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Electroless Plating on Plastic

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Abstract— To compete in the emerging global marketplace industries shows an increasing interest in the development of advanced material possessing attractive properties. Metalized product made by deposition of metallic layers on products made of plastics and composite materials is one of the ideal examples in this respect. Since the plastic products are lighter, have low cost and can be moulded into any shapes in very short time duration by reducing the manufacturing time and cost for complex products. Also if these parts can be attributed the characteristics of metal by metallization then the final part would brings out the revolutionary change in the market with increasing demands for it. The paper reviews the various ways of metalizing the plastic parts and the comparison among them.

Index Terms— Activation; Coating; Conductivity; Electroplating; Etching; Electroless plating; Metallization.

1 Introduction

Plastic parts can be coated with metal by a process called as metallization. Through metallization, the specific properties of plastics are enhanced by the addition of properties usually associated with metals. These properties include reflectivity, abrasion resistance, electrical conductivity and a variety of decorative effects [1]. The deposition of a metallic coating on these parts also gives them a more attractive look, enhances their application range and creates therefore a considerable added value. Metallization of plastics is normally undertaken for either decorative or functional purposes. Metalized plastic components can be used in similar applications as metal plated parts with relatively lower weight and have higher corrosion resistance. In addition, electrical conductivity can be controlled in metalized parts and also they involve less cost in manufacturing. Plating on plastics therefore has been developed and widely involved in manufacturing printed circuit boards (PCBs), automobile parts, and in the electromagnetic interference (EMI) shielding applications. Plastics on which plating can be done are polypropylene, polysulfon, polyethersulfone, polyetherimide, Teflon and acrylonitrile-butadiene-styrene (ABS) etc. Among them ABS has found the widest acceptance in the plating industry because of its excellent toughness, good dimensional stability, good process ability, chemical resistance and cheapness. ABS is an engineering thermoplastic composed of an elastomer (butadiene) dispersed as a grafted particulate phase in a thermoplastic matrix of styrene and acrylonitrile copolymer referred as SAN [2].

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Plating of plastics can be done with Gold, silver, aluminum, nickel, chromium, copper etc [3]. Having excellent electrical conductivity and being relatively inexpensive, copper (Cu) has has been widely used for plating on plastics and a variety of plastics have been Copper plated.

2 Methods for Metallization of Plastic

Rapid Metallization of plastics can be divided into primary and secondary metallization. Primary metallization is done to make the non-conductive parts conductive by depositing a thin layer of metal or plastic substrate usually having thickness of 10-50 µm. Secondary metallization is mainly done on the primary metalized parts for increasing the thickness of metallic layer on it. The thickness deposited by secondary metallization is more than 180 µm. The important routes for metallization of plastic are as follows:

i) Brushing a metal paint
ii) Spray metal techniques
iii) Dipping in a metal paint
iv) Sputtering
v) Electroless plating
vi) Electroplating
vii) Electroforming
viii) Vapour Deposition techniques.

2.1 Brushing a metal paint

Applying a metal paint with a brush is the most convenient method of plating on the plastic surfaces. In this the metal paint is applied on the plastic surface through a brush to form a thin coating layer of conductive paint on plastics. This method has the advantage of producing uniform layer of applied metallic coating.

2.2 Spray metal Techniques

Spray deposition is a process also known as plasma spray deposition, plasma spraying and plasma deposition. In this process molten metal is sprayed onto a surface to form a coating. This is achieved by melting of pure or alloyed metals. The molten metal is then projected towards the surface to be coated by using blast of compressed air or other suitable mechanism. The result obtained is a layer of solid metal on the surface to be treated. The number of layers applied dictates the thickness of the coating. For example "Spray silvering" is a technique in which low adhesion silver layers were applied as undercoats to the surface of plastics. Silver was deposited by the chemical reduction of ammoniacal silver nitrate with a solution of formaldehyde or hydrazine. Both these solutions were simultaneously sprayed by aerosol so that mixing occurred on the surface to be plated. The metallic silver coats produced by this method were generally thin, and needed to be overplated with other metals to increase the coating thickness. In addition aluminium, copper and other paints can be used for spraying. Alternative dry spray techniques known as the "Schoop process" or "Flame spraying" have also been used. In these techniques, molten metal was sprayed by compressed air on to a plastic substrate, with solidification occurring on contact with the surface.

2.3 Dipping in a metal paint

Applying a conductive paint through dipping the plastic part in metal paint is also an alternative method for achieving the conductive plastic parts. The conductive metal coating is applied by dipping plastic parts in metal paint and leaving it inside the paint for some duration and taking it out and drying the painted part. Thus the layer of metal paint gets deposited as thin film on the plastic surface.

2.4 Sputtering

Sputtering is usually carried out in argon plasma. By biasing the target (source of metal) negatively, argon (Ar) ions are attracted to the target. The momentum of the Ar ions is transferred to the target resulting in the ejection of one or more atoms from the surface of the target. The sputtered atoms, mostly neutral, fly into the plasma and land on the wafer. The angular distribution of the sputtered particles follows the cosine law. Therefore, like evaporation, sputter deposition occurs essentially along a line-of-sight path with a cosine distribution. Poor step coverage can result if the surface topography of the wafer is abrupt. The uniformity of the deposited film can be improved by raising the substrate temperature, using a larger target, or inserting a collimator between the sputtering cathode and the wafer.

2.5 Electroless plating

It is the most common and widely used method for achieving the plating on plastic surfaces without any electrical assistance in the process. In electroless plating, the plastic part prior to plating is first subjected to surface preparation and then it is dipped into aqueous solutions containing metal ions. The chemical reactions occur between activated surface and solution which cause the metal ion to move the plastic substrate and deposited over it to form a thin layer of metallic film. The electroless plating process consisted of various steps for achieving the plastic metallization which are:

- i) Brushing
- ii) Conditioning or Etching
- iii) Neutralization
- iv) Activation
- v) Acceleration
- vi) Electroless plating.

2.6 Electroplating

This is basically a secondary method of metallization of plastics. This is done with aid of an external current supply. Electroplating is the deposition of a metal coating onto an object by putting a negative charge onto the object to be plated and immersing it into a solution, which contains a salt of the metal to be deposited. The metal ions of the salt carry a positive charge and are attracted to the part. When they reach it, the negatively charged part provides the electrons to 'reduce' the positively charged ions to a metallic form. When this method is applied for plastic parts, this is used for increasing the thickness of coating on parts already metalized by primary techniques.

2.7 Electroforming

Electroforming is a process for producing a metal part by electro deposition in a plating bath over a base form or mandrel, this is subsequently removed. Build-up is achieved over all mandrel surfaces at an approximate deposition rate of 25µm per hour. Electroforming reproduces the form or mandrel exactly (about 1µm), without the shrinkage and distortion associated with other metal forming techniques such as casting, stamping or drawing.

2.7 Vapour deposition techniques

The plastic component is first washed and coated with a base coat, so that the metal layer is smooth and uniform. Next a metal is evaporated in a vacuum chamber. The vapour then condenses onto the surface of the substrate leaving a thin layer of metal coating. The entire process takes place within a vacuum chamber to prevent oxidation. Depending on the component's application a top coat may be applied after deposition to increase properties as abrasion resistance etc. Metalized plastic components that receive their coats via this process are found in a range of applications, from automotive interior parts to certain types of foils. This deposition process can be either physical vapor deposition (PVD) or chemical vapor deposition (CVD). The most common forms of physical vapor deposition (PVD) are evaporation, e-beam evaporation, plasma spray deposition etc. PVD is used due to the following reasons:

- i) The ability to deposit high-temperature and refractory metals.
- ii) The high deposition rate afforded by modern cathode and target design.
- iii) The capability to deposit and maintain complex alloy compositions.
- iv) The capability to maintain well-controlled, uniform deposition on large (200 mm and larger) wafers.

Chemical vapor deposition (CVD) on the other hand also offers several advantages as:

- i) Excellent step coverage.

ii) Large throughput.
iii) Low-temperature processing.

3 Research Trend

The most common and widely used method in current time for metallization of plastic is Electroless plating. In electroless plating, metal ions in aqueous solutions are deposited on the activated plastic surface by oxi-reduction reactions without the aid of an external electrical supply. This helps in formation of a thin metallic layer on the plastic surface. This electroless deposited film serves two important functions: (a) It provides an electrically conductive substrate that allows further coating by electroplating or other and (b) It provides a secure bond between the plastic substrate and the electroplated layer [1, 4]. But before carrying out the plating, preparation or cleaning of plastic surface is essential for getting the proper plating on plastics.

The electroless plating process consisted of the following steps:

i) Cleaning
ii) Conditioning or Etching
iii) Neutralization
iv) Activation
v) Acceleration
vi) Electroless plating

(i) Cleaning **–** This process is used for cleaning the plastic surface either by brushing or scouring with sand paper to remove oil, dirt, grease etc. and also to develop micro-roughness for increasing surface area. The cleaner is typically alkaline in nature, although neutral or acidic materials can also be used. Important factors to be considered about the cleaning solution are: proper cleaner choice to do the job, temperature of cleaner, concentration of cleaner, time in the cleaner, work agitation in the cleaner, cleanliness of the cleaner to dump and rinsing after cleaning. Temperature is a key factor that is often overlooked in cleaner operation. Most cleaners have a lower limit of temperature operation below which they rapidly lose effectiveness.

(ii) Conditioning or Etching **–** This is the most important stage in plating process as it is fully responsible for achieving suitable conditions for good metal–plastic bonding. The parent surface is chemically etched resulting in the development of pores which can substantially increase the surface area of plating surface. In addition, it is also believed that hydrophilic sites which can readily absorb the etchant also developed on the surface. This stage consists of the immersion of the plastic sheets in an oxidant solution. The oxidant solutions used can be either chromic acid in aqueous sulphuric acid or hydrofluoric acid with sulphuric acid or other depending on the surface to be plated. Optimum conditioning time depends on the initial surface properties, which in turn are dependent on composition and injection conditions used in production of plastic parts. Depending on the surface the etching is carried out normally for 5–15 minutes, in a bath with temperature in the range of 60–65ºC. Conditioning materials contain surfactants to do the job intended. Finally after the process the part is cautiously rinsed with water as insufficient rinsing can allow the surfactant to remain on etched surface throughout the rest of the process and act as interference to etching, activation, and ultimately the resulting metallic bond. Thus the etched surface serves a number of purposes which includes

- An increase in the surface area thereby providing more opportunity for intimate contact between metallic layers.
- A properly etched surface will provide anchoring sites for the activator material, which can mechanically bond to the metallic surfaces.
- Some residual surface contamination remaining also got remove in the etching, if the contamination was not totally removed in the soak cleaner. This is because the residual contaminant does not allow the etchant to start working on the underlying layer at the same time it starts to work on uncontaminated areas.

(iii) Neutralization **–** This stage is responsible for removing the remaining amount of oxidant with a reducing agent as meta-bi-sulphite or ferrous ions to prevent its inhibition of the catalyst because even trace may completely inhibit electroless deposition of metallic layer on plastic surface.

(iv) Activation – In this stage, the conditioned surface is contacted with an activator or catalysts usually colloidal suspension of palladium/tin (Pd/Sn) catalyst powder. The catalyst particles get deposited in the surface micro-cavities formed during conditioning for subsequent initiation of the autocatalytic electroless metal plating process. Also depending on surface, activation stage is generally carried out at 45 ºC for 3 minutes. Since activator is a layer of material between the metallic layer and the subsequent electroless deposition, it can prevent intimate metal to metal contact and interfere with adhesion. It is desirable not to put too much activator on the work being processed and to avoid too long immersion time. Improper activation will probably cause poor metallic bonding, activator consumption, and hence cost will increase.

(v) Acceleration - In this stage, the absorbed catalyst particles are activated to increase its activity. The accelerator may be an acid or basic solution which dissolves excess of activator and removes it from the surface to interfere the absorbed catalytic action. The activated surface was washed and immersed in an acceleration bath normally at 30 ◦C for 3 min.

(vi) Electroless Deposition **–** In the deposition stage the activated plastic went through the solution usually containing of metal salts and hypophosphite as the reducing agent, in either basic or acid medium. An electroless plating layer is formed by a redox reaction on the activated surface [5]. The temperatures of bath are normally in range of 45–65 ºC. The temperature and deposition time are important in this stage for achieving the metallic deposition. A typical electroless bath formulations will contain metal salts, reducing agent (formaldehyde), alkaline hydroxide, chelating agents (quadrol, EDTA, Rochelle salts, etc.), Stabilizers, brighteners. The formaldehyde and the hydroxide ions provide the reducing force necessary for the deposition of metallic ions. The deposition reaction must be initiated by a catalytic species on the surface of the work to be plated.

4 Related Work

Various researchers have found that electroless plating can be efficiently done on the plastic surfaces if a proper etchant solution is used prior to plating process. Thus etching is an important step before carrying out electroless plating on plastics. Luan B. et al. [6] study the chemical surface preparation for electroless plating of stereo lithography polymers using etching solution of chromic acid and sulphuric acid. They conducted the contact angle analysis to assess the surface hydrophilicity so as to optimize the preparation process. The applicability of this technology was verified by subsequent metallization process. It was concluded as an efficient method for metallization of SLA polymers and enhances its performance in applications. Teixeira L.A.C et al. [7] carried out electroless copper deposition on ABS plastic using etching solutions of sulphuric acid, with hydrogen peroxide and/or nitric acid replacing the conventional use of chromic acid to avoid its effect to environment. They concluded that the solution used as oxidant can be used to provide comparative conditioning or etching for good metal-plastic bonding. Li Dapeng et al. [8] conducted acidic electroless copper deposition on aluminum-seeded ABS plastics. They have used aluminium-carbon paste and applied it on prepared ABS surface. Then electroless copper deposition was performed on pasted samples using copper sulphate and hydrofluoric acid as electroless bath. They have found good deposition of metallic copper layer on pasted sample both at room temperature and elevated temperature. Lin Yi et al. [9] analyses the effect of additives and chelating agents on electroless copper plating. They have used ethylenediaminetetraacetic acid (EDTA), triethanolamine (TEA) and ethylenediamine as additives or chelating agents in electroless copper plating with formaldehyde as the reducing agent. The experimental result shows that EDTA plays an important role in chelating, while the main effect of TEA is adsorption on copper surfaces to inhibit formaldehyde oxidation. On the other hand ethylenediamine serves as a refining agent owing to its higher adsorption on strength on copper surface than formaldehyde and TEA. Fritz N et al. [10] carried out electroless deposition of copper on organic and inorganic substrates using a Sn/Ag catalyst. They investigated the electroless deposition of copper and silver on epoxy and silicon dioxide-based substrates. In their experiment they found that cost-efficient Sn/Ag catalyst can be used as a replacement for Sn/Pd catalyst currently used in board technology. Shu Z et al. [11] investigated on the environment-friendly Palladium free surface activation technics for ABS surface. They have founded that colloidal solution of sulphuric acid and magnesium oxide can be used for etching. Also the use of the copper sulphate ($CuSO_4$ and reduction with DMAB (dimethylamineborane, $(CH_3)_2NHBH_3$) solution leads to the adsorption of Cu^0 particles on the plastic substrate which can be used as a replacement for the costly palladium in activation stage and making the electroless process cost effective. Naruskevicius L et al. [12] investigated on the use of a cobalt (Co) based surface activator for electroless copper deposition. The idea is based on the deposition of a Co-based precursor film on the substrate surface to be metalized and on the reduction of the adsorbed cobalt particles. The reduction of the adsorbed cobalt oxy/hydroxy compounds was carried out by dipping the treated surface in an alkaline solution of borohydride both at room and elevated temperatures. They have found that the presence of a small amount of Cu^{2+} ions in the colloidal solution of cobalt compounds catalyzes the reduction of adsorbed Co-based precursor on the dielectric surface. Also they concluded that formed Co seeds initiate electroless copper deposition.

5 Problem and Challenges

The electroless plating on the plastic can be done successfully but the process has got some limitation too. Even though the various steps of electroless plating can be carried out by using different alternative option, but still there are many problems which needs to be overcome for achieving good metallic deposition on plastic substrates. Thus the various problems encountered during various stages can be listed as following.

Etching - The etchant is the most critical step in obtaining an acceptable finished part. Since an under etching and overetching a part can degrade the surface and cause poor adhesion. The various problems in etching are as shown in table 1:

TABLE 1
Problems in Etching

Problem	Cause	Solution
Parts very light	Low temperature	Raise temperature, Agitate parts
Parts very dark	High temperature	Lower temperature, Check chemistry
Roughness on the parts	Particulates in the bath	Batch filter to the bath
Skip plate after electroless bath	Low temperature	Raise temperature, Check chemistry

Neutralizers - They are designed to eliminate excess etchant from the parts usually by chemical reduction. Thus the related problems in neutralizing stage are as listed in table 2:

TABLE 2
Problems in Neutralization

Problem	Cause	Solution
Parts very light	Low temperature	Raise temperature, Agitate parts
Parts very dark	High temperature	Lower temperature, Check chemistry
Roughness on the parts	Particulates in the bath	Batch filter to the bath
Skip plate after electroless bath	Low temperature	Raise temperature, Check chemistry

Activation - The main goal of activator is to provide catalytic sites on the surface of plastic. The associated problems are shown in table 3:

TABLE 3
PROBLEMS IN ACTIVATION

Problem	Cause	Solution
Parts very light	Low temperature	Raise temperature, Agitate parts
Parts very dark	High temperature	Lower temperature, Check chemistry
Roughness on the parts	Particulates in the bath	Batch filter to the bath
Skip plate after electroless bath	Low temperature	Raise temperature, Check chemistry

Accelerators are used to increase the action of absorbed catalysts. Thus problems occurring in this stage are as shown in table 4:

TABLE 4
PROBLEMS IN ACCELERATION

Problem	Cause	Solution
No plate on edge of part	Over acceleration, high temperature	Low temperature, Low time
Parts have no plate in major area	Under acceleration, low temperature	High temperature, Increase time
No plate at all out of electroless bath	Contamination that causes aggressiveness	Increase temperature and / or decrease temperature

Electroless deposition - Finally in the electroless bath which deposits a thin, adherent metallic film, usually copper or nickel, on the plastic surface by chemical reduction. Nickel baths are relatively easy to control, while copper baths generally require automatic analysis for control. Copper baths are more susceptible to problems than nickel. The various problems in this stage are listed in table 5:

TABLE 5
PROBLEMS IN ELECTROLESS DEPOSITION

Problem	Cause	Solution
Roughness	Particulates in bath	Filter bath, Agitate work
Burn off in strike	Electroless coating too thin	Increase time and temperature, Check bath rate
Overactive bath	High temperature, High reducer, Low stabilizer	Low temperature, Check chemistry, Check stabilizer
Sluggish bath	PH out of range, High stabilizer, Low reducer, Low temperature, Contamination.	Check chemistry, Rise temperature, Check for contamination

5 APPLICATION

Figure The electroless plating on plastic has got very widespread application in all the fields as includes oil & gas, chemical processing, textile etc. Varieties of metals can be deposited including copper, nickel, chromium, silver etc. Among the all copper and nickel find the most extensive application. Electroless nickel plating been used widely in aerospace industry. In aircraft engines, turbine or compressor blades are plated with electroless nickel to protect them against the corrosive environment. In automotive industry electroless nickel plating is used to plate gear and fuel injectors etc. In the field of chemical processing industries the electroless nickel plating is used by material engineers to solve many unresolved problem. Tubular used in oil and gas production are an excellent application for electroless nickel plating. Electroless nickel plating is also used to plate molds and dyes. It also found wide application in foundry tooling, printing industries, textiles, and medical. Electroless plating of copper films have been used as conductor and connector in printed circuit boards (PCB). Copper plating also serves many useful functions in electronic devices, corrosion protection, diffusion barriers, conductive circuit elements, via-hole filling for semiconductor integrated circuits and flexible circuits. Plating is also used to enhance solderability. Tin, tin-lead, tin-bismuth, various silver alloys, gold and gold alloys, electroless nickel-boron and electroless nickel-phosphorus alloys are common materials for soldering.

6 CONCLUSION

The The increasing possibilities of electroless plating on plastics with low cost and time through different methods shows a great potential. Since the plastic parts itself posses many useful properties and if they are imparted with metallic properties on it, the properties of resulting part will be greatly enhanced with high increase in its demand in global market. As it is simple, cost effective method since it don't involves the use of expensive equipments as required by other deposition processes for achieving good bonding between plastic substrate and metallic layer it really enhanced its application. Also it is less intensive because the metal deposition rate is limited by metal ion reduction in the bulk of the solution. These lead the electroless plating on varieties of plastics from earlier polypropylene to ABS for different applications. These all factors help it in becoming an ideal process which provides part with attractive properties.

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