

**CHAPTER - III**

**ELECTRODEPOSITION  
OF  
NICKEL**

## CHAPTER III

### ELECTRODEPOSITION OF NICKEL

#### 3.1 INTRODUCTION AND REVIEW OF EARLIER WORK

Nickel is the most important metal applied by plating in terms of not only of the tonnage of metal consumed but also of the wide diversity of its uses( 8, 9), with respect both to the many basis metals covered and to the numerous types of articles plated. Nickel deposition is also important because it illustrates and involves many of the important factors in electrodeposition such as high cathode polarisation, stressed deposits, pH control, fitting and the effect of addition agents . Intensive study of nickel plating is therefore useful not only directly but also because it throws lights on many other problems of plating (10, 11). Again because of favourable mechanical properties , nickel deposits are also used for electroforming of printing plates, phonograph record, stamper tubes, screens and many other articles (12, 13).

Electrodeposition of nickel has been known from ancient times . Adams (14) in 1869 was probably the first to do nickel plating on truly commercial basis. He used double salt , baths including both sulphate and chloride. Upto 1913 , many bath composition were proposed (15). Since then the rate of development has been quite rapid . High speed plating began by Watts with his famous Watts bath (16).

For bright nickel plating number of brightners were used by different workers (17 to 22).

Thus striking effects produced by small concentration of brightners indicate there adsorption on growth sites , on points and edges of crystals, locations and possibly preferentially on certain crystal faces producing an inhibiting effect on the most active growing sites (22 to 24). Different baths like nickel flouboraste bath (25, 26), nickel sulphament bath (27, 28) alkaline nickel bath (29) and many others (30 to 34) have been tried by different workers to obtain satisfactory deposits. Other organic and inorganic additives were also successfully tried by number of worker from different baths (35 to 39).

Inversigation of properties and structure of nickel deposits has also been carried out during electrodeposition of nickel (40 to 45).

The review of the earlier work clearly shows that there is a a lot of scope for electrodeposition of nickel from some new bath. The bath is ammonical acetate bath. It is non - poisonous simple to prepare and dilute.

### **3.2 ELECTRODEPOSITION OF NICKEL FROM AMMONICAL ACETATE BATH:**

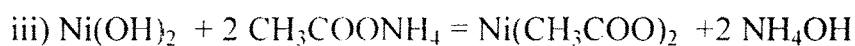
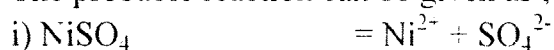
The bath solution is prepared by slowly adding requisite quantity of 25 % ammonia solution to a desired quantity of 30 % freshly prepared NiSO<sub>4</sub> till the colour changes from dark bluish green to pale green. Then to this solution requisite quantity of 60% ammonium acetate is added till blue colour is obtained. The whole solution is then diluted to 100 ml and is used for eletrodeposition work.

Influence of various factors such as conc. of NiSO<sub>4</sub>, ammonium acetate, pH and temperature of the bath is then studied in greater details to arrive at the optimum condition for the production of satisfactory deposits of nickel.

### **3.3 A PROBABLE MECHANISM OF ELECTRODEPOSITION OF NICKEL FROM AMMONICAL ACETATE BATH :**

Here in the formation of bath solution ammonia acts as a precipitating agent while ammonium acetate acts as a complexing agent.

The probable reaction can be given as ,

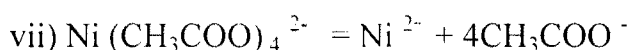


It appears from the values of the stability constants that the complexes of Nickel formed in this bath are  $\text{Ni}(\text{CH}_3\text{COO})_3$  and  $\text{Ni}(\text{CH}_3\text{COO})_3^{2-}$ .

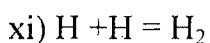
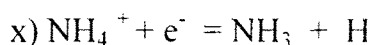
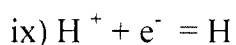
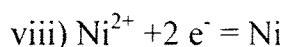
However because of the uncertainty of the nature of the complexes and their subsequent stability constants we are led to assume the possibility of these complexes and to depend in the data available with us.

The formation of complex is further there confirmed by the polarisation study.

The complex formed may slightly be dissociated as ,



During electrodeposition following electrochemical reactions might occurs at the cathode



The reactions x & xi might bring about a deminution in the yield of the metal product.

Therefore it become obvious, that if a very high efficiency is desired the reaction viii only should occur in preference to reactions ix , x & xi .

### **3.4 INFLUENCE OF VARIOUS CONTROLLING PARAMETERS ON C.C.E. AND CHARACTER OF DEPOSITS**

#### **1. INFLUENCE OF CONCENTRATION OF NICKEL SULPHATE**

(TABLE 3.1, GRAPH 3.1)

Concentration of  $\text{NiSO}_4$  is varied from 1 to 6 % of the bath solution. Concentration higher than 6 % could not be tried due to restricted solubility of nickel hydroxide in ammonium acetate solution. Usually higher concentration of the metal salt are used in commercial plating and then it is difficult to extract the metal content from waste solutions. Here this difficulty is overcome by using dilute solution. Again from this dilute bath, equally effective, good quality deposits are produced, apart from cost consideration.

Our results indicate that at low conc. of  $\text{NiSO}_4$  black- white deposits are obtained.

With increasing conc. of  $\text{NiSO}_4$  the quality of deposits gets improved considerably. However at higher conc. of  $\text{NiSO}_4$  (6% ) the deposits are bright but non adherent.

Further observations indicate that percentage CCE also goes on increasing up to maximum (83.27%), which is optimum condition and then it gradually decreases.

Hence with increase in the concentration of nickel sulphate from 1% to 6%, the nature of deposits improved considerably but the deposits are non-adherent at higher concentrations of nickel sulphate.

Considering quality and quantity (C.C.E %) of deposits, 2% nickel sulphate is selected as optimum condition for further studies.

#### **2. INFLUENCE OF CONC.OF AMMONIAM ACETATE :**

(TABLE 3.2, GRAPH 3.2)

Ammonium Acetate is introduced in the bath as a complexing agent concentration is varied from 3 to 33 % of the bath solution. It is observed that when the conc. of Ammonium Acetate is 6% there is no deposition of nickel. The solution is also turbid. It indicates that such concentration of ammonium acetate is insufficient for the formation of complex. However at 9 % the bath solution remains

**TABLE NO. 3.1 INFLUENCES OF NICKEL SULPHATE  
CONCENTRATION**

**OPERATING CONDITIONS :**

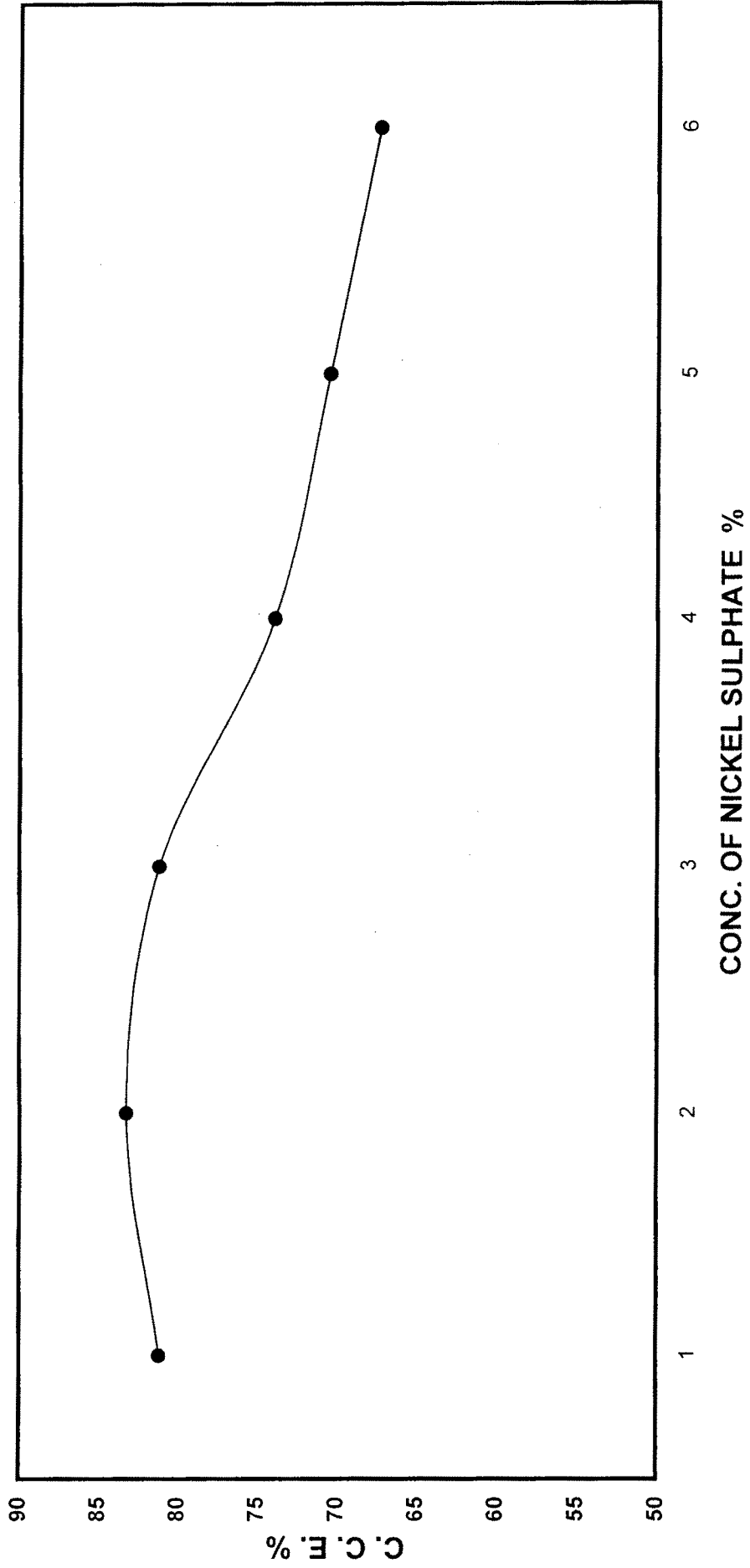
- 1) Ammonia – (25%) Requisite amount
- 2) Ammonium acetate – Requisite amount
- 3) Total Volume – 100 ml
- 4)  $p^H$  of bath Solution – 7
- 5) Temperature – 25<sup>0</sup>C
- 6) Current density – 1.00 A/Sq. dm.
- 7) Inter electrode distance – 2 cm
- 8) Duration of electrolysis – 20 minutes

| Obs. No. | Conc. of Nickel Sulphate % | Wt. of Nickel deposited gms | Wt. of Copper deposited in Coulometer gms. | CCE % | Nature of deposit  |
|----------|----------------------------|-----------------------------|--|-------|--|
| 1        | 1                          | 0.030                       | 0.040                                      | 81.19 | Adherent, dull, black-white .                                |
| 2        | 2 *                        | 0.030                       | 0.039                                      | 83.27 | Uniform, adherent, white, throwing power increases .         |
| 3        | 3                          | 0.030                       | 0.040                                      | 81.19 | Uniform, adherent white.                                     |
| 4        | 4                          | 0.028                       | 0.041                                      | 73.94 | Uniform, adherent brightness improves considerably decreases |
| 5        | 5                          | 0.028                       | 0.043                                      | 70.49 | Bright but slightly non-adherent .                           |
| 6        | 6                          | 0.028                       | 0.045                                      | 67.36 | Bright but non-adherent at edges .                           |

- **OPTIMUM CONDITION.**

INFLUENCE OF NICKEL SULPHATE CONCENTRATION

GRAPH NO.3.1



clear throughout electrolysis and there is considerable improvement in the nature of deposit. At very high concentration of ammonium acetate, white & dull deposits are obtained. Percentage CCE also decreases with increase in the concentration of Ammonium Acetate. It may be due the increase in the cathodic polarisation which may be explained later in chapter IV. From the observations 9% of Ammonium Acetate is taken as optimum, as it gives satisfactory deposit, good %CCE and in addition gives stability to the plating bath.

### 3. Influence of pH

#### (TABLE 3.3, GRAPH 3.3)

The  $p^H$  of the bath solution is adjusted to the desired value by addition of ammonia or by acetic acid solution. Here these two reagents are selected because either addition of small amounts of ammonia or acetic acid in the bath solution does not interfere the composition of the bath solution.

pH of the bath solution is then varied from 6 to 8. It is observed that  $p^H$  has a very conspicuous effect on the nature of the deposit. The deposit obtained at 6 (acidic) as well as at 9 (basic), are not satisfactory. However those obtained at 7 (neutral) are quite satisfactory. Hence the bath may be termed as neutral bath.

Percentage CCE is low at lower pH. At low pH,  $H^+$  ion concentration in the bath and hence at cathode is comparatively large, as a result metal ion concentration is less near the cathode. Hence non adherent deposits are obtained and %C.C.E. is also low. However with increase in pH,  $H^+$  ion concentration in bath and hence in the vicinity of cathode decreases. Thus metal ion concentration increases and quality as well as quantity of deposits increases to considerable extent. At higher pH, however percentage CCE decreases to a considerable extent. This may be attributed to the fact that at such pH excess of  $NH_4^+$  ions are present in the solution. Hence there is evolution of ammonia gas near the cathode which lowers the percentage CCE. Hence 7 is taken as an optimum  $p^H$  for future work.



**TABLE NO. 3.2 INFLUENCES OF AMMONIUM ACETATE CONCENTRATION**

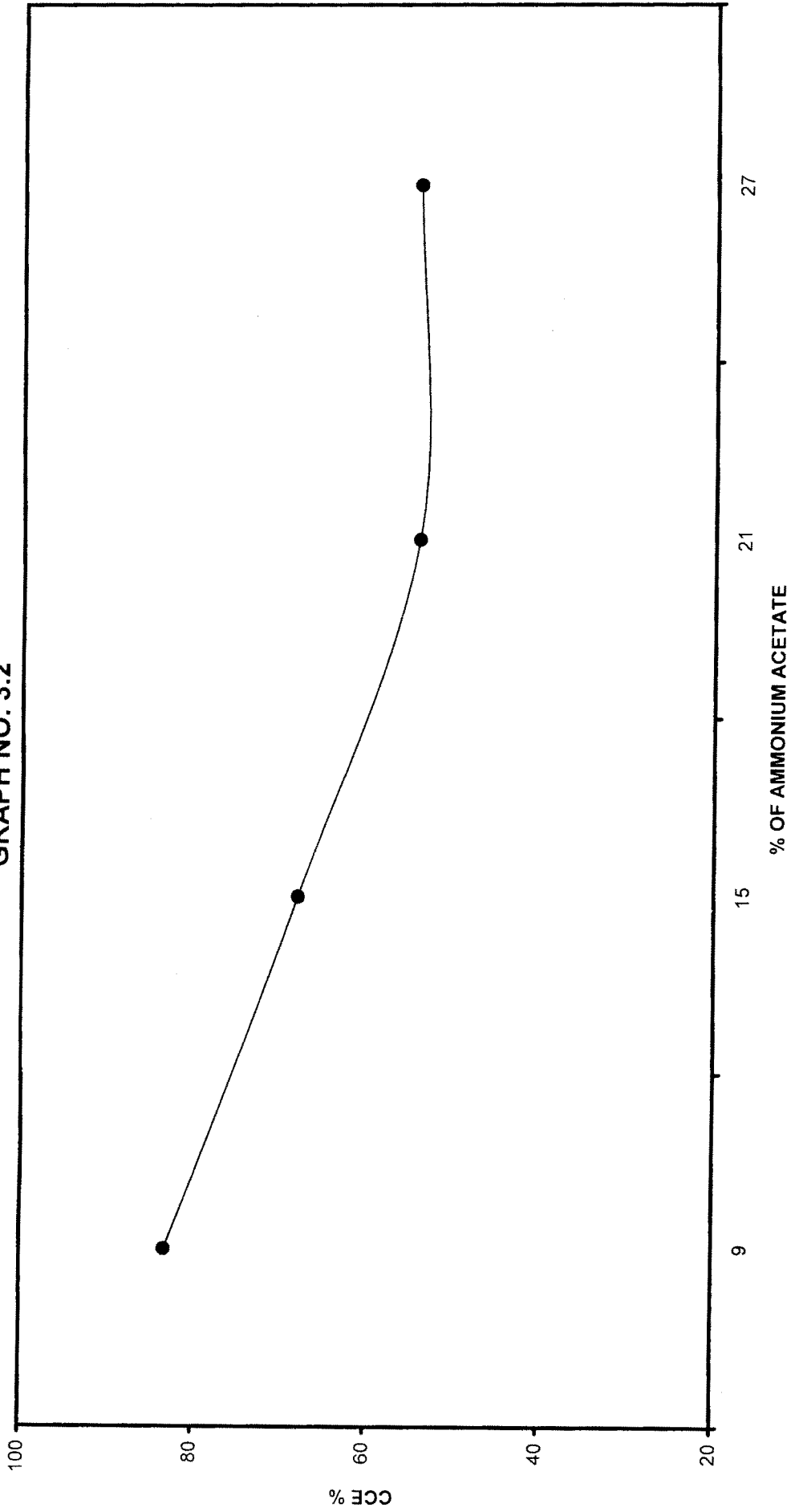
**OPERATING CONDITIONS :**

- 1) Nickel Sulphate – 2%
- 2) Ammonia – (25%) Requisite amount
- 3) Total Volume – 100 ml
- 4) pH of bath Solution – 7
- 5) Temperature – 25<sup>0</sup>C
- 6) Current density – 1.00 A/Sq. dm.
- 7) Inter electrode distance – 2 cm
- 8) Duration of electrolysis – 20 minutes

| Obs .<br>No. | Conc. of<br>Ammonium<br>Acetate<br>% | Wt. of<br>Nickel<br>deposited<br>gms | Wt. of Copper<br>deposited in<br>Coulometer<br>gms. | CCE<br>% | Nature of deposit                         |
|--------------|--------------------------------------|--------------------------------------|---|----------|---|
| 1            | 6                                    | -                                    | -   | -        | Solution is turbid<br>no deposition       |
| 2            | 9 *                                  | 0.030                                | 0.039   | 83.27    | Uniform ,adherent<br>white.               |
| 3            | 15                                   | 0.027                                | 0.043   | 67.97    | Uniform<br>,brightness<br>improves slowly |
| 4            | 21                                   | 0.021                                | 0.042   | 54.13    | Adherent-white,<br>dull at edges          |
| 5            | 27                                   | 0.020                                | 0.040   | 54.13    | White, slightly<br>non-adherent.          |
| 6            | 33                                   | --                                   | --  | --       | No deposition                             |

\* OPTIMUM CONDITION.

INFLUENCE OF AMMONIUM ACETATE CONCENTRATION  
GRAPH NO. 3.2



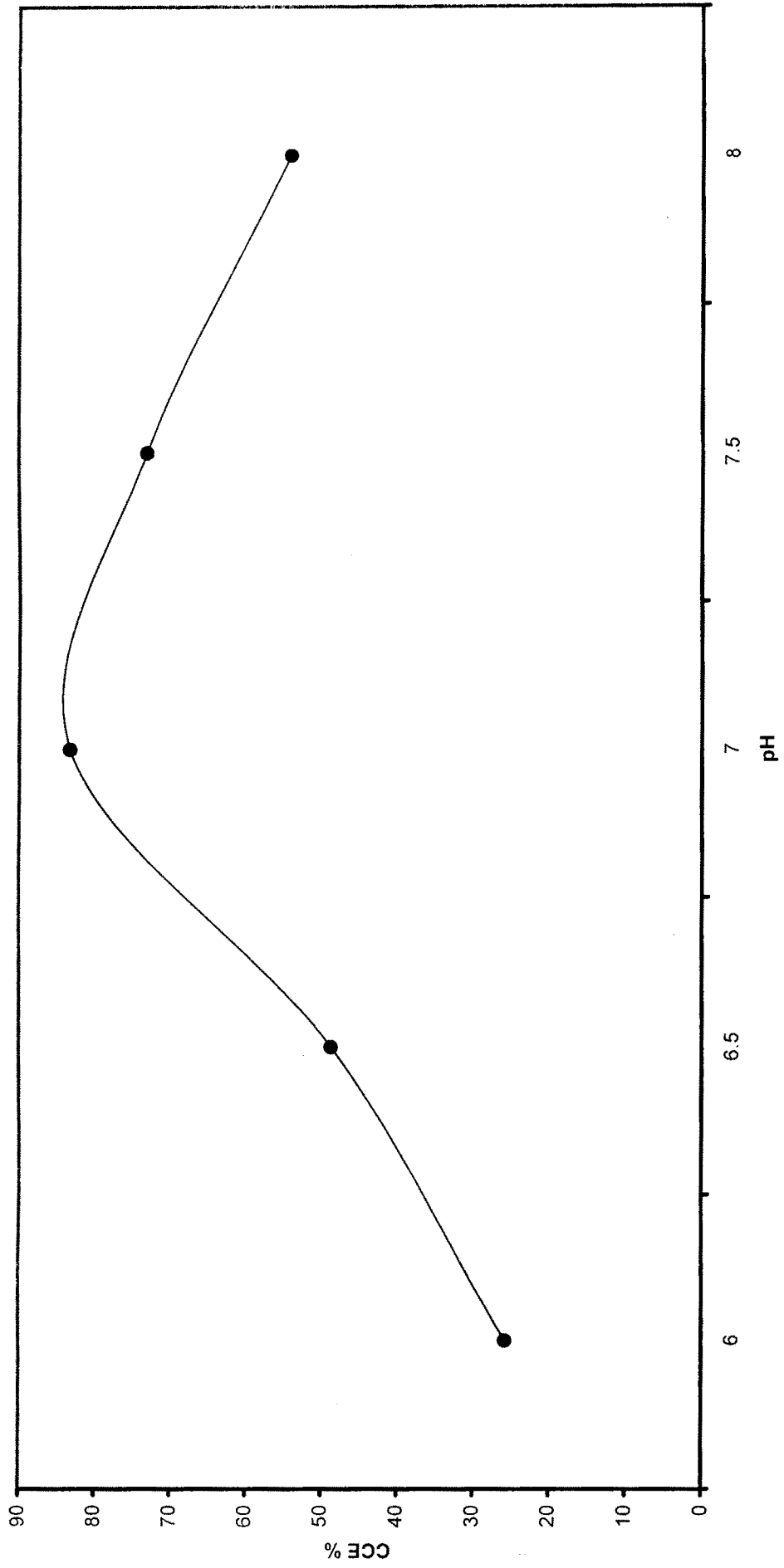
**TABLE NO. 3.3 INFLUENCES OF pH OF THE BATH SOLUTION****OPERATING CONDITIONS :**

- 1) Nickel Sulphate – 2%
- 2) Ammonia – (25%) Requisite amount
- 3) Ammonium acetate – 9%
- 4) Total Volume – 100 ml
- 5) Temperature – 25<sup>0</sup>C
- 6) Current density – 1.00 A/Sq. dm.
- 7) Inter electrode distance – 2 cm
- 8) Duration of electrolysis – 20 minutes

| Obs. No. | p <sup>H</sup> | Wt. of Nickel deposited gms | Wt. of Copper deposited in Coulometer gms. | CCE % | Nature of deposit                               |
|----------|----------------|-----------------------------|--|-------|---|
| 1        | 6.0            | 0.010                       | 0.042                                      | 25.77 | Non-adherent, black rough                       |
| 2        | 6.5            | 0.018                       | 0.040                                      | 48.70 | Black – white, uniform                          |
| 3        | 7.0 *          | 0.030                       | 0.039                                      | 83.27 | Uniform, brightness improves, adherent          |
| 4        | 7.5            | 0.027                       | 0.040                                      | 73.07 | Bright , adherent                               |
| 5        | 8.0            | 0.021                       | 0.042                                      | 54.12 | Bright non -adherent , Evolution of ammonia gas |

\* OPTIMUM CONDITION.

INFLUENCE OF pH  
GRAPH NO. 3.3



#### **4. INFLUENCE OF CURRENT DENSITY :**

**(TABLE 3.4, GRAPH 3.4)**

Current densities ranging from 0.5 to 2.5 A/Sq. dm are applied. At low C.D. (i.e.0.5) deposits obtained are bright & non- adherent. Probably because at low C.D. discharge of ions occur slowly. With increase in C.D. the quality of deposits improves and uniform fine grained and smooth deposits are obtained. This may be due to the fact that ,at such low current densities the rate of formation of nuclei is greater than the rate of growth of nuclei .Also percentage CCE increases with increase in C.D. .But at high current densities the solution in the vicinity of cathode becomes deficient of  $\text{Ni}^{2+}$  ions, as a result rough and treed deposits are obtained. Moreover, there is evolution of ammonia gas at higher current densities and thus percentage CCE decreases. Hence, for further work 1 A/Sq dm is taken as an optimum current density.

#### **5. INFLUENCE OF TEMPERATURE:**

**(TABLE 3.5 ,GRAPH 3.5)**

The temperature of the bath is varied from 5<sup>0</sup>c to 45<sup>0</sup>c. It is observed that the deposits obtained at low as well as at high temp. are dull, black-white and rough .However those obtained at moderate temperate are quite satisfactory. At lower temperature the deposits are dull and there is tendency towards treeing. With increase in temperature it decrease to remarkable extend. This might be due to increase in the mobility of metal ions with increase in temperature, so that the cathode film is more rapidly replenished which reduces the tendency towards treeing.

It is further observed that percentage CCE increases with increases in temp. This may be attributed to increase in ionic mobilities with temperature. Thus more metal ions diffuse in and out from the electrode at higher temperature resulting in the increase of percentage C.C.E. At higher temperature, percentage C.C.E decreases. It may be because of decreasing throwing power of bath.

The optimum condition selected is 25 °C

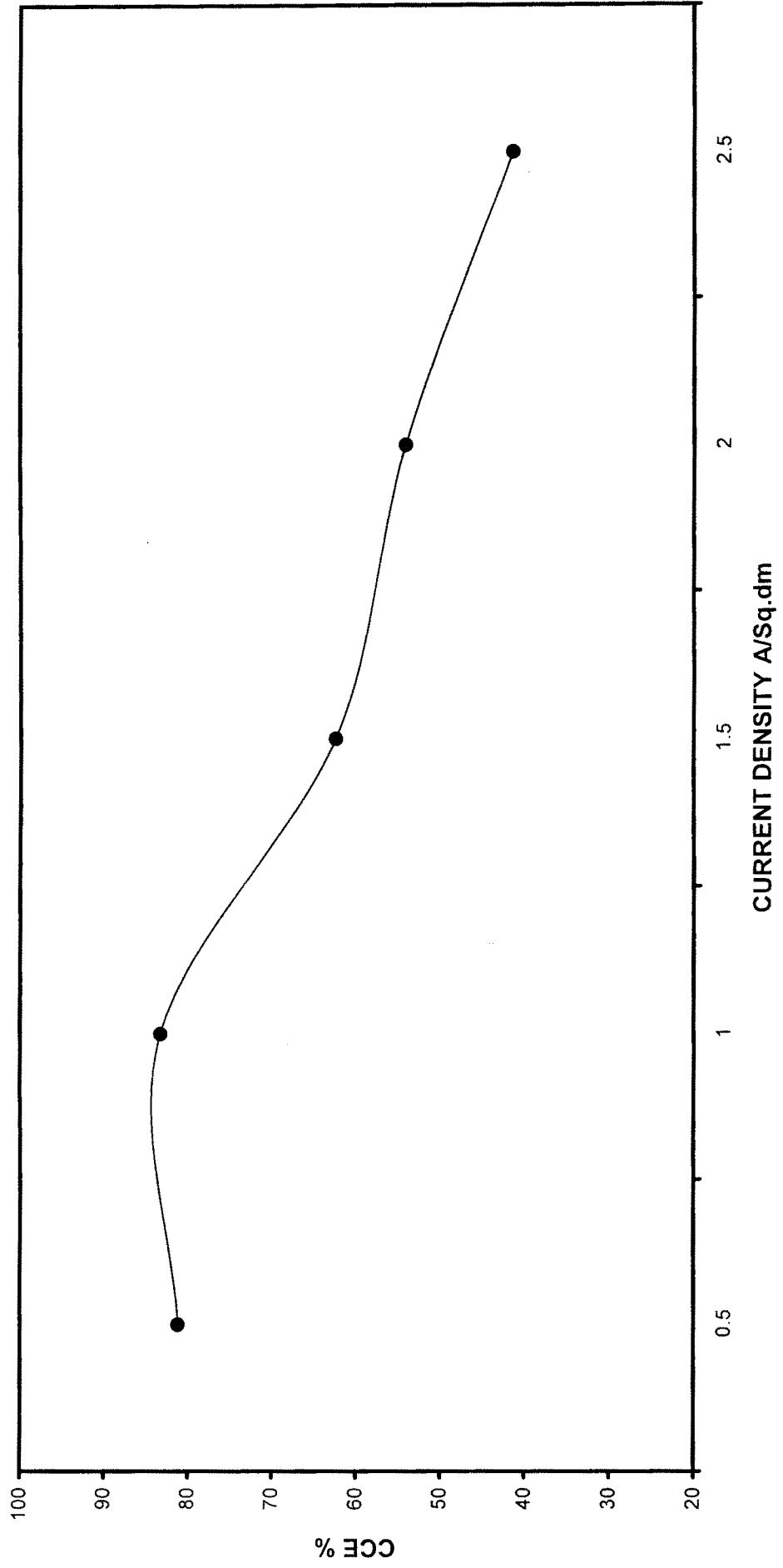
**TABLE NO. 3.4 INFLUENCES OF CURRENT DENSITY****OPERATING CONDITIONS :**

- 1) Nickel Sulphate – 2%
- 2) Ammonia – (25%) – 1.5 ml
- 3) Ammonium acetate – 9%
- 4) Total Volume – 100 ml
- 5) pH – 7
- 6) Temperature – 25<sup>0</sup>C
- 7) Inter electrode distance – 2 cm
- 8) Duration of electrolysis – 20 minutes

| Obs. No. | C. D. A/ sq. dm. | Wt. of Nickel deposited gms | Wt. of Copper deposited in Coulometer gms. | CCE % | Nature of deposit                          |
|----------|------------------|-----------------------------|--|-------|--|
| 1        | 0.5              | 0.018                       | 0.024                                      | 81.18 | Bright, non-adherent                       |
| 2        | 1.0 *            | 0.030                       | 0.039                                      | 83.27 | Uniform, bright, adherent                  |
| 3        | 1.5              | 0.030                       | 0.052                                      | 62.45 | Uniform, slightly rough                    |
| 4        | 2.0              | 0.035                       | 0.070                                      | 54.12 | Black-white, rough                         |
| 5        | 2.5              | 0.038                       | 0.100                                      | 41.43 | Non-satisfactory spongy, evolution of gas. |

\* OPTIMUM CONDITION.

INFLUENCE OF CURRENT DENSITY  
GRAPH NO. 3.4



**TABLE NO. 3.5 INFLUENCES OF TEMPERATURE****OPERATING CONDITIONS :**

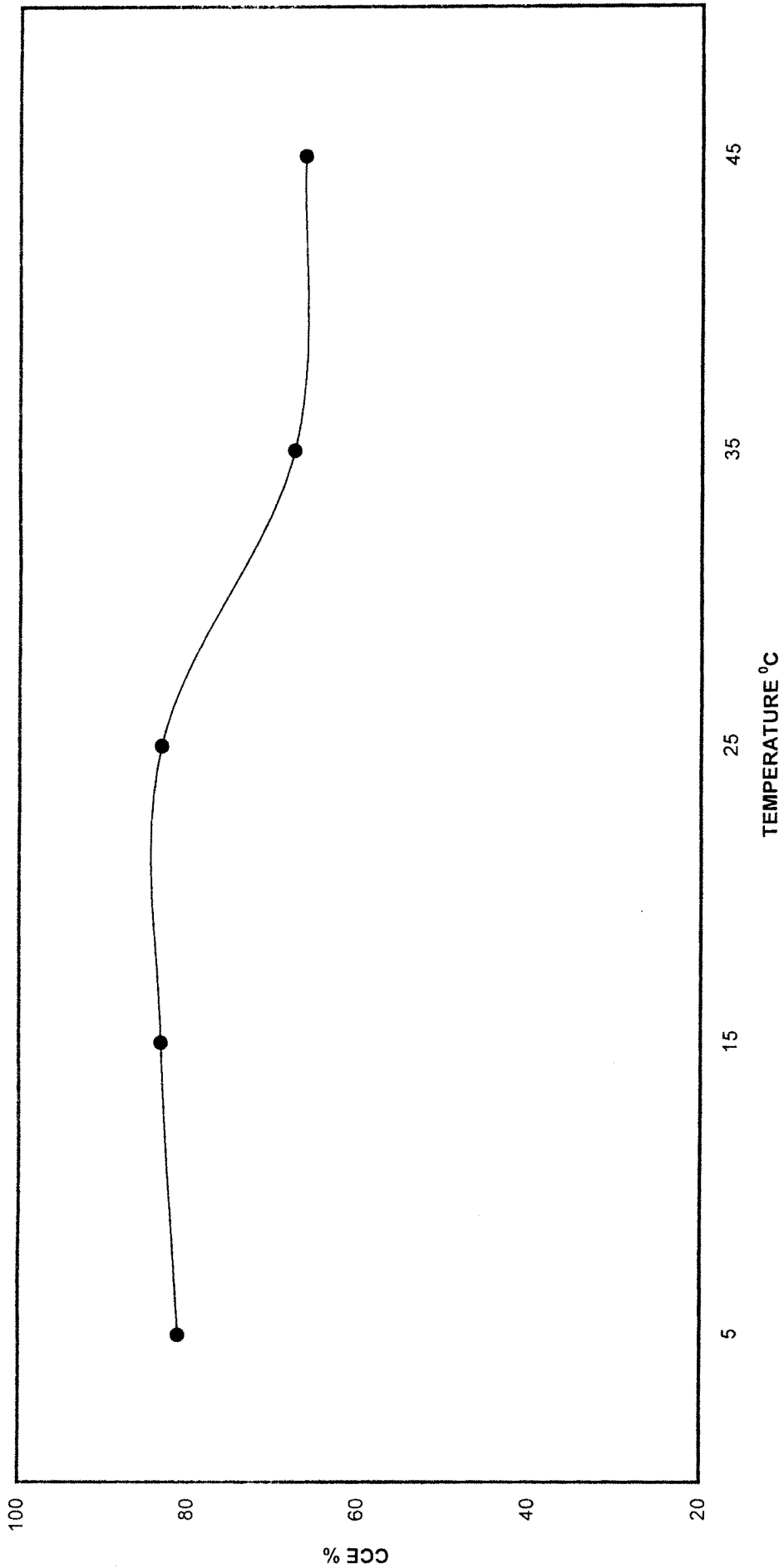
- 1) Nickel Sulphate – 2%
- 2) Ammonia – 1.5 ml
- 3) Ammonium acetate – 9%
- 4) Total Volume – 100 ml
- 5) pH – 7
- 6) C. D. – 1 A/sq dm.
- 7) Inter electrode distance – 2 cm
- 8) Duration of electrolysis – 20 minutes

| Obs. No. | Temp. °C | Wt. of Nickel deposited gms | Wt. of Copper deposited in Coulometer gms. | CCE % | Nature of deposit                 |
|----------|----------|-----------------------------|--|-------|-----------------------------------|
| 1        | 5        | 0.030                       | 0.040                                      | 81.18 | Milky white ,dull                 |
| 2        | 15       | 0.030                       | 0.039                                      | 83.27 | Uniform, bright, adherent         |
| 3        | 25*      | 0.030                       | 0.039                                      | 83.27 | Uniform, bright, adherent         |
| 4        | 35       | 0.025                       | 0.040                                      | 67.66 | Black-white                       |
| 5        | 45       | 0.027                       | 0.044                                      | 66.42 | Black-white,non-adherent at edges |

**OPTIMUM CONDITION.**



INFLUENCE OF TEMPERATURE  
GRAPH NO. 3.5



**TABLE NO 3.6 NICKEL SYSTEM**

The ranges over which the different parameters were studied and optimum conditions arrived at by experiments are summarised below –

| <b>Obs. NO</b> | <b>Parameters studied &amp; range</b>   | <b>Optimum Condition</b> |
|----------------|---|--------------------------|
| 1              | <b>COMPOSITION OF BATH</b><br>a) Conc. of NiSO <sub>4</sub><br>1 to 6 %<br><br>b) Conc. of Ammonium Acetate<br>6 to 33% | 2%<br><br>9%             |
| 2              | <b>pH OF THE BATH SOLUTION</b><br>6 to 8%   | 7                        |
| 3              | <b>C.D.</b><br>0.5 to 2.5 A/sq.dm.  | 1 A/sq.dm.               |
| 4              | <b>TEMPERATURE</b><br>5 to 45 °C  | 25 °c                    |

\* INTER ELECTRODE DISTANCE :- 2 cm.

\* DURATION OF ELECTROLYSIS :- 10 minutes.

## **6. INFLUENCE OF ADDITION AGENTS :**

**(TABLE NO. 3.7 , GRAPH NO. 3.7)**

Addition agents are widely used in plating industry as brighteners. Various substances like organic, inorganic and colloidal in nature are added to the plating solution in small quantities. With a view to see whether they produce any desirable effect on the nature of the deposit. Results of such observation are summarized in the table 3.6. It is observed that for number of addition agents the appearance of deposit improves (e.g. Urea, Agar agar ) .With the addition of urea, throwing power increases which can be tested quantitatively with bent cathode test ( Sec. 2.10).although appearance of the deposits improves considerably with addition above mentioned addition agents ,it is observed that percentage C.C.E. more or less remains the same except Agar agar where although deposits are satisfactory the percentage efficiency decreases to considerable extent .The opposite effect is observed with the addition of Ammonium molybdate and ammonium salicylate. The deposits obtained are not satisfactory and percentage C.C.E. also lowers.

The effect of addition agent with reference to cathodic polarisation is discussed in the section (4.2.6) .

**TABLE NO. 3.7 INFLUENCE OF ADDITION AGENTS****OPERATING CONDITIONS:-****VIDE – SUPRA TABLE NO. 3.6**

| Obs. No. | Addition Agent in traces | Wt.of nickel deposited gms. | Wt.of copper deposited in coulometer gms. | CCE % | Nature of deposit                           |
|----------|--------------------------|-----------------------------|---|-------|---|
| 1        | ----                     | 0.030                       | 0.039                                     | 83.27 | Uniform,white adherent(Reference plate)     |
| 2        | Ammonium molybdate       | 0.025                       | 0.040                                     | 60.74 | Black ,dull, patchy                         |
| 3        | Ammonium salicylate      | 0.022                       | 0.040                                     | 59.54 | Dull ,adherent, not satisfactory            |
| 4        | Glucose                  | 0.030                       | 0.039                                     | 83.27 | Uniform ,slightly dull than reference plate |
| 5        | Ammonical silver nitrate | 0.028                       | 0.040                                     | 75.77 | Slightly black,adherent                     |
| 6        | Urea                     | 0.029                       | 0.040                                     | 78.48 | Brightness increases,fine grained plate     |
| 7        | Agar Agar                | 0.017                       | 0.039                                     | 48.42 | Brilliant ,adherent satisfactory            |