CuSO}_4$ ) and weight percentage(%) of the (Cu):-



Table(3.2) show the relationship between the PH of electrolyte solution and weight percentage(%) of the deposited(Cu):

<b>pH</b>	<b>Weight percentage(%)</b>
4	4.82
7	30.40
10	5.06

The constant operating condition :

- ✓ The temperature =25<sup>0</sup> C.
- ✓ The concentration = 0.1(M).
- ✓ Current value = 0.38

Fig(3.2) show the relationship between pH of electrolytic solution ( $\text{CuSO}_4$ ) and weight percentage (%) of the (Cu) -





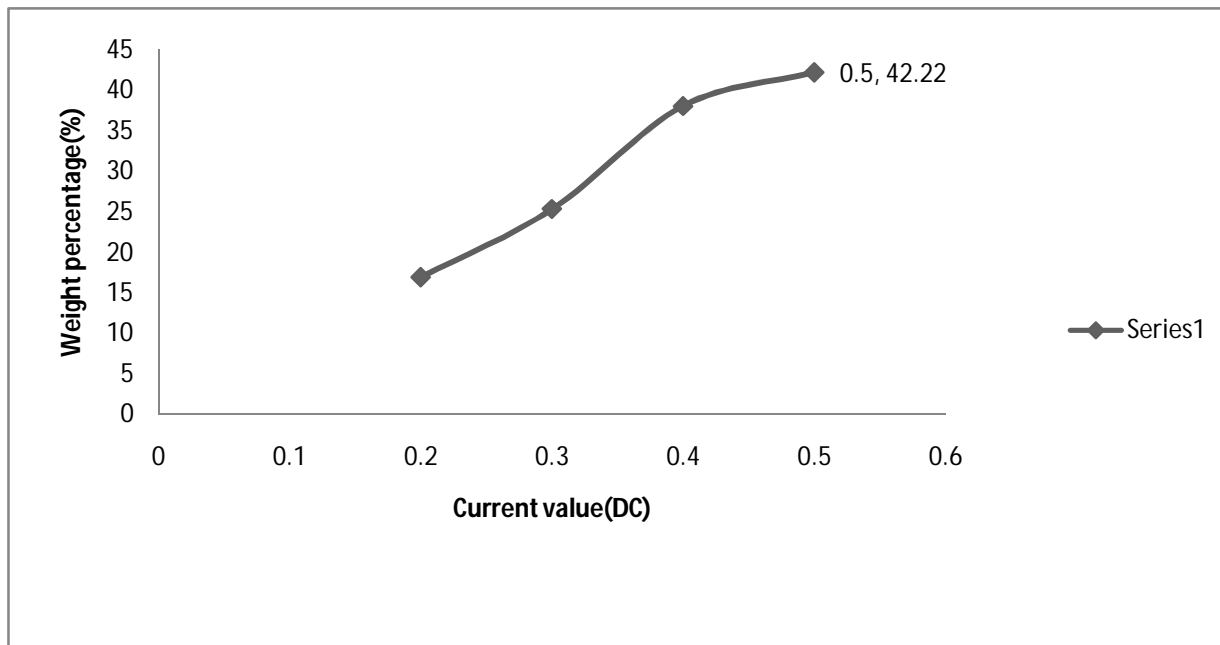
Table(3.3) show the relationship between a current value and weight percentage(%) of the deposited (Cu):-

Current value(DC)	Weight percentage(%)
0.2	16.89
0.3	25.33
0.4	38.05
0.5	42.22

The constant operating condition:

- ✓ The temperature =25<sup>0</sup> C.
- ✓ The concentration = 0.1(M).
- ✓ pH = 7.

Fig (3:3) show the relationship of current value and weight percentage (%) of the (Cu) -



## 4. Discussion

### Electroplating of Plastics

#### 4.1. The Problem

The basic problem in attempting to electroplate onto plastics substrates is, of course, that they are electrically non-conductive and cannot be immersed in a plating solution and coated in the way that metal objects can. Some method was therefore needed whereby a conductive film could be deposited onto the plastics surface to provide the basis for subsequent electrodeposition. It was, of course, vital that this surface layer, in addition to being electrically conductive, should adhere well to the substrate if the final coating system was to show good adhesion

In addition to this, there have also been two very significant developments in nickel/chromium electroplating technology that have ultimately greatly improved the quality of electroplated plastics.

- Double layer nickel systems consisting of a semi-bright under layer with bright nickel topcoat - have been developed which give much improved corrosion resistance compared to single layer bright nickel coatings of the same total thickness.
- It has also become widely accepted that microdiscontinuous chromium systems, where the chromium layer exhibits either an extensive microcracked structure or is microporous, further increase corrosion resistance of nickel/chromium deposits.

Modern specifications for electroplated plastics that are to be employed in severe environments (e.g. external automotive applications) all call for the use of double layer nickel together with microdiscontinuous chromium<sup>(6)</sup>

## 4.2. Discussion of results:

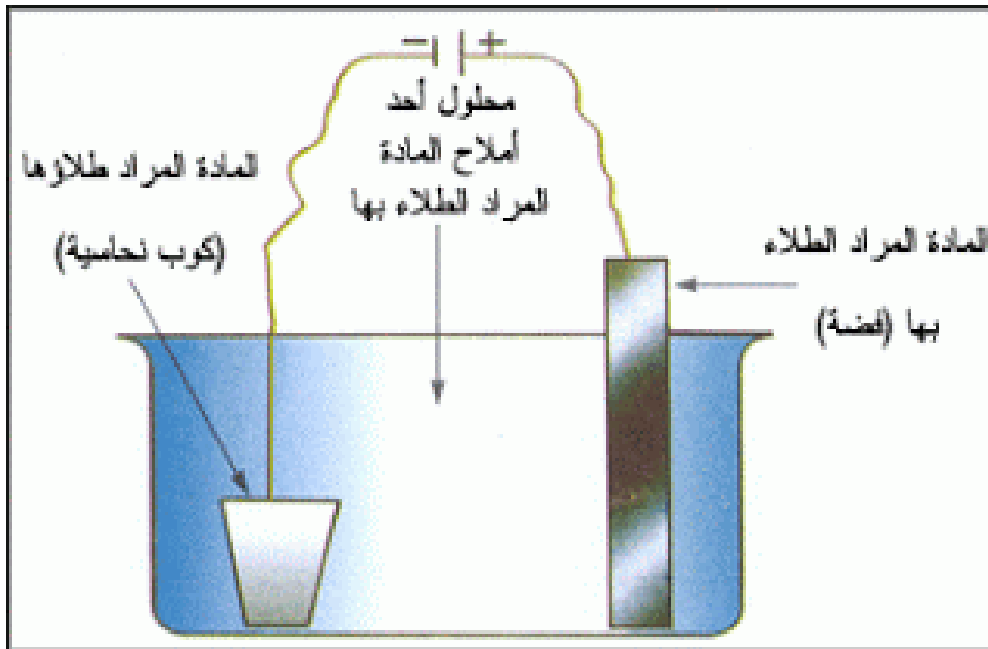
- From the table(3.1) and figure(3.1) it was found that when the concentration of the electrolytic solution increased, the amount material deposited on the surface of the plastic was also increased as stated by Faraday's law according to F.L equation (Q) page (2)
- From the table (3.2) and figure (3.2)It's clear that the deposited weight increased as the pH was increase and decreased below pH 10 due to formation e.g. of copper hydroxide.
- From the table (3.3) and figure (3.3) no doubt that whenever greater the current value density . the amount material deposited on surface of the plastic increased.

## 5.1. References

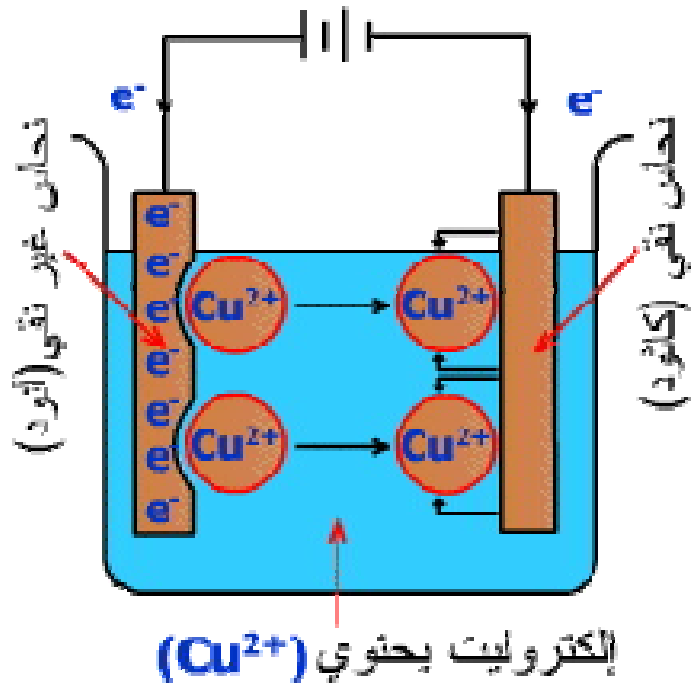
1. [www.answers.com/topic/electroplating-of-metals#ixzz30ek1RiXD](http://www.answers.com/topic/electroplating-of-metals#ixzz30ek1RiXD)
2. [./www.ehow.com/how\\_5019748\\_electroplate-metal.html#ixzz30ejhdCT](http://www.ehow.com/how_5019748_electroplate-metal.html#ixzz30ejhdCT)
3. [www.skplating.com](http://www.skplating.com)
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5. [www.faqs.org/patents/app/20090255823#ixzz34UjAAfLA](http://www.faqs.org/patents/app/20090255823#ixzz34UjAAfLA)
6. [en.wikipedia.org/wiki/Electrophoretic\\_deposition#city\\_note-1](http://en.wikipedia.org/wiki/Electrophoretic_deposition#city_note-1)

## 5.2Appendix:

- the metal to be repainted is copper by silver :-



- purification of copper from alloy :-



- Process of electroplating deposition :

