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Electrochemical Pollution Control – Substitute for Cyanide Bath for Copper

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Abstract

In the age of raising industrial production the problem of environmental protection becomes a vital aspect in all questions of the human society. The problem involves questions of careful utilisation of natural resources, the prevention of useless or harmful side products, environmentally – tailoring of products. Chemical industry in the widest meaning plays a major role in the solution of these questions. Also electrochemistry can contribute as its main scientific interest lays in the interaction of energy and chemical matter.

Electrochemical processes my influence the environment mainly as follows.

- *production of harmful substances in the course of the electrochemical reaction.*
- *generation of harmful substances in the course of the electrochemical reaction.*
- *indirect generation of harmful side – products at the electrode or the electrolyte by chemical reaction sequences.*
- *decomposition products of the electrode materials*
- *formation of residual electrolytes and electrode wastes*

Electrochemical processes offer certain of advantages in comparison in classical chemical processes. The electrochemical reaction can easily be controlled by the electric current. In this way also the electrical conditions, potentials, reaction rate are observable and can be monitored. Therefore, the level of disturbance of the environment should be lower than in classical chemical processes. On the other hand electrochemical processes are usually very selective due to the opportunity to control the electrode potential. They can be used to remove certain harmful substances from the environment. The flash or strike bath for copper deposition on MS (Mild Steel) Components prior to other plating involves at present in the industry, the use of Cyanide complex baths. The hazards from the use to find a substitute for cyanide bath. An attempt is made in this work, to formulate a Copper –EDTA disodium salt complex bath and its suitability to obtain a Copper strike on MS component. The optimum operating conditions like current density, composition of bath, temperature, and pH are evaluated. The cost of this EDTA bath is also estimated.

Keywords: *Copper-EDTA salt solution; Cost analysis; Electrochemical reactions; MS sheet.*

1. INTRODUCTION

Electrodeposition or commonly known as electroplating consists of depositing a thin layer of nobler metal over a lesser one by passing a direct current through the electrolytic solution containing the metal ion to be deposited. The metal is plated on this cathode Job), whereas the anode is made up of the coating material or an inert material of good electrical conductivity.

1.1 Electroplating

The basic components of an electroplating unit are a cathode, an anode, an AC-DC rectifier and a suitable plating bath. Ancillary equipments may be

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necessary for stirring, for purification of the electrolyte and to provide any automation.

1.2 Role of electrolyte

The electrolyte is normally an aqueous solution containing the plating metal in an ionic form. There are some metals which cannot be plated from aqueous simple salts solutions because of their large negative discharge potentials. Attempts to deposit such metals from aqueous solution only lead to the liberation of hydrogen at the electrode (Stotand Ashby, 1999).

1.3 Role of cathode

The metal or non-metal substrate, in which the metal is deposited, is made negative and is called the "Job". In most of the cases the substrate is MS component and plated metals are copper, nickel and chromium. Less frequently employed substrates are copper, brass alloys and plastics, less frequently plated metals are zinc, cadmium, silver, gold etc. Whatever may be the substrate it requires an extensive pre-treatment. Surface contamination in the form of rust, scale, oil, grease and dirt is often obvious. Invisible contamination may also be present and represents, on the whole a greater hazard example soldering fluxes, sulphate and cyanide from industrial atmosphere.

The surface of the substrates needs to be prepared mechanically and chemically. The mechanical preparation means removal of surface undulations by buffing, polishing etc. Chemical cleaning involves removal of grease, dirt and scale or other film by solvent cleaning (example, trichloroethylene), alkali cleaning (example, sulphuric acid) and the modern method ultrasonic cleaning (using alkaline cleaner in which the soundwaves are being converted into vibration waves). Electroforming is a special process in which the cathode is given a very thick coating and the coating is separated from the cathode, later which has the same counteras that of the cathode. Here metals or non-metals are used as substrates. In the case of non-metal being used as a substrate, after heavy deposition the plastic is melted and removed (Expendable substrate). The widely used plastic ABS and for the pre-treatment, it is etched in sulphuric acid, sensitised in a solution of stannous chloride and hydrochloric acid and activated in palladium chloride solution. It is then metallised in a Fehling's type solution where in a thin coating of copper is formed on the plastic by chemical reduction. After this, it functions as a metal cathode on which any electrode position can be carried out. Typical industrial applications of this process are production of metal screens, waveguide, record stampers which cannot be made by other conventional metal forming processes (Ohms and Wiesener, 1990).

1.4 Role of anode

The normal practice is to use soluble anodes of the plating metal. It is preferable to have an anodic current efficiency equal to the cathode efficiency. If the anodic current efficiency is higher than the cathode value, insoluble auxiliary anodes may be used together with soluble anodes which is a common practice in cadmium plating (Brenner, 2009). When a high current density is required the surface area of the anode can be increased by the use of shots, pellets held in double – cotton or poly propylene bags. Basket anodes have the additional advantages that they have constant shape and may be designed to give improved distribution of the deposited metal on the component being plated. Insoluble anodes, example in plating of chromium from hexavalent bath, inert lead-tin or lead-antimony anodes are used. They are free from the problems of particle formation (Dennis and Such, 2003).

2. OPERATING CONDITIONS

2.1 Role of applied potential

The rate at which the reaction proceeds is extremely critical as it determines not only the duration of the reaction and the economic but also other plating parameters. From an industrial point of view, the rate of deposition must be fast. In electrical terms, the rate of deposition is nothing but the current that is passed through the system. In order to pass the current, energy must be supplied to the system in the form of potential which becomes the limiting factor. From Ohm's law, it follows that current can be increased by increasing the potential.

$$\text{i.e.,}\quad V \propto I \qquad \text{.........} \ (1)$$

But current cannot be just increased indeterminately by increasing the applied potential because the plating reaction requires and optimum rate beyond which it becomes difficult to control the quality and nature of the deposit. Such practical difficulties limit the current that can be passed through the system. Let the two copper plates be dipped in a Cu^{+2} solution (say copper sulphate). The system now constitutes an electrochemical cell. In the absence of any external applied potential, the system is under the dynamic equilibrium:

$$Cu^{2+} + 2\,e^{-} \rightleftharpoons Cu \qquad \text{.......} \ (2)$$

The standard equilibrium potential for this system under ambient conditions is + 0.340V (from EMF series). The flow of charge (current) across this system in dynamic equilibrium will be to a very small extent of approximately 10^{-8} – 10^{-10} A. This small current is called “exchange current”. In such a case, practically no reaction (electrodeposition) will be observed. The above concept is purely thermodynamic.

For this system to acquire any practical significance, the rate of the reaction must be increased manifold, i.e., the current flowing should be increased to say 10 or even 100A. In other words, the equilibrium between the two electrodes must be disturbed so that one electrode becomes electron rich and the other electron deficient. As a result, the reaction will now proceed in one direction only. For achieving this, the application of an external potential becomes imperative. On application of an external potential, the copper electrode attached to the positive terminal of the power supply becomes electron deficient and undergoes oxidation. Consequently, reduction occurs at the other electrode as it becomes electron rich. Both the reactions, namely oxidation and reduction, occur at a rate many times greater than the exchange current rate i.e., the reversible condition is transformed into an irreversible condition. In other words, the equilibrium state is replaced by a non-equilibrium state or a transition from thermodynamics to kinetics occurs. In the example cited above, the reaction that predominates at the cathode on application of external potential during electroplating is:

$$Cu^{2+} + 2\,e \rightleftharpoons Cu \qquad \ldots\ldots\ldots\ldots (3)$$

and the reaction at the other electrode (anode) will be

$$Cu \rightleftharpoons Cu^{2+} + 2\,e^{-} \qquad \ldots\ldots\ldots (4)$$

Hence for an electrochemical reaction to occur at a practical rate a much higher potential than the equilibrium potential is required. But the magnitude of this extra-potential over the equilibrium value depends upon the desired rate of deposition which in turn depends upon the current flowing through the system. But one cannot increase the potential to a very high extent in order to achieve very high deposition rates because at very high applied potentials, not only copper deposition will take place but also hydrogen will be evolved. This simultaneous evolution of hydrogen gas along with copper deposition makes the deposit porous and non-adherent. Also the current spent for this unwanted reaction is a waste. Thus, in any plating process, the operating limit is the hydrogen evolution. The voltage requires for the process is decided based on this factor. (Peterspiro –Robert Draper, 1991)

2.2 Role of complex baths

Though simple baths are economical and are used widely in plating, the use of complex baths is resorted to a few cases where a simple baths fail. The failure bath necessitates the use of complex baths. Following details illustrate this point.

Case 1: Zinc

The standard reduction potentialfor Zn ($Zn^{2+} + 2e^{-} \rightleftharpoons Zn$) is – 0.76 V. The high negative value indicates the difficulty of reducing zinc ions from aqueous solutions in which Hydrogen ions are also present. Application of a potential negative to this value will be required to exceed the over potential required for this reaction. That means the potential will be much higher negative value than the standard electrode potential of hydrogen which is zero. Hence the tendency for hydrogen ions getting reduced will be more than that of zinc ions from aqueous solutions. Therefore, it is very difficult to deposit zinc from simple zinc sulphate solutions. In practice zinc deposition is carried out from alkaline zinc cyanide solutions where the electrolytic profile changes such that at normal applied potential zinc deposition takes place. In recent years highly acidic zinc chloride baths have been developed, which have its own merits and demerits.

Case 2: Silver and Gold

Simple salt solution for silver is silver nitrate bath, in which the deposit of silver obtained by plating is very hard and rough. A high standard reduction potential (+0.8V) is the cause. Though reduction of silver ion concentration may decrease this potential, the magnitude of reduction is very less. For example, 10 times dilution of Ag^{+} ion from 1 to 0.1M reduces, the equilibrium potential approximately by 60mV, which is evident from the application of Nernst equation. Attempt made to reduce the concentration further to 10^{-3} to 10^{-4}M results in only hydrogen evolution and not silver deposition.Hence, it is complexed with cyanide, which is stable under alkaline conditions. Non cyanide bath for silver plating has not so far been reported. For gold no simple salt is available and hence the only alternative is going for complex bath. Gold-cyanide baths are widely employed in gold plating industry and till date a non-cyanide bath has not been developed, despite the hazards of cyanide. (Brenner, 2009).

Case 3: Copper

Though several baths are available for copper plating, the most economical and widely used one is acid copper sulphate bath. The most important engineering material for fabrication is mild steel and to avoid its getting corroded, mild steel component is coated with bright nickel and chromium. Bright nickel deposit is known for its porosity. Hence a copper undercoat is advised to increase the life of the electrodeposit of nickel and chromium.

The standard reduction potential for Iron ($Fe^{2+} + 2e^- \rightleftharpoons Fe$) is -0.44V and that of copper ($Cu^{2+} + 2e^- \rightleftharpoons Cu$) is +0.337V. Hence when an MS component is dipped in an acid copper sulphate solution, copper and hydrogen are displaced and iron goes into solution (A metal with a lower reduction potential is displaced by one with a higher reduction potential from the solution of the latter). The displaced copper presents as a loose, porous deposit on the MS component, the porosity being due to inclusion of displaced hydrogen. From a platter's point of view this loose deposit cannot be called an electrodeposit at all. To narrow down the wide gap of two equilibrium potentials the concentration of Cu^{2+} ion in the solution should be reduced.

Nernst equation it is apparent that the reduction in concentration by 10 times of the solution leads to a small decrease of potential by approximately 30 mV only. To reduce the equilibrium potential by 300 mV, that is to bring it to zero, the concentration should be approximately 10^{-10}M which is practically water. Hence the alternate method of reducing the metal ion concentration is by complexing.

But copper for a cyanide complex only in monovalent state. Cuprous copper complex with potassium cyanide producing $K_3[Cu(CN)_4]$ (Potassium Tetracyano copper-I). This is water soluble and dissociates completely into potassium and complex anion.

$$K_3[Cu(CN)_4] \text{ ------> } 3\,K^+ + [Cu(CN)_4]^{3-}$$

Dissociation of anion occurs to a very low extent and the dissociation constant value (k) is 5.6 x 10^{-28}

$$[Cu(CN)_4]^{3-} \rightleftharpoons Cu^+ + 4CN^+$$

This complex ion is very stable. Hence, the concentration of free cuprous ion in solution is extremely small of the order of 10^{-8} to 10^{-9} M and this reduces the equilibrium potential from +0.34 to 0.1 V (approximately).This shifting of potential to higher negative value narrows down the gap, thereby preventing the displacement of copper from the solution (copper deposition). On application of a potential the following reaction will occur.

$$Cu^+ + e^- \rightarrow Cu$$

Removal of this copper ion from the equilibrium causes further dissociation of the anion producing Cu^+ for the reduction or deposition. Virtually, copper does not exist as free cuprous ion but entrapped in the anion which acts as a reservoir. On demand by way of applied potential cuprous ions are released from the reservoir.In copper plating of MS objects, copper flash/strike in copper cyanide bath is carried out upto a thickness of about 1 to 2 microns and further build up of deposit is done from regular acid copper sulphate bath.For copper deposition use of acid copper sulphate baths has been a well established one and is employed in electro refining of copper, production of printed circuit boards in electronic industry and electroforming.

The complex baths used for copper deposition are cyanide and pyrophosphate. The cyanide copper complex bath has a wide area of application and is generally employed for commercial electroplating. Both ferrous and non-ferrous metals may be copper plated from solutions of this type. In addition, the cyanide copper baths solutions have much higher throwing power than the other types of copper plating solutions (Sequira, 2000). Copper pyrophosphate bath solution has a good throwing power and is cyanide free. The solution is approximately neutral and less corrosive than acid copper solutions. The industrial applications include electroforming, production of printed circuit boards and the plating on plastics. A method for continuous coating of copper on steel wire has been developed by non-cyanide acid copper baths (Ramesh Babu *et al.* 1999). At present in plating industry where a copper undercoat is given on MS sheet, prior to nickel or chromium depositions, copper cyanide complex bath is used as a strike bath, since copper cannot be plated on MS sheet directly from acid copper sulphate bath for reasons discussed earlier. The use of cyanide bath possesses several problems in storing, usage, handling and disposal. Cyanide baths though stable in alkaline conditions, slowly decompose on exposure to air giving rise to hydrogen cyanide fumes. On contamination with acid it gets decomposed fast to hydrogen cyanide, which is highly toxic. Special fume exhaust is to be provided for removing toxic fumes. Letting it out to atmosphere violates pollution board regulations. Further, disposal of cyanide effluent and washings create also serious pollution problems and calls for extensive and expensive treatment to meet the pollution board regulations (Visalakshi Ravindran *et al.* 1995).

Attempts are going on to substitute this hazardous cyanide bath, with this view in mind the project work has been taken to develop a non-cyanide bath involving EDTA and optimise the operating variables. Cost comparison with cyanide bath is also made.

3. EXPERIMENTAL WORK

AC –DC power supply (westinghouse) 0 -12 V DC continuous variable is used for DC supply. Elecrolysisis the cell consists of a 250ml borosil glass beaker with a copper anode and a hollow cylindrical platinum as the cathode. A PVC rod was inserted Tight fit into the hollow platinum cathode and the other end of the platinum cathode was closed with a rubber cork to avoid plating on the inner side. The electrical connection was taken from the platinum cathode. The electrolysis was conducted in the beaker scale to study the effort of all variables and based on these results,scaling up was done from the beaker to trough glass from 250 ml to 2 litre baths. For this the cathode specimen used were made up of mild steel. The size of the specimen was approximately 5 cm X 1 cm.TheCathode specimen was hung from the centre and facing the two sides of it were two copper anodes, to ensure uniform plating on both sides of the cathode. Sysronics 335 was used to find the pH of the bath. The bath was agitated or stirred using magnetic stirrer. Chemicals used were BDH/ E merck brand laboratory grade Duco Auto clear DucoThinner from Ducopaint company. De-ionized water was used for washing and for preparing the solutions.

4. ELECTROLYSIS

4.1 Preparation of the baths

Copper sulphate-EDTA bath employed for the complex non-cyanide bath.required quantity of copper sulphate and EDTA were weighed, copper sulphate was firstdissolved and then EDTA was added. After EDTAdissolves, this solution was filtered to remove insoluble impurities, and was made upto 500 mL. This was the stock solution. From this stock solution,required quality of this electrolyte was measured out for each electrolysis run. Like this, mixtures of copper sulphate and EDTA were prepared in different molar ratios as shown in the following table.

Table 1. Mixtures of copper sulphate and EDTA were prepared in different molar ratios

Bath A	Copper sulphate EDTA	0.1M 0.1M
Bath B	Copper sulphate EDTA	0.2M 0.1M
Bath C	Copper sulphate EDTA	0.3M 0.1M

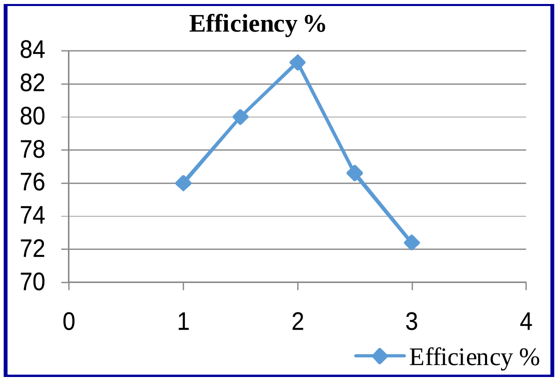

Fig. 1: Current density A/dm^2

The electrolysis was carried out at various current densities (1 A/dm^2, 1.5 A/dm^2, 2 A/dm^2, 2.5 A/dm^2 and 3 A/dm^2) and at various temperatures (Room temperature, 40 °C and 50 °C). The cathode, each time after deposition was dried and weighed. The deposit was stripped in a stripping solution containing a mixture of sulfuric acid and hydrogen peroxide. This solution was made upto 50m/L and used for analysis. Copper sulphate in the made up solution prepared from the stripped deposit was estimated iodometrically as follows. Approximately 0.01 N sodium thiosulphate was prepared and was standardized using standard potassium dichromate solution.Copper present in the made up solution from the deposit was determined iodometrically following the standard procedure. The weight of copper is determined from stripping of deposit and by volumetric analysis. The coating thickness was determined using “Weigh” plate weigh method”. Samples were weighed accurately before and after plating digital balance. Before weighing the sample was thoroughly cleaned, dried in an air oven, cooled in a desiccators and finally weighed (Ramesh Babu *et al.* 1999).

The coating thickness is determined as

$$\text{Thickness} = \frac{M_2 M_1}{QA} \text{ microns}$$

M_1= mass in grams of the test specimen before plating

M_2= mass in grams of the test specimen after plating
Q =density in grams per cubic centimeters of coating
A = area in square centimeter of the plated surface of the test solution

5. RESULT & DISCUSSION

The results of copper deposition carried out at various current density values.The weight of deposit increases from 0.92mg at 1 A/dm^2 current density to 2.02 mg at 3 A/dm^2 current density. The appearance of the deposit is good upto 2 A/dm^3 current density and there after becomes dark. Also the deposit is not adherent beyond the current density of 2 A/dm^2.The efficiency can be calculated by taking the ratio of the weight of deposit directly measured (Dg) to the theoretical weight of deposit which is calculated (Tg), but this is often highly erroneous because of the following factors.

1. Inclusion of impurities
2. The current fluctuations which occur during electrolysis.

For example the variance control is adjusted for 150 mA. But it cannot be definity ascertained that 150 mA current is passed for the entire duration of 15 minitues. The current fluctuations occur and are set right by manual adjustment which cannot be done continuously.If a coulometer is available the exact quantity of electricity passed can be determined. Since the facility is not available, the weight of deposit determined by direct method Dg is not taken for efficiency calculation, instead of this the weight determined volumetric method is taken. For this the deposited was stripped in dilute sulphuric acid and hydrogen peroxide mixture and the weight of copper in the solution was estimated. The efficiency thus determined is found to increase upto a current density of 2.0 A/$dm^2$and thereafter to decreases in the bath of copper sulphate 0.1 M and EDTA 0.1 M. The decrease in efficiency beyond a current density of 2 A/$dm^2$is attributed to the formation of loose deposits.It is washed off and the adherent portion of the deposit is taken for efficiency calculation. For the determination of direct weight of deposit, loose portion was not dislodged or wiped off completely. Hence the weight is found to increase continuously with current density, but even this increase is not proportional weight of deposit based on the weight obtained at 1 A/dm^2 will be 1.38 mg at 1.5 A/dm ^{2} 1.84 mg for 2 A/dm^2, 2.30 mg for2.5 A/dm ^{2} and 2.76 mg for 3 A/dm ^{2}. But the weight obtained at these current densities are less and the decrease is more at higher current densities. The reason for this is the evolution o f hydrogen at higher current densities, in which a part of the current is wasted in hydrogen evolution. This factor along with non adherent portion with the one obtained in commercial cyanide plating bath, which is of the order of 80 -85 % (Dennis and Such , 2003)

Hydrogen evolution can be accounted from a different angle. For increasing the current density higher applied potential is necessary as shown in all the tables. For example the applied potential is increased from 2.5 V to above 6.0V to achieve the increase in current density from 1 – 3 A/dm ^{2}.This increase in applied potential leads to increase in cathode potential also which is given in the second rows of these tables. For example in Table 2 0.35 V – 0.68 V in Table 3 0.1 V – 0.6 V and Table 4 0.6 V – 2.0 V.The higher applied potential and hence cathode potential exceeds the hydrogen over potential. Hence hydrogen is also covered along with copper deposition, when the applied potential is high. Actually hydrogen bubbles were observed very slightly in the I bath at 2 A/dm ^{2}, when the applied potential is 4.18 V and the cathode potential is 0.40 V.
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The hydrogen evolution is slightly more at 2.5 – 3 A/dm^2 current densities at applied potentials of 5.18 and 6.62 V and cathode potentials of 0.54 – and 0.68 respectively. In the bath II also similar observation has been made. But in bath III a significant increase in cathode potentials from 0.61 – 1. 3 V is occur, when current density was increased from 1.5 - 2.0 A/dm^2. Hydrogen was found to evolve vigorously at this stage, resulting in the black porous deposit at 2.0 A/dm^2. The steep increase in cathode potential shows that the hydrogen over potential is far exceed, so that a considerable quantity of hydrogen gas is evolved. From the platter's point of view hydrogen evolution is the limit of any electro deposition and hence this increase in cathode potential assumes significance.

The results obtained with the other baths containing copper sulphate and EDTA in different ratios are given in table 3 and 4. The deposits obtained from IIand III bath shows a similer trend, i.e. increase in the weight of deposit with increase incurrent densities and increase inefficiency upto 2.0 A/dm^2 and then a decrease. Of the three baths (I,II and III) bath II is better in the sense that very high efficiency of 88% observed at 1.5 A/dm^2 At the same current density the effieiency in the I bath is 80% and bath III is 86 %.The deposit at 3 A/dm^2 from the bath III the copper sulphate concentration is much higher than the other two, giving raise to highly porousdeposits.The appearance of deposit is extremely good from bath II than from the other two baths.Good quality deposits are not obtained from bath III,through some of them were adherent.Bath I gave raise todeposits of acceptable quality, bath II to very shiny,adherent and non porous deposits.Hence bath II found to be the best of the three and is chosen for further study.

Regarding current densities 1.5 – 2.0 A/dm^2 is found to be optim- um range for obtaining deposits of acceptable standards. All the three baths gave a similar observation leadings tothe conclusion that 1.5 – 2.0 A/dm^2 is the optimum current density range. The results of the experiments carried out at a higher temperatures 40 ºC, 50 ºC, involving baths II at different current densities are given in the table 5 and 6. The required current density is achieved at lesser applied potential than required at room temperature.(the first rows of three tables)This is expected because the conductivity of the bath increases with temperature, thereby reducing the Internal Resistance Over Potential (IROP). The energy saved by way of applied potential is spent in hearing the bath, Obviously this is not advantage. Also no other significant improvement is observed by carrying out the electrolysis at higher temperatures. Efficiency valves are also less in baths operated at 40 ºC and 50 ºC. Provisions for heating the bath involve higher investment costs, as well as recurring expenses. It is rather a blessing in disguise that heating is not required. Hence room temperature electrodeposition is advised.

Table 2. Copper deposition at various current densities

Bath: CuSO4 (0.1M) + EDTA (0.1M) **pH = 6**
Temp: Room temperature **Duration = 15minutes with agitation**

0zs	1	1.5	2	2.5	3
Applied Potential (V)	2.5	3.2	4.18	5.18	6.62
Cathode Potential(V)	0.35	0.37	0.4	0.54	0.68
Weight of deposit Direct (Dg)mg	0.92	1.02	1.32	1.42	2.02
Weight of deposit Therotical(Tg)mg	0.45	0.68	0.9	1.12	1.33
Weight of deposit Experimental (Eg)mg	0.34	0.54	0.75	0.86	0.96
Appearance	Uniform, Adherent	Uniform, Adherent	Uniform, Adherent	Black, Porous	Black, Porous
Efficiency %	76	80	83.3	76.6	72.4

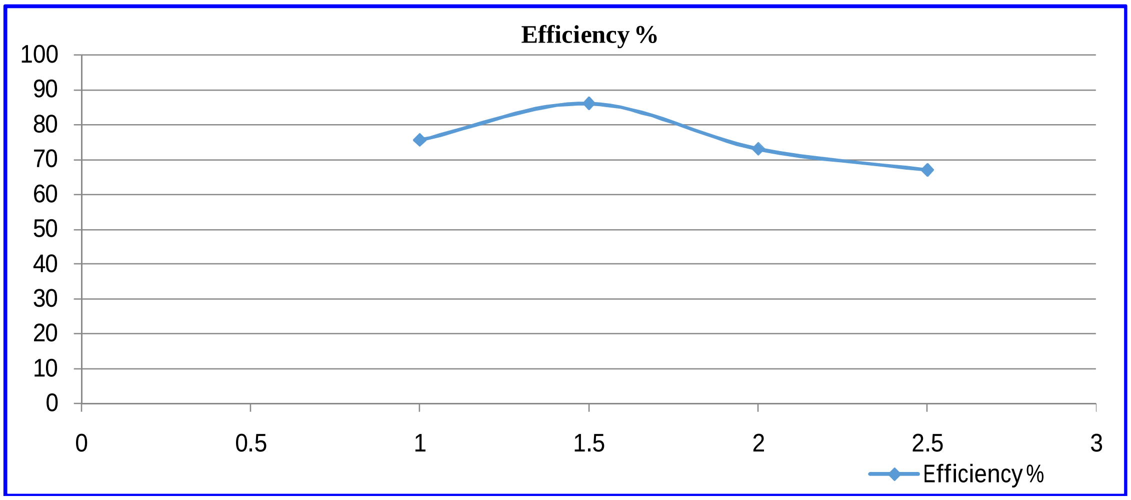

Fig. 2: Current density A/dm^2

Table 3. Copper deposition at various current densities

Bath: CuSO4 (0.2M) + EDTA (0.1M) **pH = 6**

Temp: Room temperature **Duration = 15minutes with agitation**

Current density A/dm^2	**1**	**1.5**	**2**	**2.5**	**3**
Applied Potential (V)	2.5	3.18	4.18	5.12	5.54
Cathode Potential(V)	0.1	0.37	0.4	0.54	0.59
Weight of deposit Direct (Dg)mg	0.72	0.85	95	1.25	2.22
Weight of deposit Therotical(Tg)mg	0.45	0.68	0.9	111	1.33
Weight of deposit Experimental (Eg)mg	0.35	0.59	0.62	0.65	0.68
Appearance	Uniform, Adherent	Uniform, Adherent	Uniform, Adherent	Black, Porous	Black, Porous
Efficiency %	78.71	88	70	58.8	51

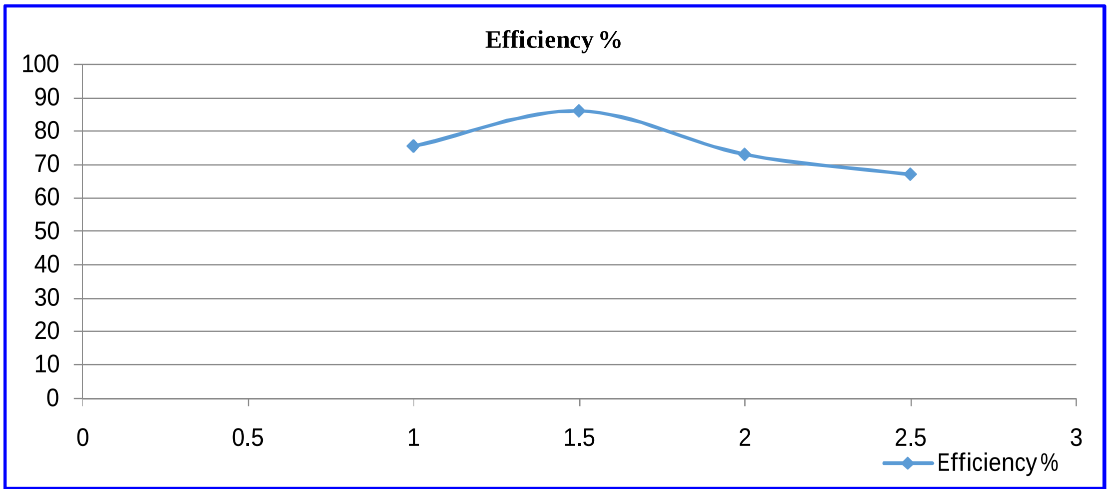

Fig. 3: Current density A/dm^2

Table 4. Copper deposition at various current densities

Bath: CuSO4 (0.3M) + EDTA (0.1M) **pH = 6**

Temp: Room temperature **Duration = 15minutes with agitation**

Current density A/dm^2	**1**	**1.5**	**2**	**2.5**
Applied Potential (V)	2.12	2.48	3.52	3.79
Cathode Potential(V)	0.6	0.61	1.3	1.5
Weight of depositDirect (Dg)mg	1.71	1.82	2.12	2.16
Weight of deposit Therotical(Tg)mg	0.45	0.68	0.89	1.11
Weight of deposit Experimental (Eg)mg	0.34	0.58	0.68	0.75
Appearance	Uniform, Adherent	Uniform, Adherent	Uniform, Adherent	Black, Porous
Efficiency %	75.5	86	73	67

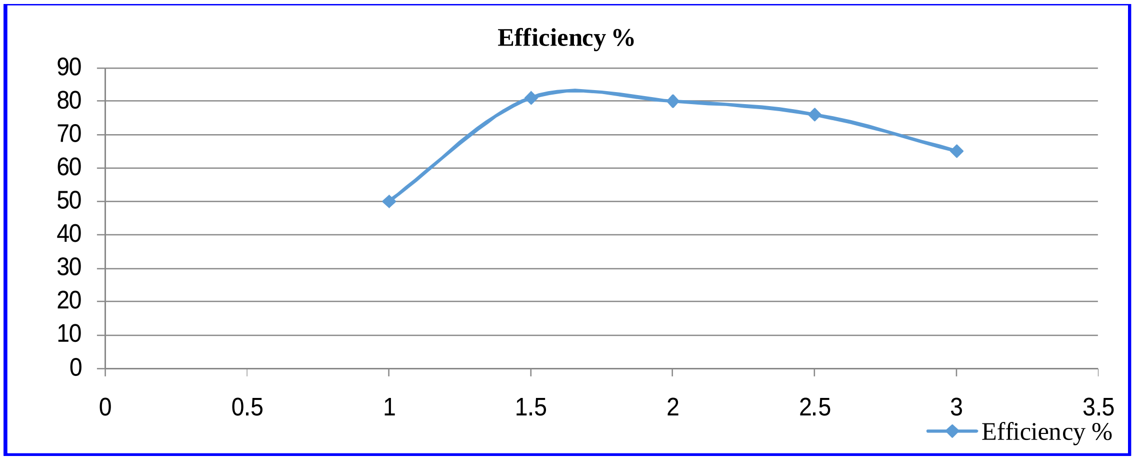

Fig. 4: Current density A/dm^2

Table 5. Copper deposition at various current densities

Bath: CuSO4 (0.2M) + EDTA (0.1M) **pH = 6**

Temp: 40 ^{0}C **Duration = 15minutes with agitation**

Current density A/dm^2	**1**	**1.5**	**2**	**2.5**	**3**
Applied Potential (V)	1.58	1.99	3.2	3.95	4.01
Cathode Potentia(V)	0.35	0.65	0.87	0.96	1.12
Weight of deposit Direct (Dg)mg	1.62	1.82	2.15	2.32	3.82
Weight of deposit Theoretical (Tg)mg	0.45	0.68	0.89	1.11	1.33
Weight of deposit Experimental (Eg)mg	0.3	0.54	0.72	0.85	0.87
Appearance	Uniform Adherent	Uniform Adherent	Uniform Adherent	Black Porous	Black Porous
Efficiency %	50	81	80	76	65

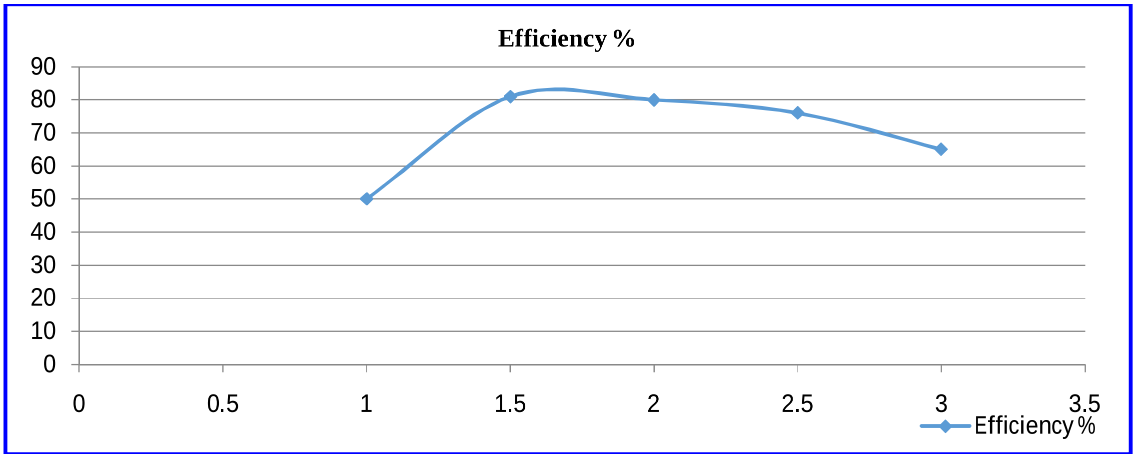

Fig. 5: Current density A/dm^2

Table 6. Copper deposition at various current densities

Bath: CuSO4 (0.2M) + EDTA (0.1M) **pH = 6**

Temp: 50 ^{0}C **Duration = 15minutes with agitation**

Current density A/dm^2	**1**	**1.5**	**2**	**2.5**	**3**
Applied Potentia (V)	1.02	2.17	2.52	3.92	4.2
Cathode Potential(V)	0.33	0.6	0.85	0.94	1,12
Weight of deposit Direct(Dg)mg	1.66	2.32	2.52	2.52	3.32
Weight of deposit Theoretical Tg)mg	0.45	0.68	0.89	1.12	1.33
Weight of deposit Experimental(Eg)mg	0.36	0.58	0.72	0.86	1.01
Appearance	Uniform Adherent	Uniform, Adherent	Uniform Adherent	Black Porous	Black Porous
Efficiency %	77	86	80	77	74

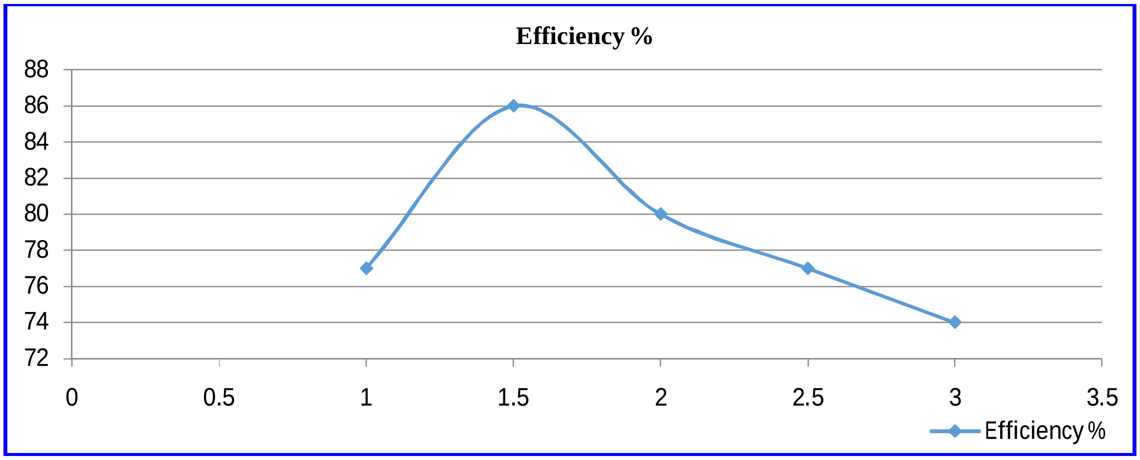

Fig. 6: Current density A/dm^2

5.1 Optimum conditions

The optimized operating conditions are

i) Applied Potential = 3 – 4 V
ii) Current density = 1.5 -2.0 A/dm ^{2}
iii) Agitation = mild
iv)Temperaure = Room Temperature
v)pH = 6

5.2 Cost effectiveness

The comparisonof Cost effectiveness was carried out with Copper – EDTA and Copper Cyanide complex baths.

1.Material Cost on basis of 100 L

Copper cyanide cost around Rs. 2300/= where as Copper sulphate (0.2 M) and EDTA (0.1 M) is Rs. 900/=. The comparison of commercial copper cyanide complex bath consists of cuprocyanide excess of Potassium cyanide and sodium hydroxide.The cost of this readymade salt mixture from a standard company like Growers and Wheel or CMP is around Rs. 860 per kg, so there is considerable reduction in the cost of plating salts.

5.3 Other cost factors

Labour cost can be the same

Cyanide complex bath is operated at 50 -55 C while EDTA bath is operated at room temperature. The cost of heating by way of electrical charges(electrical heating) or conventional direct heating (Fuel cost) will be additional and recurring which is not required in EDTA bath.Since cyanide bath is slowly decoposingreflenishment of cyanide content by way of addition of Potassium cyanide and potassium hydroxide is necessary, whereas no additional is required in EDTA bath. Copper dissolution from the anode almost matches the copper loss by deposition from solution ,and copper concentration doesnot decrease significantly.Over a long period say once in 3 months slight additions may be required, the cost of which is not much.

As per as non recurring cost is concerned the following points are noteworthy.

1.No equipment is necessary for heating since no fumes are evolved, fume exhaust system which is essentisl in cyanide bath is not required here.This eliminates fume dust , exhaust motors etc., which reduces the investment cost considerably.

2.The important and significant factors is, there is no need for effluent treatment plant for cyanide.

The process becomes Eco – friendly.

6. CONCLUSION

The bath of copper sulphate0.2M and EDTA 0.1 M is suitable.

Increase of EDTA and Copper sulphate from the above ratio resulted in unsatisfactory coating.The bath is highly stable which is a primary requite inplatingindustry.The optimum current density range is 1.5 - 2 A/dm^2. The above current density is to be achieved at an applied potential of 3 -4 VThe bath is operated at room temperature .The anode dissolves freely in the bath and hence frequent replenishment of the salt is not necessary which is definite advantage in plating industry.

Continuous stirring is essential. About 6 microns thick coating obtained in 30 minutes.A coating thickness of 1-2 microns is enough for strike, and hence the duration can be reduced considerably.Since the bath is primarily developed as a flash or strike bath no brightener or addition agents is required at this stage. Further building up of copper can be done from the conventional acid and copper sulphatebath.Since the bat offers good quality deposit it can also used in applications where the requirement is about 10 microns thick coating and further coating is not required.Cost wise the bath is highly economical. Last but not the least, the baths and the process are eco friendly.

6.1 Scope for the further work

The process can be scaled up pilot plant level and investigation can be carried out. The possibility of its use for other industrial applications than using it as a mere flash bath can also be explored.

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