Effect of Organic Additives and Current Efficiency on Electrodeposition of Nickel from Sulfate Bath

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Abstract

The properties of nickel metal electrodeposited in presence of organic additives in various concentrations were studied with respect to current efficiency of the bath. Films were electrodeposited in various pH and temperatures, for different durations in order to get high current collection efficiency (CCE) and uniform deposition. Locally available salt of sulfate was preferably used as source of nickel. Sodium sulfate was used to improve the conductivity of the bath. The optimum concentration of nickel sulfate was found to be 0.5 M/50 ml and that of sodium sulfate was 0.5 M/ 10 ml. It was observed that the rate of deposition linearly increases with the increase in concentration of the sodium sulfate in the electrolytic bath. Further, it was observed that the rate of deposition and current efficiency increases with the increase in pH up to pH 6 and above this pH both the rate of deposition and current efficiency decreases due to the formation of nickel hydroxide in the electrolytic bath. Nickel chloride was primarily added to the bath not only to increase the corrosion of the anode but also to enhance the uniformity of the deposited layer. Surface structure analyses were carried out using scanning electron microscopy (SEM). Elemental analyses were performed using energy dispersive x-rays (EDX). Reasons for variation in properties and structural characteristics of metal deposit are discussed.

***Keywords:** Nickel Chloride, SEM, EDX*

1. Introduction:

Electro-deposzition is the process by which an applied current is used to deposit a film of metal or alloy by the reduction of metallic ions on to a conductive substrate [1]. It is a simple, inexpensive, accurate and rapid technique to produce dense metallic nanocrystal [2]. Nano crystalline films have attracted much attention because of their unique properties that arise from effects of size reduction and large amount of interfaces [3-5]. These unique chemical and electrical properties, which give, rise to their potential use in the fields of nonlinear optics, luminescence, electronics, catalysis, solar energy conversion, and optoelectronics, as well as other areas [4]. Dimensions of the particle size affect physical properties of the materials. Several methods like sputtering, laser ablation, inert gas condensation, severe plastic deformation, electro less deposition and electrodeposition etc are used to prepare these films [5]. Electroplated nickel has found widespread applications as decorative as well as functionally suitable metal coatings [6]. Numerous studies have shown that the physico-mechanical properties of

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nickel coatings depend strongly on the deposition parameters and bath composition [7]. Recently new buffer components, mainly organic acids have been extensively studied because they offer higher buffer capacity than the boric acid does [8]. Several studies [8-10] show Nickel depositions with respect to current collection efficiency (CCE) and structural characteristics. In all these studies, sulfate, chloride or sulfamate baths were used. To prepared high quality micrometer thick films (smooth and bright deposit) at a reasonable high deposition rate, plating baths with a high concentration of metallic ions and small amount of organic additives must be used [10]. In the absence of these additives, even in concentrated metallic-ion-containing solutions and under surface reaction control could derive the interface to an unstable growth regime. In this case branched and low adherent deposits are formed [11]. Further, It has been reported [12] that Structural properties of electro-deposits are controlled using current density during DC plating or applying a periodically changing current signal. DC method is used to achieve Nano-scale grain sizes compared to periodically changing current method. These nanostructured materials have recently attracted great attention due to the improvement produced specially in the mechanical response (e.g., wear resistance) of the films [12-14].

The purpose of the present investigation is to evaluate the effect of temperature, pH and time on the electrodeposition characteristics of nickel from acidic sulfate solution in relation to CCE and deposit morphology using DC method.

2. Experimental procedure:

2.1 Reagents:

A conventional two-electrode set-up was employed for the deposition of nickel from sulfate bath. The electrolyte solution consisted of $NiSO_4.6H_2O$ (nickel sulfate hexahydrate, 0.1 M), as an electro active specie and H_3BO_3 (boric acid, 0.4 M) as buffering agent. $NiCl_4. 6H_2O$ (nickel chloride hexahydrate, 15g/L) was added to the bath in order to reduce the polarization and prevent passivation of anode. The effects of several bath additives were studied. Saccharin additive was used in nickel electroplating as sodium saccharin salt ($NaC_7H_4NO_3S$) at a concentration of 0.5-4.0 g/L [12].

2.2 Preparation of cell assembly:

A 250ml Pyrex beaker was used as a plating container. The working electrode was connected with negative terminal and the counter electrode was connected with positive terminal of the DC power supply. The cathode and anode were fixed in position. The inter electrode distance was 1.5 cm.

Each of the plating solution was placed in beaker (bath). The pH was adjusted with dilute NH_4OH solution or H_2SO_4 solution. The pH of the bath was measured with a pH meter. Prior to that, pH meter was calibrated with two buffers, i.e. first one at pH 2.10 (0.05 M HCl + 0.09M KCl) and second one at pH (0.01M Na_3PO_4). The control parameters were temperature, cathodic current density, pH, voltage, stirring rate, amount of primary metal ions, electrode potential and plating time. As the substance deposited in this work were magnetic in nature, very effective stirring was achieved by magnetic bar. For optimization of temperature, an ordinaryz thermostat capable of controlling temperature within $0.1^{\circ}C$ was used. After each of the plating the specimen was taken out, rinsed with distilled water followed by conductive water and air-dried. The deposit was stored for further analysis. All electrochemical deposition was performed by DC plating. All depositions were carried out using galvanostat. All the electrochemical depositions were perform at different temperature. In the galvanostatic technique, the current is controlled while potential between the working electrode and counter electrode is measured as a function of time. The potential is a dependent variable, which is recorded using a suitable recording system. The cathode was weight by a balance before deposition, when the deposition finished; cathode was carefully removed from the solution. The cathode was then rinsed by deionize water and acetone to get rid of the acidic bath solution residue. An electric balance obtained the mass of the cathode after deposition. The net mass of the film was calculated from the mass difference before and after deposition.

2.3 Hydrogen evolution and cathode efficiency:

The discharge of nickel ions is not the only reaction that can occur at the cathode, a small percentage of current is consumed in discharge of hydrogen ions from water. This reduces the cathode efficiency for Ni deposition from 100 percent to 92 to 97 percent depending on the nature of the electrolyte. The discharge hydrogen ions form bubbles of hydrogen gas at the cathode surface. In a plating operation, it is expected that the entire current passed to be utilized for electroplating. If a fraction of the current is used for any other reaction (including heating of bath) it is a waste. In the present case, the cathode efficiency was calculated by using following formula, cathode efficiency is defined as the percentage of the total current usefully employed for the cathodic deposition of the metal [13].

$$\text{Cathodic current efficiency} = W_1 / W_2 \text{ X } 100 \qquad (1)$$

.Where

W_1 : weight of metal actually deposited.

W_2: weight of metal theoretically calculated from the quantity of electricity passed.

Weights of metal actually deposited (W_1) were calculated by using following formula;

$$W_1 \quad = \quad X_1 - X_2$$

Where

X_1: weight of the sample before deposition.

X_2: weight of the sample after deposition.

Weight of metal was calculated theoretically by using following formula,

$$W_2 \quad = \text{ I x t x A } / \text{ 96500 x Z}$$

Where

I: current passed in ampere.

t: time for plating in seconds.

A: atomic weight of coated metals.

z: valence of the metal to be coated.z

3. Results and discussion:

During the course of investigation, we used watts bath for electrodeposition of nickel on the copper electrode. The basic constituents used for a watts nickel-plating solution include, nickel sulfate (131.43g/L) as the primary source of nickel ions and nickel chloride (20 to 30 g/L) as a secondary source of nickel ions. Solution of nickel chloride is also used to improve anode corrosion. Boric acid (24g/L) is used to stabilize the pH of the solution, enhances the whiteness of deposit and improves the performance of leveling agent. Nickel sulfate and nickel chloride are nonvolatile, highly conductive and soluble in water. The broadest range of operating conditions for the nickel-plating solution from sulfate bath was a temperature range of 20 to 60 °C, a pH range of 2 to 6, a current density range from 60 to 300 mA/cm^2 and mechanical agitation of 100 to 300 rpm. The plating solution is agitated to maintain optimum placement of the nickel deposit, prevent anode or cathode polarization effects and improve coverage. Inadequate levels of agitation can result in dull, burnt, pitted and streaky deposit.

3.1 Effect of sodium sulfate and nickel sulfate:

The effect of sodium sulfate and nickel sulfate on quality of deposited nickel from an optimized electrolytic bath containing organic additive with 0.1 M boric acid as buffers was studied using DC method. The primary effect of sodium sulfate is to improve the conductivity of the bath. The results are shown in Table 1 and 2.

Table 1: Effect of sodium sulfate on nickel deposition. 0.5M NiSO$_4$, 0.5M Na$_2$SO$_4$, 0.4M H$_3$BO$_3$, 0.1M vitamin C, pH 3, time 15 min, inter electrode distance 1.5cm, stirring rate 100 rpm, and cathodic current density 8 mA/cm^2.

0.5M Na$_2$SO$_4$.10H$_2$O (mL)	Ni deposit (mg)	C.C.E. (%)
2	3.5	64.8
4	7.4	67.2
6	15.9	75.7
8	18.0	78.2
10	28.0	87.5
15	40.0	97.5

Table 2: Effect of nickel sulfate on nickel deposition.

0.5M $NiSO_4$, 0.5M Na_2SO_4, 0.4M H_3BO_3, 0.1M vitamin C, pH 3, time 15 min, inter electrode distance 1.5cm, stirring rate 100 rpm, cathodic current density 8 mA/cm^2.

0.5M $NiSO_4.6H_2O$ (ml)	Ni deposit (mg)	Appearance of deposit
20	15.3	Black gray, smooth deposit.
30	17.4	Yellowish gray smooth deposit.
40	19.1	Gray, dull silver color deposit.
50	22.9	Smooth, silver shiny deposit.
60	27.7	Silver color slightly brown deposit.
70	40.5	Silver color smooth, slightly pitted.

It is evident that there is an increase in the deposition rate with increase in amount of sodium sulfate in the bath. There results are consistent with earlier published results by Horkan *et al.* [15]. At low concentration of sodium sulfate, the deposits are found to be loose and non-adherent, i.e. can be removed easily just by washing the electrode. However, it is observed that at very high concentration the deposits are also non-adherent, loose and powdery in nature. Sodium sulfate is used to liberate hydrogen gas bubbles from the cathode surface [16]. This is useful because hydrogen pitting can be controlled by vigorous agitation. The optimum concentration of sodium sulfate is noted to be 0.5 M in 10 ml solution of electrolytic bath, where the deposits of nickel are smooth, shiny and adherent. The concentration of nickel sulfate has a remarkable effect on the electrodeposition of nickel on the cathode surface. As is evident from the Table 1 and 2. The current efficiency is found to increases with the concentration of nickel ions and decrease with increasing current density. Similar results are reported elsewhere [17]. The electrodeposition of nickel is found to be yellowish in color when the concentration of nickel sulfate is lower in the bath. Whereas, at high concentration of nickel the deposit obtained are silver white indicating more deposition of nickel. The rate of nickel deposition increases when concentration of nickel is increased in the electrolytic solution in the intermediate range from 0.5 M /30 ml to 0.5 M /50 ml. Further increase of the nickel concentration is insignificant because high nickel concentration in the deposit leads to change the physical and mechanical properties of the deposit material. Consequently, the optimum amount of 0.5 M nickel sulfate is 50 ml. The deposited films obtained at this concentration of nickel from the electrolytic bath are more acid resistant as compared to other deposits.

3.2 Effect of nickel chloride:

The concentration effect of nickel chloride on the electrodeposition of nickel was studied. During the course of electrodeposition oxygen comes from water molecule and oxidizes on the anode surface blocking the anode for further nickel dissolution, hence after an experiment the low deposition of nickel is observed. To maintain the nickel concentration, 0.1 M nickel chloride is added to the electrolytic bath. Nickel chloride primarily increases anode corrosion, conductivity and uniformity of coating thickness distribution. The chloride forms a complex with nickel, which might otherwise have formed a passive film [18]. From the Table 3 it is seen that the final pH of the electrolyte is lower at low concentration of nickel chloride. In the presence of nickel chloride the process of nickel deposition is followed by the proton reduction. It can be concluded that the kinetic effect observed at the beginning of deposition is attributed to the slow reaction step (1). This is rate determining step the second electron transfer is then faster.

Table 3: Effect of nickel chloride on nickel deposition.

0.5M NiSO$_4$,   0.5M Na$_2$SO$_4$, 0.4M H$_3$BO$_3$, 0.1M vitamin C, voltage 2.5V, cathodic current density 7.4mA / cm^2, stirring rate 100 rpm.

0.1M NiCl$_2$ (ml)	Ni deposit (mg)	Initial pH	Final pH
10	4.5	3.00	2.30
15	8.6	3.00	2.30
20	13.4	3.00	2.80
25	15.0	3.00	3.04
30	17.3	3.00	3.40

It can be concluded that the kinetic effect observed at the beginning of deposition is attributed to the slow reaction step (1). This is rate determining step the second electron transfer is then faster.

Ni + H$^+$ + e$^-$ Ni-H$_{ads}$ (1)

2Ni - H$_{ads}$ 2Ni + H$_2$ (2)

Ni - H$_{ads}$ + H$^+$ + e$^-$ Ni + H$_2$ (3)

Table 3 also shows that when the concentration of nickel chloride is increased the final pH of the electrolyte slightly increases because at high concentration the hydrogen evolution reaction takes place at the cathode and reactions 1-4 occur simultaneously [19]. The optimum concentration of nickel chloride is 20 to 30 g/L in the solution to promote anode corrosion.

Ni^{2+} + Cl$^-$ NiCl$^+$ (4)

NiCl$^+$ NiCl$^+_{ads}$ (5)

NiCl$^+_{ads}$ +   e$^-$ NiCl$_{ads}$ (6)

NiCl$_{ads}$ +   e$^-$ Ni + Cl$^-$ (7)

3.3 Effect of time and temperature on nickel deposition and cathodic current efficiency:

The effect of both the time and temperature on the rate of nickel deposition and cathodic current efficiency from sulfate bath containing vitamin C as an additive, operating at an output voltage of 2.5v, at pH 3 was undertaken in this study. Experimental results are shown in Figure 1. The data shows that the rate of deposition increases and the current efficiency decreases with increasing time. This may
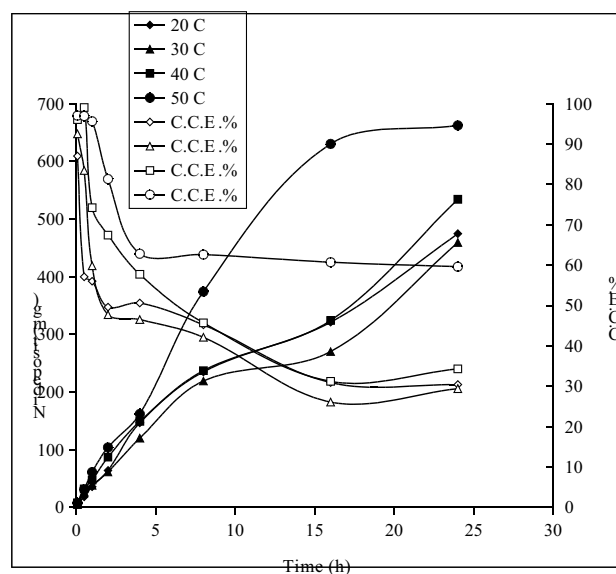
Figure 1: Effect of time and temperature on nickel deposition and current efficiency.

Be attributed to the fact that with increasing deposition time the concentration of hydrogen molecule increases which form bubbles on cathode surface and reduces its efficiency [20]. It contradicts the result reported by Yin and Lin [21] where the current efficiency remains constant and the coating thickness increases with increase in time. The different results may be due to the different experimental conditions. The data also shows that the current collection efficiency (CCE) increases with increase in temperature because the conductivity of ionic solution increases and there is adequate supply of ions to the cathode at higher temperatures [22].

3.4 Effect of pH and temperature on nickel deposition and current efficiency:

Effect of pH at different temperatures on current efficiency was studied during nickel deposition from sulfate bath in presence of vitamin C additive, by DC method. It was observed that the rate of deposition and current efficiency increases with increase in pH up to pH 6 and above this pH both the rate of deposition and current efficiency decreases due to the formation of nickel hydroxide in the electrolytic bath at high pH value. The effect of temperature shown in Figure 2 indicates that the current efficiency and deposition rate increases linearly when the temperature is raised from 20 to 60°C. This is because of increase in conductivity with temperature. However, the electrodeposition of nickel at temperature higher than 60°C was not studied due to evolution of volatile components and increase resistivity of the metal ions. The efficiency of the bath at the above mentioned pH and temperature is found in the range of 32 to 65%. The deposits obtained at pH 3 and 4 at 30 and 40°C are smooth, adherent, silver color and acid resistant as compared to other deposits.
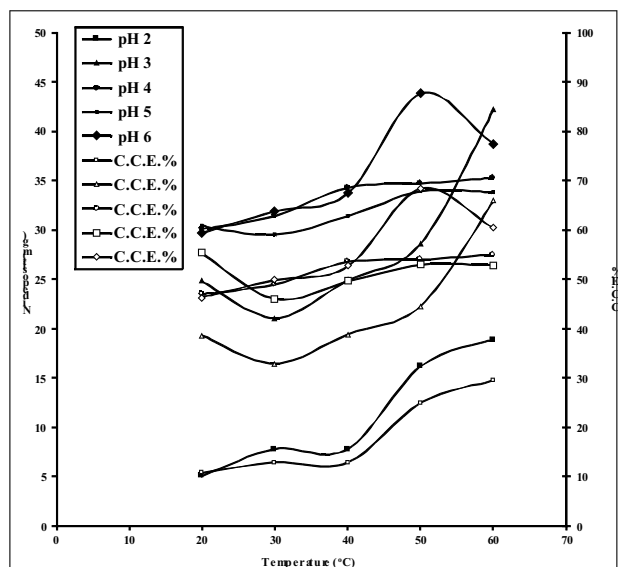

Figure 2: Effect of pH and temperature on nickel deposition and current efficiency.

3.5 Effect of temperature on nickel deposition at different concentrations of NiSO$_4$:

The influence of temperature on nickel deposition from different concentrations of nickel sulfate bath is given in Figure 3. From the Figure it is seen that temperature behaves differently on nickel deposition at different concentrations of nickel sulfate. However, the temperature effect becomes more significant on the bath of nickel deposition when the nickel concentration is increased from 0.001 to 0.5M. Moreover, it is pertinent to mention here that the rate of deposition substantially increases when the initial concentration of nickel is increased. From the Figure 4, it is also clear that the current efficiency increases with increase in temperature and concentration of the electrolyte. Similar findings were represented elsewhere [22].
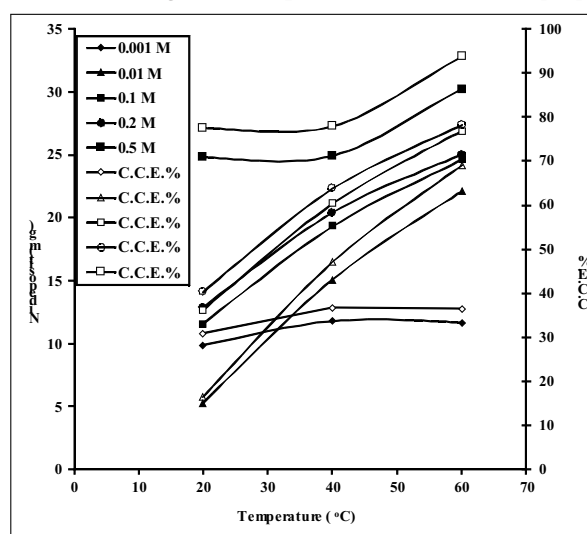

Figure 3: Effect of temperature on nickel deposition at different concentrations of NiSO4.
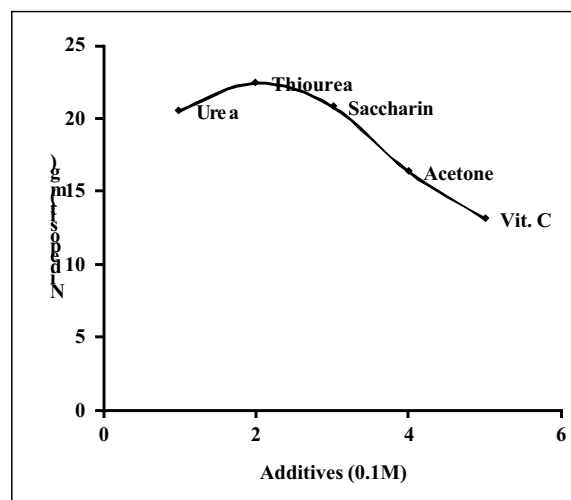

Figure 4: Effect of organic additives on nickel deposition from sulfate bath.

3.6 Effect of organic additives and saccharin concentration on nickel deposition:

Organic additives are often used in electroplating operations to moderate deposit growth rates and control film quality. It is often assumed that additives act by preferentially adsorbing on to asperities on the cathode surface, thereby blocking the attachment of metal ions at those sites and favoring growth at other locations. It is also known that organic additives display a polishing and leveling effect by increasing the density of nuclei in the deposited layer. The organic surfactants, therefore, reduce roughness and as a consequence avoid electrolyte and solid particle entrapment in the deposited metal [23]. In this work different kinds of organic additives were used to obtain the electrodeposited films by DC method from sulfate bath. The effects of different additives on characteristics of nickel deposition are shown in Tables and Figures 4, 5.

Table 4: Effect of organic additives on nickel deposition from sulfate bath.

0.5M $NiSO_4$, 0.5M Na_2SO_4, 0.4M H_3BO_3, pH 3, time 30 min, cathodic current density 8 mA/cm^2, inter

Additive (0.1M)	Ni deposit (mg)	Appearance
Urea	20.5	Smooth, shiny silver color deposit.
Thiourea	22.4	Blackish rough, deposition.
Saccharin	20.8	Adherent, smooth, shiny silver color deposit.
Acetone	16.3	Yellowish silver deposit on one side.
Vitamin C	13.1	Smooth, yellowish silver color deposit.

Table 5: *Effect of saccharin concentration on nickel deposition from sulfate bath.*

0.5M $NiSO_4$, 0.5M Na_2SO_4, 0.4M H_3BO_3, pH 3, time 30 min, cathodic current density 8 mA/ cm^2, inter electrode distance 1.5 cm, stirring rate 100 rpm, temp. 30 °C.

Saccharin concentration (g/L)	Ni deposit (mg)	Appearance
0.5	11.7	Silver color deposit on both side rough on edges.
1.0	15.1	Smooth, silver color deposit on front side.
1.5	13.8	Yellowish silver color, smooth deposit rough on edges.
2.0	15.6	Smooth, yellowish silver color deposit on one side.
2.5	15.1	Silver shiny, smooth deposit on one side.
3.0	13.1	Silver color non-uniform deposit on one side.
3.5	15.3	Silver shiny, smooth deposit.
4.0	13.9	Rough, yellowish silver color deposit. Small blackish spots on one edge.

The deposits obtained from saccharin and vitamin C additive baths are adherent, smooth, silver shiny while the one obtained from urea, thiourea, and acetone are yellowish rough. It is observed that vitamin C is playing an important role in changing the characteristics of the deposits, such as hardness, porosity and ductility of the deposited film. As discussed in earlier section, in the absence of vitamin C the deposited film is not uniform and is blackish dull in color. Effect of saccharin on nickel deposition is strongly dependent on the concentration of the additive. As shown in Figure 5 that changing concentration of saccharin additive do not has a significant effect on the rate of deposition, however it affect the surface morphology of the deposited nickel (Table 5).
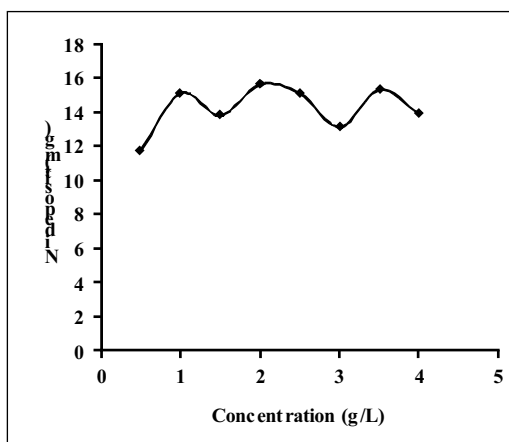

Figure 5: Effect of concentration of saccharin on nickel deposition from sulfate bath.

The deposits obtained at lower concentration from 0.5 to 3.5g /L are more uniform and adherent as compared to higher concentration.

The percent composition of the deposited nickel changes under different additives. Figure 6 show that the deposited layer contains 82, 94, 95 and 91% of nickel in the presence of urea, acetone, saccharin and vitamin C additives respectively. The deposits do not contain any other impurities. Surface morphology of the deposited nickel shows uniform growth of columnar crystals in the presence of vitamin C as compared to deposits in presence of
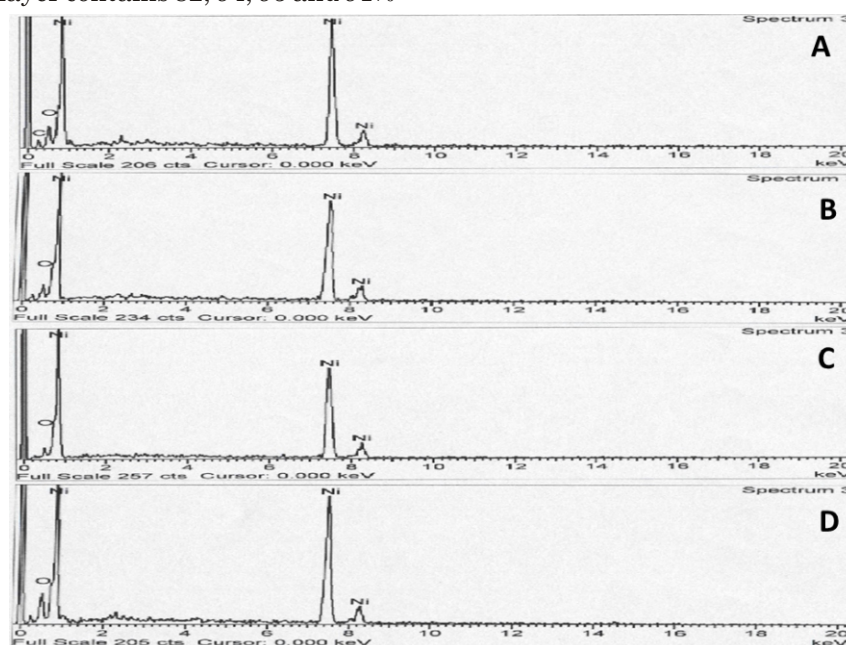

Figure 6: EDX analyses of nickel deposit at different additive a) urea, b) acetone, c) saccharin, d) vitamin C.
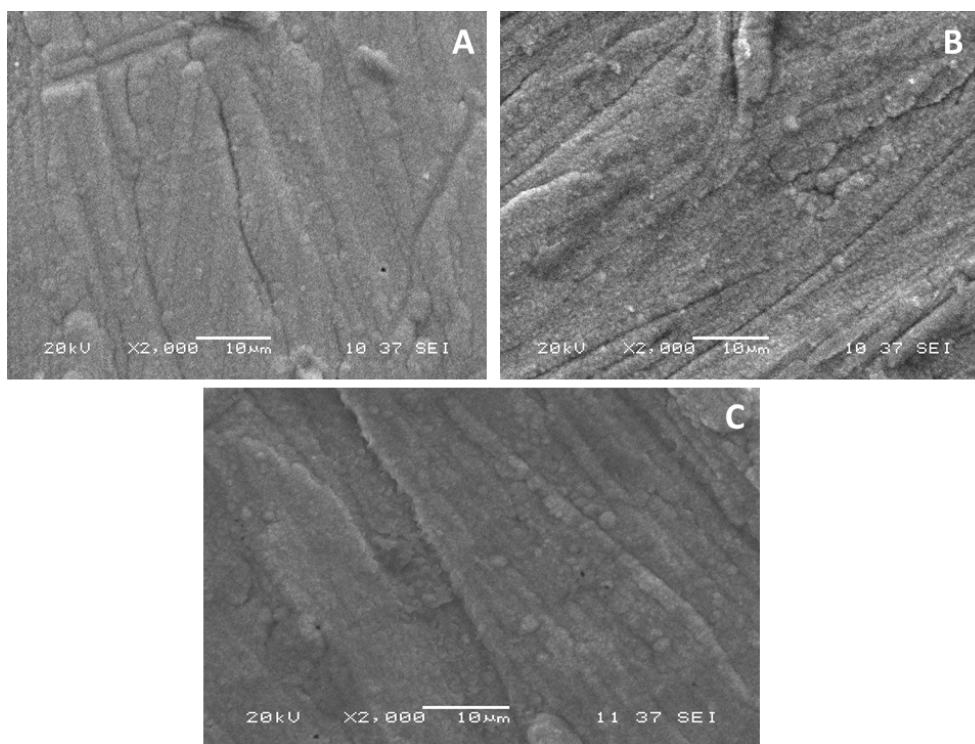
Figure 7: Scanning electron micrograph   (X2,000) of nickel   deposited in presence of a) urea, b) acetone and c) vitamin C as an organic additive.

4. Conclusion:

The optimum concentration of nickel sulfate is found to be 0.5 M/50 ml and that of sodium sulfate is 0.5 M/ 10 ml. The nickel ion concentration is maintained by the addition of 0.1 M nickel chloride in the electrolytic bath. The rate of deposition increases with the increase of time while the current efficiency decreases with the increase in time. It is observed that the rate of deposition and current efficiency increases with the increase in pH up to pH 6 and above this pH both the rate of deposition and current efficiency decreases due to the formation of nickel hydroxide in the electrolytic bath.

Saccharin and vitamin C are found to be good additives as compared to urea and acetone.

Changing concentration of saccharin additive has no effect on the quantity of nickel deposited. However, the characteristics of deposit change with changing concentration in the sulfate bath. The maximum concentration of saccharin is found to be 3.5g/L.

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