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## Electrochemical Deposition Of Nickel From Local Nickel Sulphate Solution On Copper Substrate

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### Abstract

*In this work, nickel was deposited on copper substrate through electrodeposition which was abstracted from local sulphate salt. Nickel deposition on copper substrate was done in both presence of vitamin C and saccharin additive. Boric oxide was used as buffering agent and pH of the solution bath was maintained through sulfuric acid and ammonium hydroxide. Round shape deposition on copper substrate was observed in the presence of vitamin C, while columnar shape particles were observed in the presence of saccharin additive. Deposition of nickel was done through sulfate bath on copper substrate. Boric acid was used as buffering agent and direct current electrolysis were conducted throughout this experimental work. PH of the solution was kept constant with the help of diluted sulfuric acid and ammonium hydroxide. The deposited nickel particles were obtained in round shape in the presence of vitamin "C" additive, while columnar shape particles obtained in saccharin additive. The experimental conditions were optimizing to get smooth, adherent, and acid resistance surface. This research work reported that, rate of sulfate bath deposition increases lineally with increase in temperature and PH of the solution.*

**Keywords:** Electrical Deposition, Current density, pH, Nickel, Sulfate bath, Copper substrate.

### 1. Introduction:

Electro-deposition is a surface coating method, where deposition of cathode occurs by immersing both cathode and anode into an electrolytic bath [1]. Electro-deposition is one of the technologically and economically route to produce metal alloy and composite materials [2]. Electrodeposited coating increases the resistance to corrosion and it produces metal-base composite with specific properties [3]. It is widely used in micro devices electroplating as thin films and three-dimensional thick structures

due to its superior properties such as high corrosion resistance; wear resistance, thermal, magnetic and optical characteristics [4] which is widely used in applications such as printed-wiring boards, connectors, and magnetic recording heads [5]. Electro-deposition offers great advantages over other techniques such as physical and chemical vapor deposition, mostly due to simple operating conditions [6]. With the trend toward miniaturization, electro-deposition has established itself as the manufacturing technology of choice [7].

Electro-deposition as a fabrication technology in the

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electronic industry is quite advantageous due to its cost effectiveness, easy maintenance and quality deposits [8]. A wide range of composite films has been used for a variety of applications by tailoring the composition of films via electro-deposition [9].

Market demand of nickel matrix composites is increasing tremendously because of its novel application in aerospace and defense sectors [10]. Naturally, nickel is strong and threatening metal which resists cutting erosion and corrosion phenomenon [11]. Electroplated nickel is a promising material to realize movable structures for micro-electromechanical systems (MEMS) [12]. Since the process of electro-deposition is greatly influenced by the nature of electrolyte, concentration of ions, pH, bath temperature, degree of agitation, substrate and counter electrode geometry and material of construction, current density, mode of deposition (DC versus pulse plating), and presence of additives in the electrolyte [13].

The work presented here has looked into the electrical deposition of nickel through sulfate bath on copper substrate. Nickel deposition was investigated at different experimental conditions to produce uniform physical and chemical properties.

## 2. Experimental set-up:

A conventional two-electrode set-up was employed for the deposition of nickel from sulfate bath in Pyrex glassware as shown in Figure 1. Before each experiment, all the glass wares were first washed by

commercial detergent solution followed by dipping in distilled water and then soaking in 0.1 M nitric acid for 5 minutes [14]. Finally, the glass wares were thoroughly rinsed with nano-pure water. Copper sheets of desired area were used as working electrodes. A nickel sheet with an area of  $4\text{ cm}^2$  was used as soluble counter electrode. Before the electrodeposition, working electrode was first polished with sand paper and then washed with commercial detergent and water, immersed in dilute  $\text{HNO}_3$  solution for a few minutes. Finally, the electrode was degreased with acetone. An adhesive tape was used to cover all the substrate except the area on which deposition of film was desired. The anode was chemically cleaned by 1 M  $\text{HNO}_3$  solutions and then rinsed by double distilled water before deposition. The open end of the nickel rod was out of the solution and connected with the positive (+) terminal of the DC power supply.

## 3. Preparation of Cell Assembly:

In this work, 250 mL Pyrex beaker was used as plating container. Negative terminal of DC power source was connected to the working electrode and positive terminal was connected to counter electrode. The distance between the cathode and anode was fixed at 1.5 cm. Plating solution's pH was adjusted using  $\text{NH}_4\text{OH}$  or  $\text{H}_2\text{SO}_4$  solution and recorded with pH meter which was calibrated with two buffers solution. First one was at pH 2.10 (0.05 M  $\text{HCl}$  + 0.09 M  $\text{KCl}$ ) and second one was at pH 11.72 (0.01 M  $\text{Na}_3\text{PO}_4$ ).

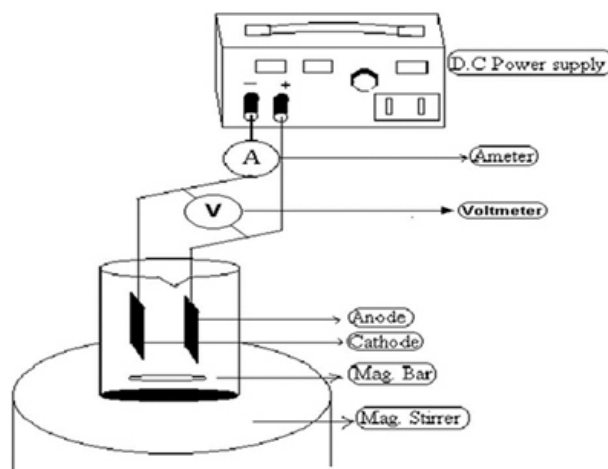


Figure 1: Schematics of nickel electrolytic cell for nickel plating.

Each of the plating solution was poured in the beaker. All electrochemical deposition was performed by DC plating and was carried out using galvanostatic technique. The cathode was weight by digital balance before deposition, when deposition was finished; cathode was carefully removed from the solution. Cathode was then rinsed by deionized water and acetone to get rid of the acidic bath solution residue. Finally, cathode deposited mass was obtained through balance (Model: Model 8460, Manufacturing: Mettler Toledo). The net mass of the film was calculated from the mass difference before and after deposition. To prevent anode and cathode polarization and improve coverage, the plating solution was agitated to maintain optimum placement of the nickel deposit. Inadequate levels of

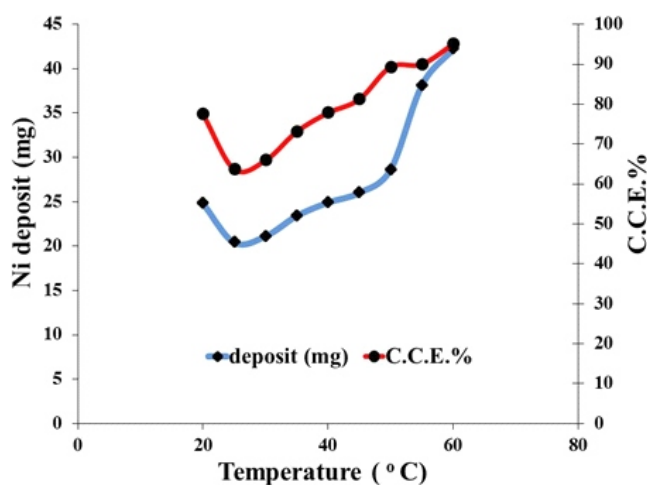
agitation can result in dull, burnt, pitted and streaky deposit.

For temperature control, an ordinary thermostat capable of controlling temperature within  $\pm 0.1$  °C was mounted in the beaker. All the electrochemical deposition was performed at different temperatures.

#### 4. Results and discussion:

##### 4.1 Effect of temperature:

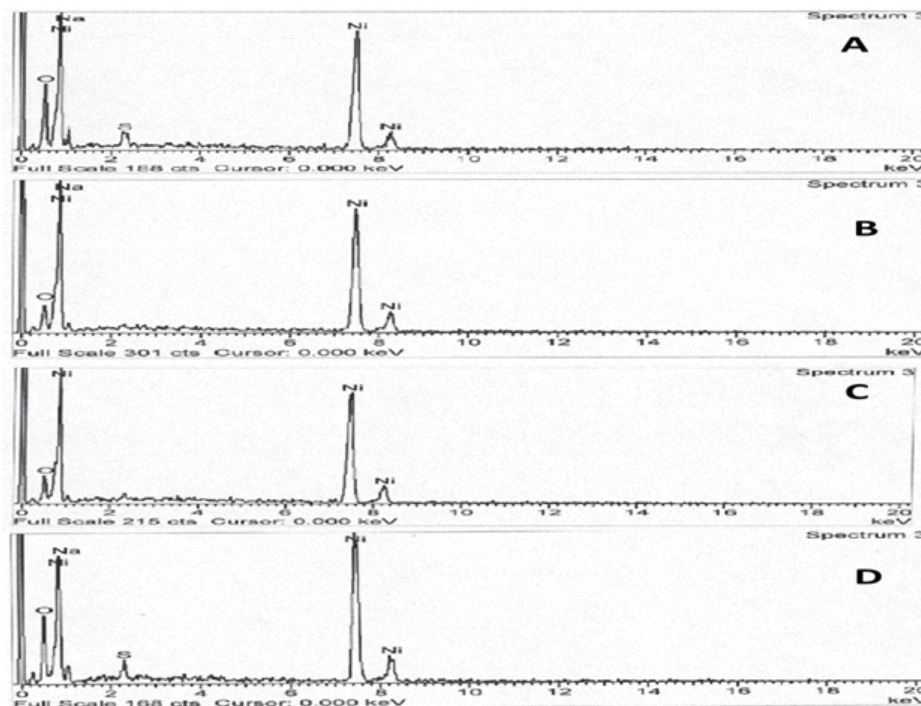
Electrodeposited coating on copper substrate from salt bath was carried out in 0.1 M boric acid as buffer solution containing 0.1 M vitamin “C” and 3.5 g/L saccharin as an organic additives using DC method. Electric current was passed for 30 minutes which changes the quantity of the deposited Ni with change in temperature as shown in Figure 2.



**Figure 2:** Effect of temperature on nickel deposition in presence of vitamin C Additive.

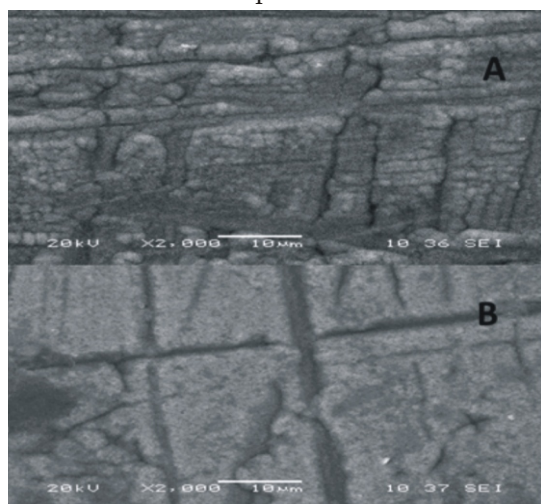
It clearly shows that there was no deposition of nickel at 15 °C under the experimental conditions employed. Furthermore, nickel deposition almost remained constant from 20 to 40 °C. It was observed that the deposit nickel was smooth and grayish in the range of 20 °C, where at 40 °C the deposit was smooth along with adherent and silver shiny small black spots on edges. However, there is a gradual increase in electro-deposition of nickel with increase in temperature up to 60 °C. In addition, the coating thickness and cathode efficiency simultaneously increased. This may be attributed to increase in hydrogen evolution at the cathode surface. The cathodic current efficiency (C.C.E) increased with an increase in temperature, which led to enhance nickel deposition. In the presence of saccharin additive, the nickel deposition occurs at 15 °C as compared to vitamin “C” additive where

there is no deposition occur at 15 °C. We limited the study of nickel deposition to the temperature range 20–60 °C in order to avoid the loss of volatile components of the bath [15]. Luke et al, [16] reported that increase in temperature would enhance the concentration of metal ions in the cathodic diffusion layer due to an increased diffusion rate at high temperature. Figure 4, shows that the grain size increases with an increase in temperature. The velocity of metal ions also increases with an increase in temperature due to decrease in the viscosity of the electrolyte. Figure 3, shows elemental analyses done by EDX at different temperatures, which reveals that at 15 °C and 50 °C the deposited nickel contains oxygen and sulphur impurities while no impurities were detected at 25 and 40 °C. The maximum composition of nickel deposit is 91 % at 40 °C.



**Figure 3:** EDX analyses of nickel deposit on copper substrate at (a) 15 °C (b) 25 °C (c) 40 °C, and (d) 50 °C.

Surface morphology of the deposited film at different temperatures at a potential of 2.5 V is shown in Figure 4. The surface morphology of the film at 25 °C showed compact uniform packed layered deposition due to which the deposited film is smooth, adherent and acid resistant. At 25 °C small cracks were observed while at 40 °C large cracks were observed in the deposited film.

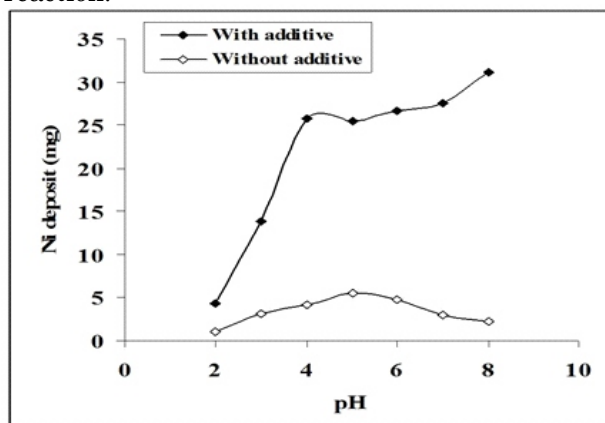


**Figure 4:** Scanning electron micrograph (X 2000) of nickel film in presence of Saccharin additive by DC method at (a) 25 °C and (b) 40 °C.

#### 4.2. Effect of pH

Effect of pH on the deposition of nickel was studied

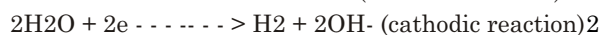
in pH range of 2 to 8. Dilute solution of sulphuric acid and NaOH were used to control the pH of bath solution. Effect of solution's pH on nickel deposition in presence and absence of vitamin "C" additive is shown in Figure 5. Results showed that the nickel electro-deposition from sulfate bath increases with an increase in solution pH. Namely, in the absence of additive, the rate of nickel deposition increased from 3.1 to 5.5 mg in the pH range of 2-5. Above pH 5, linear decreased in the amount of nickel deposition was observed due to metal hydroxide ( $\text{Ni}(\text{OH})_2$ ). At pH 1, negligible amount of nickel deposition occurred due to hydrogen evolution reaction.



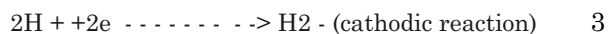
**Figure 5:** Effect of pH on nickel deposition in presence and absence of vitamin "C" Additive.



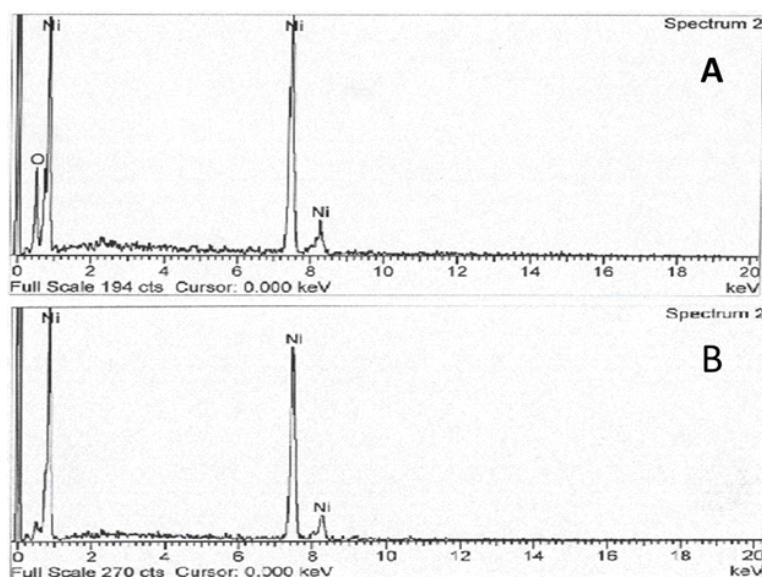
Equations 1-3 summarize the electric deposition [17].



At the surface of electrode, level of pH tends to increase which results in an insoluble formation of nickel species that blocks the electrode surface and prevents further deposition of nickel on the substrate.



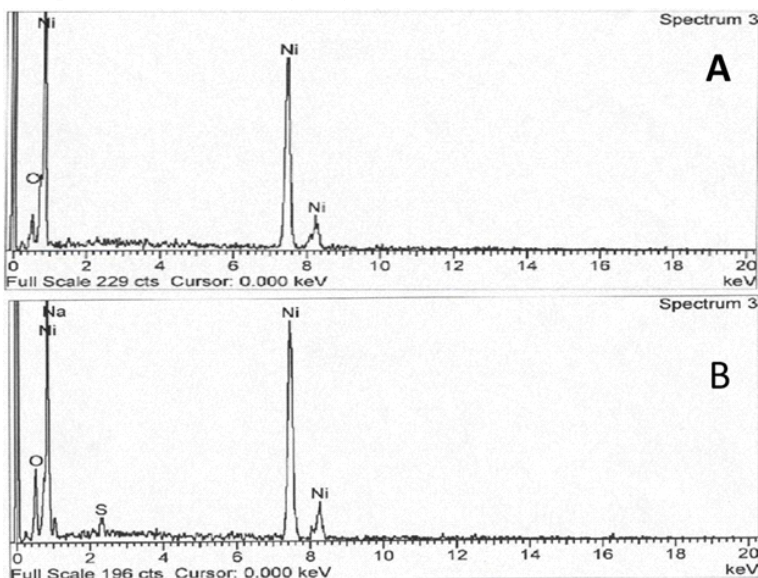
Hydrogen evolution reaction also results in low cathodic current efficiency and lack of deposit uniformity and increased surface roughness due to gas bubbles which blocked the electrode surface. The EDX analyses of the nickel deposits in the presence of vitamin C and saccharin additives are shown in Figures 6 and Figure 7, respectively. In presence of vitamin C additive at pH 3 and pH 5, the elemental composition of nickel is 86 and 100%, respectively.



**Figure 6:** EDX analyses of nickel deposit in vitamin C additive at (a) pH 3 and (b) pH 5.

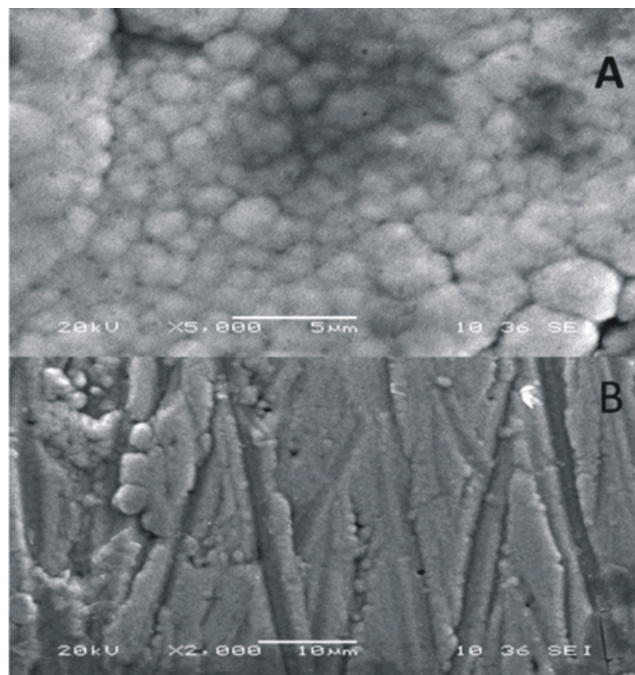
In saccharin additive, the percent composition of nickel at pH 3 and pH 5 is found to be 93 and 80% respectively. The low composition of nickel (80%)

from saccharin additive may be assigned to contamination of nickel deposits.



**Figure 7:** EDX analyses of nickel deposit in saccharin additive at (a) pH 3, b) pH 5.

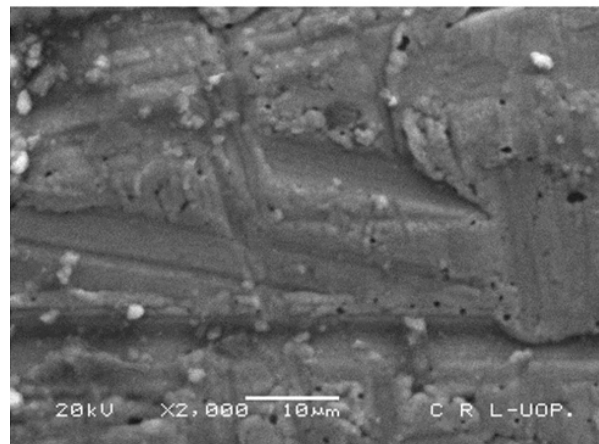
EDX analysis of nickel deposit in saccharin additive at pH 3 and pH 5 is shown in Figure 7. Deposition of nickel is accompanied by sulphur at pH 5 in the presence of saccharin additive. From EDX analysis it is clear that vitamin C performs relatively better than saccharin additive. SEM micrographs in Figure 8 A, show nickel deposition from sulfate bath in the presence of vitamin C and additive at pH 5. The particles of nickel deposits are in ball shape, smaller size and regular pattern at pH 5, while in the presence of saccharin additive (Figure 8 B) show that deposited nickel are in columnar particle shape. The uncovered spherical spots only correspond to hydrogen bubbles which attached to the electrode surface (Figure 8 B). In presence of saccharin additive, columnar particles are obtained. The uncovered spherical spots corresponding to hydrogen bubbles attached to the electrode surface are observed at pH: 5.



**Figure 8:** Scanning electron micrograph) of nickel film in presence of (a) Vitamin C and (b) saccharin additive, pH: 5.

SEM analysis was also carried out for copper substrate after nickel deposition as shown in Figure 9. It was observed that substrate was comparatively smooth after Ni deposition. From experimental results, it is concluded that rate of nickel deposition in the presence of vitamin “C” is almost five times

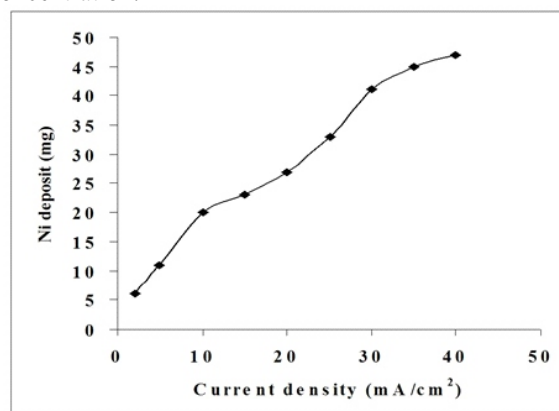
more than absence of additive. Comparative studies indicate that appearance of nickel deposits from sulfate bath in the presence of additive is relatively better than in the absence of additive.



**Figure 9:** Scanning electron micrograph (X2, 000) of copper substrate.

#### 4.3. Effect of cathodic current density

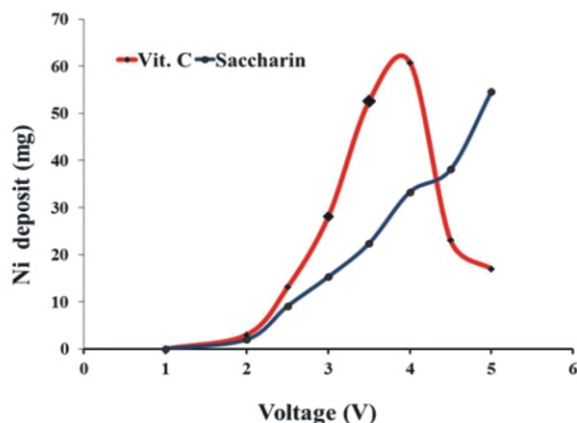
This work also focused on effect of cathodic current density on nickel deposition as shown in Figure 10. It was clearly observed that the rate of nickel deposition increases linearly with increase in current density. Deposits obtained at lower current density is very small and non-adherent, while at higher current density the deposited films are neither adherent nor acid resistance. At high current density, the temperature of the bath increases and reached to the boiling temperature. For this reason high current density is avoided for deposition. The deposits were obtained from the range of 10 to 12 mA/cm<sup>2</sup> adhere on the surface and resist acid. C. Larson et al., [18] found that current density increase the rate of deposition. Overall nickel deposits efficiency decreases with an increase in current density, which can be interpreted as a relative decrease in the nickel ion concentration.



**Figure 10:** Effect of current density on nickel deposition from sulfate bath.

#### 4.4. Effect of voltage

Optimization of voltage for effective deposition of nickel deposition from sulfate bath in the presence of vitamin C and saccharin additives was carried out at constant pH 3 and temperature of 30 °C with deposition time of 30 minutes. Figure 11, shows that the rates of nickel deposition from sulfate bath increase in the presence of saccharin additives with an increase in voltage. Nickel deposition was smooth, silver shiny, adherent and acid resistant in the range of 2.5 V to 4 V. Above and below this range of voltage, coating quality is deteriorated slowly. Figure 11, shows the rate increase of nickel deposition in the presence of vitamin C additive up to 4 V and linearly decrease in deposition quality above this voltage. It was also noticed that nickel deposits are in silver shiny, adherent and acid resistant at 2.5 V. Rashwan et al., [19] reported that deposition have linear relation with increasing voltage. However, nickel deposits are lousy, powdery and can be easily removed by cotton swab at high voltage. Therefore, in both cases of low and high voltage may be avoided for the formation of uniform protective deposit of nickel from sulfate bath on the copper substrate.

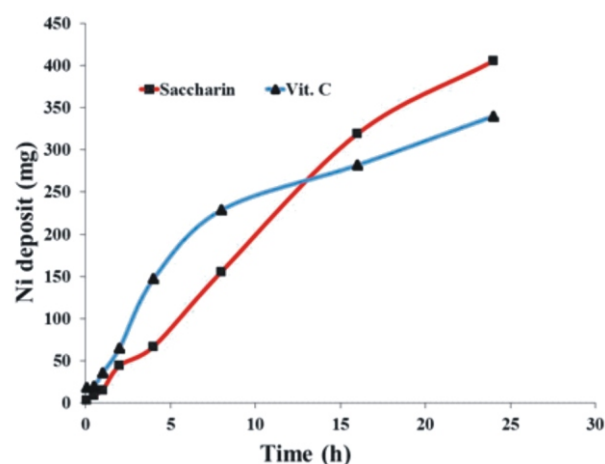


**Figure 11:** Effect of voltage on nickel deposition in saccharin and vitamin C additive.

#### 4.5. Effect of Time:

Figure 12 show the effect of time on nickel deposition from sulfate bath in the presence of vitamin C and saccharin additive at fixed voltage of 2.5 V, pH 3.08 and temperature of 30 °C. It was observed that coating thickness increases with an increase in deposition time. Deposition rate of nickel from sulfate on copper substrate increases

linearly with time for both additives. Nickel deposition quality in the presence of vitamin C is relatively greater than saccharin additive but saccharin additive deposition is shinier, adherent and acid resistant. Krishna et al., [20], reported that deposition thickness increase linearly with time. No significant changes occur in cathodic current density with time, while cathodic efficiency is found to be decreased gradually with time due to small consumption of current in the discharge of hydrogen ions from water. Similarly, with the passage of time hydroxyl ions may be discharged in preference to the dissolution of  $\text{Ni}^{2+}$  and oxygen is evolved. Results show that coating deposition time is increased to enhance coating thickness with aim to superior surface quality.



**Figure 12:** Effect of time on nickel deposition from sulfate bath in presence of saccharin and vitamin C additive.

#### 5. Conclusion:

It was concluded that electro-deposition of nickel from sulfate bath on copper substrate is multi factors dependent technique. Deposition rate of nickel from sulfate on copper substrate increased linearly with an increase in temperature and pH. It was also observed that the quality of deposit deteriorated above 40 °C due to  $\text{Ni}(\text{OH})_2$  formation. At high cathodic current density, the rate of nickel deposition increased linearly while current efficiency decreased with an increase in the current density. The optimized voltage was recorded in the range of 2.5 V to 3.5 V. The decreased in the current efficiency was observed with time and rate of deposition, while no significant changes occurred in



cathodic current density with the passage of time. Deposit obtained in the range of 10 to 12 mA/cm<sup>2</sup> were adhere and acidic resistant in nature.

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