CHAPTER-3

ELECTRODEPOSITION OF SINGLE METALS (NICKEL)

CHAPTER 3

" Electrodeposition of Single Metals " (Nickel).

Deposition of most metals from aqueous solutions especially at copper cathode takes place with different overvoltage and hence i_t essentially reversible potentials.

Overvoltage studies on the cathodic deposition of metals indicate that the deposition of metals takes place with small overvoltage. Metals such as Zinc, Copper and cadmium exibit low overvoltage, while metals of the Iron group i.e. Nickel, Iron and Cobalt, show higher over-voltages.

Had there been only the metal ions as the cations, these potentials would alone determine the process of deposition. However, in any aqueous solution hydrogen ions are also present, and consequenty two cathodic reactions are possible, the deposition of the metal and the evolution of hydrogen.

Hence it is of great interest to study the conditions under which a metal can be deposited from aqueous solution before evolution of hydrogen sets. If the potential required for metal deposition is that for the hydrogen, the products of electrolysis at the cathode will be the metal. If the reverse is true, cathodic liberation of hydrogen will occur. However, whereas the cathodic deposition of metals involves only the reversible metal electrode potentials, the liberation of hydrogen involves not only the reversible potential of the hydrogen electrode in the particular solution, but also the overvoltage of hydrogen at the material composing the cathode. In fact, it is because of this factor that many metals can be deposited, from aqueous solutions under conditions which in absence of overvoltage, which yeild hydrogen.

It can readily be shown that in a solution, the activity of hydrogen ions is 10^{-7}, and hence the potential for the reversible evolution of hydrogen would be --

$$E_{H_2} = - \frac{0.059}{1} \log_{10} \frac{1}{10^{-7}}$$

$$E_{H_2} = - 0.41 \text{ volt.}$$

The deposition of most metals above hydrogen in the electromotive series would be impossible,.

For example, the deposition potentials for metals such as Ni (-0.236 Volt) or Zn (- 0.44 Volt) suggest that hydrogen would preferentially be discharged first or along with the metals. But it has been shown that hydrogen overvoltage at copper or other cathodes is much above the stated value.

In order to discharge hydrogen from netural solution or even acidic ones containing Nickel or Zinc salts, a potential of about 0 - 1 volt would be necessary and as such the metals can easily be plated with relatively higher voltage.

3.2 Electrodeposition of Nickel from Ammonical Bath :

Nickel can be deposited from both acid and alkaline baths. The acid baths consist of sulphate, chlorides borates, sulphnic acid compounds, aliphatic unsaturated carboxylic compounds, carboxylic acid, crotonic acid, 2 - 5 diol, cinnamic acid and alkaline baths usually contain ammonia, alkaline citrate, cyanide and phosphate baths are also alkaline.

The alkaline baths have better throwing power and are therefore commonly used to plate irregulary shaped articles. The acid baths are used to plate wire and sheet metal stainless steel strips, where good throwing power is not required.

As indicated in introduction, nickel has high over voltage. Nickel can be deposited with a good cathode efficiencies from ammonical bath, i.e. alkaline bath.

It is the purpose of the present work, to obtain good quality deposit of nickel on copper from ammonical bath (alkaline) which is very simple to prepare.

Nickel is much used for "nickel plating" because of its silvery appearance, and it does not readily tarnish in air. Nickel plating is one of the most important electroplating industries. It is used as a protective coat on steel, zinc brass etc. because of its untarnishable property.

Nickel has the unique characteristic of improving one or more of the properties of most metals and alloys. It ranks ninth in the world's consumption of metals. Nickel and more than 3,000 of its alloys are used principally for resistance to corrosion in addition to strength and ductility.

Nickel was isolated by Cronstedt in 1751. The copper-nickel-zinc alloy known today as nickel silver was produced in England (1835). Nickel platting was developed by Faraday in 1843. Nickel is moderately strong, tough, ductile and nickel plates are resistance to corrosion in chemical fields and also in engineering field.

Commercially pure nickel and most of the high nickel alloy's are used for the fabrication of equipment in the chemical and process industries because of their corrosion resistance. Nickel has ability to protect it self against corrosion resisting.

The nickel is deposited from high sulphate bath, if particularly hard nickel deposits are required, then simple nickel sulphate is used. Nickel sulphate is so called as "single nickel salt". Nickel sulphate has been widely used as nickel compound. It is an important constituent of nickel-plating baths, and is generally used because of dip in enameling to strengthen adherence. It is commonly used as the constitutent of nickel-plating because it is cheap nickel salt and readily available.

In recent years the deposition of nickel has undergone considerable transformation as a result of specialised research into the conditions which control the properties of their deposits.

The following plating parameters have been studied in order to obtain a good quality, lustrous and fine deposits.

1) Composition of bath, with their concentrations.
2) Current density
3) Temperature
4) Duration of electrolysis
5) Electrode distance
6) Addition agents.

TABLE : 3.1 : The effect of concentration of $NiSO_4$ on the metal content and the percentage cathode current efficiency (CCE%) of the Nickel deposit.

Ammonia : 25 ml per 100 ml
Current Density : 2 amps per sq.dm.
Duration of Electrolysis : 20 minutes
Boric acid : 1 gm per 100 ml
Temperature : 30°c
Electrode distance : 4 cm.

Sr. no.	Concn.of Nickel Sulphate (gms. per 100 ml)	Wt.of copper deposited in coulometer (in gms.)	Wt.of Nickel deposited (gms).	CCE%	Nature of deposit.
1	5	0.081	0.031	41.9	Dull and black at the edges
2	10*	0.069	0.029	46.1	Uniform good,adherent and white bright
3	15	0.077	0.036	51.5	Quite satisfactory
4	20	0.076	0.042	60.7	Non adherent & black
5	25	0.081	0.052	69.7	-do-
6	30	0.065	0.051	84.3	-do -unsatisfactory

* Optimum condition.

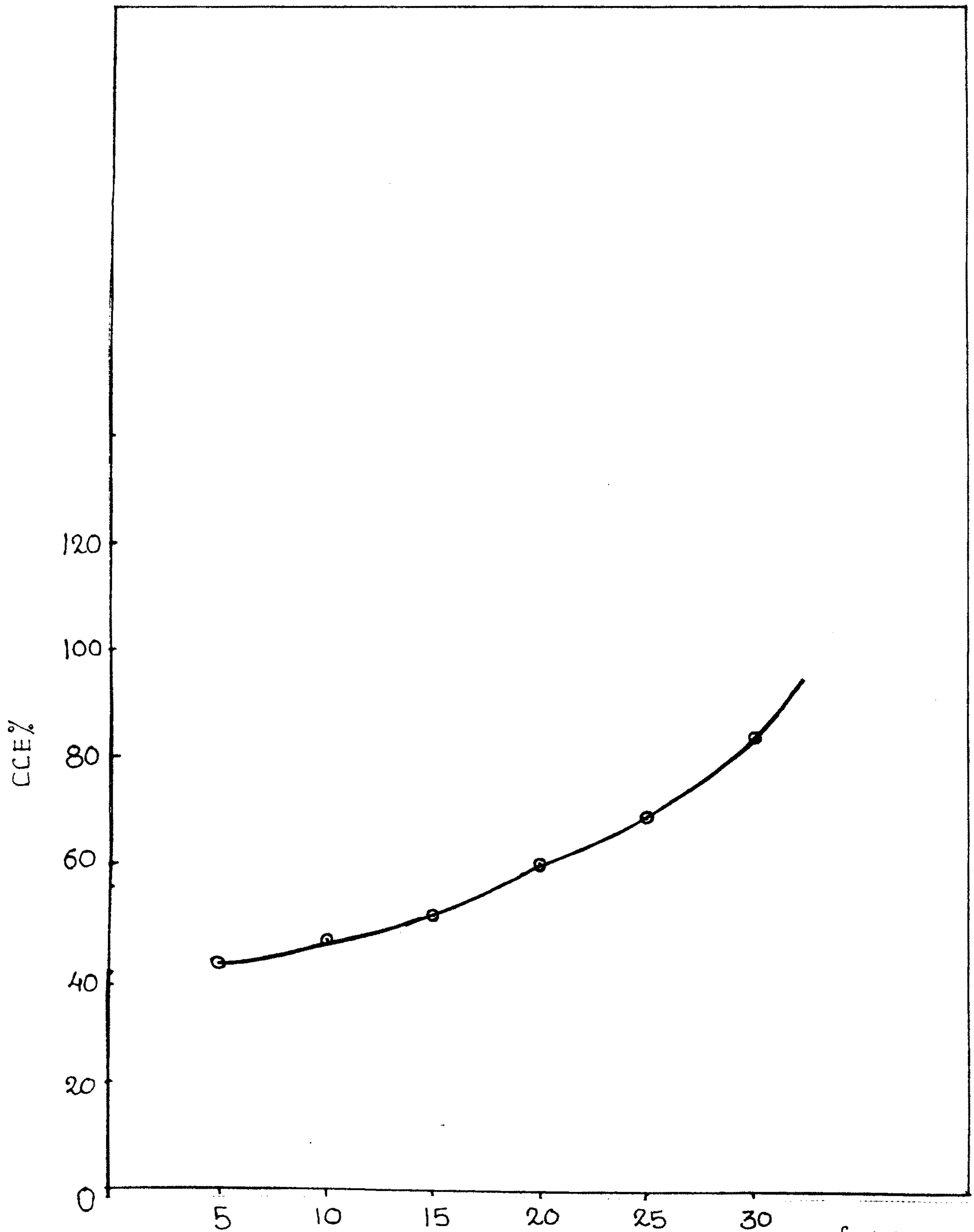


FIG: 1

Effect of conc. of $NiSO_4$ on the CCE% of Nickel deposit

TABLE NO.3.2 : The effect of concentration of Ammonia on the metal content and the percentage cathode current efficiency (CCE%) of the Nickel deposit.

Nickel sulphate : 10 gms per 100 ml — Boric Acid : 1 gm . per 100 ml

Current density : 2 amps. per sq. dm. — Temperature : $30^{o}c$

Duration of electrolysis : 20 minutes — Electrode distance : 4 cms.

Sr. no.	Concn. of NH_3 gml per 100 ml.	Wt. of copper deposited in coulometer gms.	Wt.of Nickel deposited gms.	Percentage CCE %	Mean	Nature of deposit
1	5	0.085	0.044	55.99		Dull deposit
2	10	0.070	0.038	58.72		Uniform but unsatis-factory
3	20	0.068	0.038	60.53		- do -
4	25*	0.062	0.036	62.81		Improvement in quality
5	30	0.070	0.045	69.54		Good & uniform deposit but black at the edges.
6	40	0.078	0.51	70.73		Non uniform & spa-ctchy.

* Optimum condition.

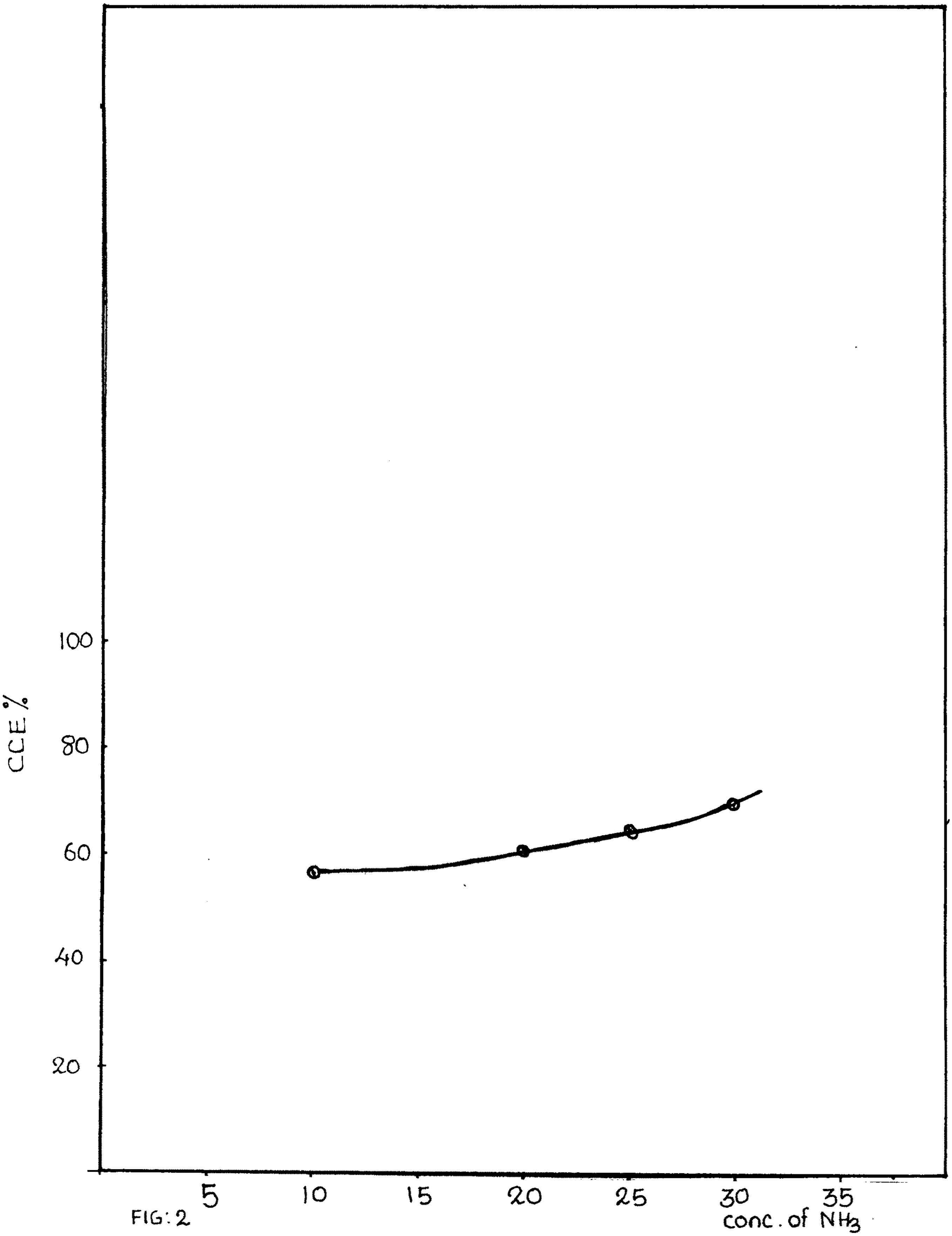


FIG: 2

Effect of Ammonia on cathode current efficiency of Nickel deposit

TABLE NO.3.3 : The effect of concentration of Boric Acid on the metal content and the cathode current efficiency (CCE%) of the Nickel deposit.

Nickel deposit : 10 gms per 100 ml
Ammonia : 25 ml per 100 ml
Current density : 2 amps. per sq. dm.
Temperature : $30^{o}c$
Duration of Electrolysis : 20 minutes
Electrode distance : 4 cms.

Sr. no.	Conc. of Boric Acid gms. per 100 ml.	Wt.of copper deposited in coulometer (gms.)	Wt. of Nickel deposited in gms.	Percentage CCE %	Nature of deposit
1	1 * ※	0.070	0.047	72.63	Uniform, bright, smooth & good
2	2	0.056	0.40	77.43	Uniform but slightly dull
3	3	0.51	0.039	82.82	Uniform but black at the edges
4	4	0.062	0.046	88.01	Dull deposit, unsatisfactory Patchy
5	5	0.065	0.055	95.53	-do-

* Optimum condition.

※ Microphotograph - 1

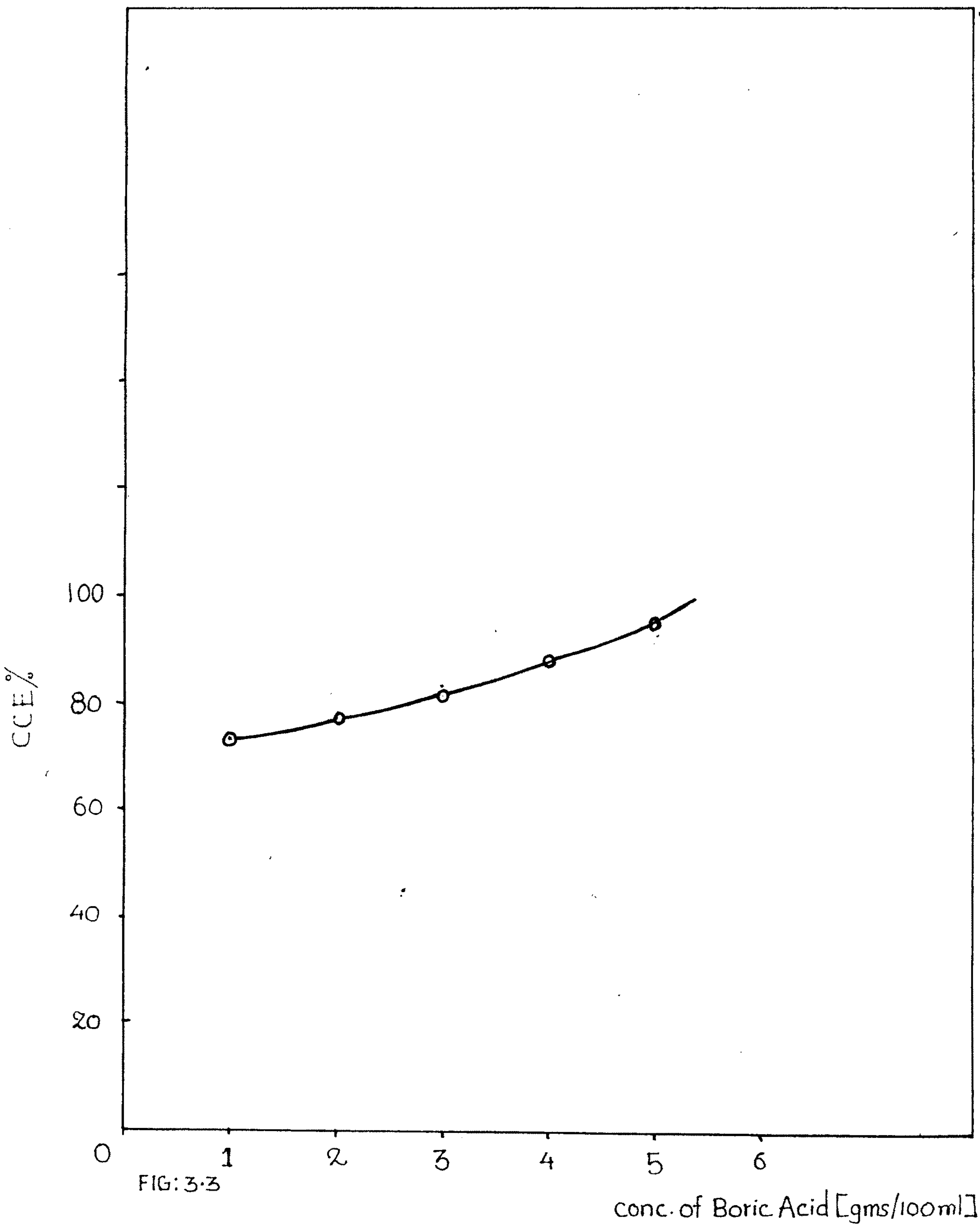


FIG: 3·3

TABLE NO.3.2 : The effect of current density on the metal content and the percentage cathode current efficiency (CCE%) of th Nickel deposit.

Nickel sulphate : 10 gms. per 100 ml — Ammonia : 25 ml per 100 ml

Boric acid : 1 gm . per 100 ml — Temperature : $30^{o}c$

Duration of electrolysis : 20 minutes — Electrode distance : 4 cms.

Sr. no.	Current density amp.per sq.dm.	Wt.of copper deposited in coulometer in gms.	Wt. of Nickel deposited in gms.	Percentage CCE %	Nature of deposit
1	1	0.089	0.030	86.46	Unsatisfactory
2	1.5	0.077	0.041	57.60	Uniform, dull deposit
3	2	0.068	0.041	65.22	Uniform, bright & smooth deposit
4	2.4 * ※	0.065	0.045	74.89	Bright, adherent, uniform and good deposition.
5	3	0.065	0.050	83.21	Unsatisfactory, black at the edges
6	4	0.076	0.060	85.40	-do-

* Optimum condition.

※ Microphotographs - 2

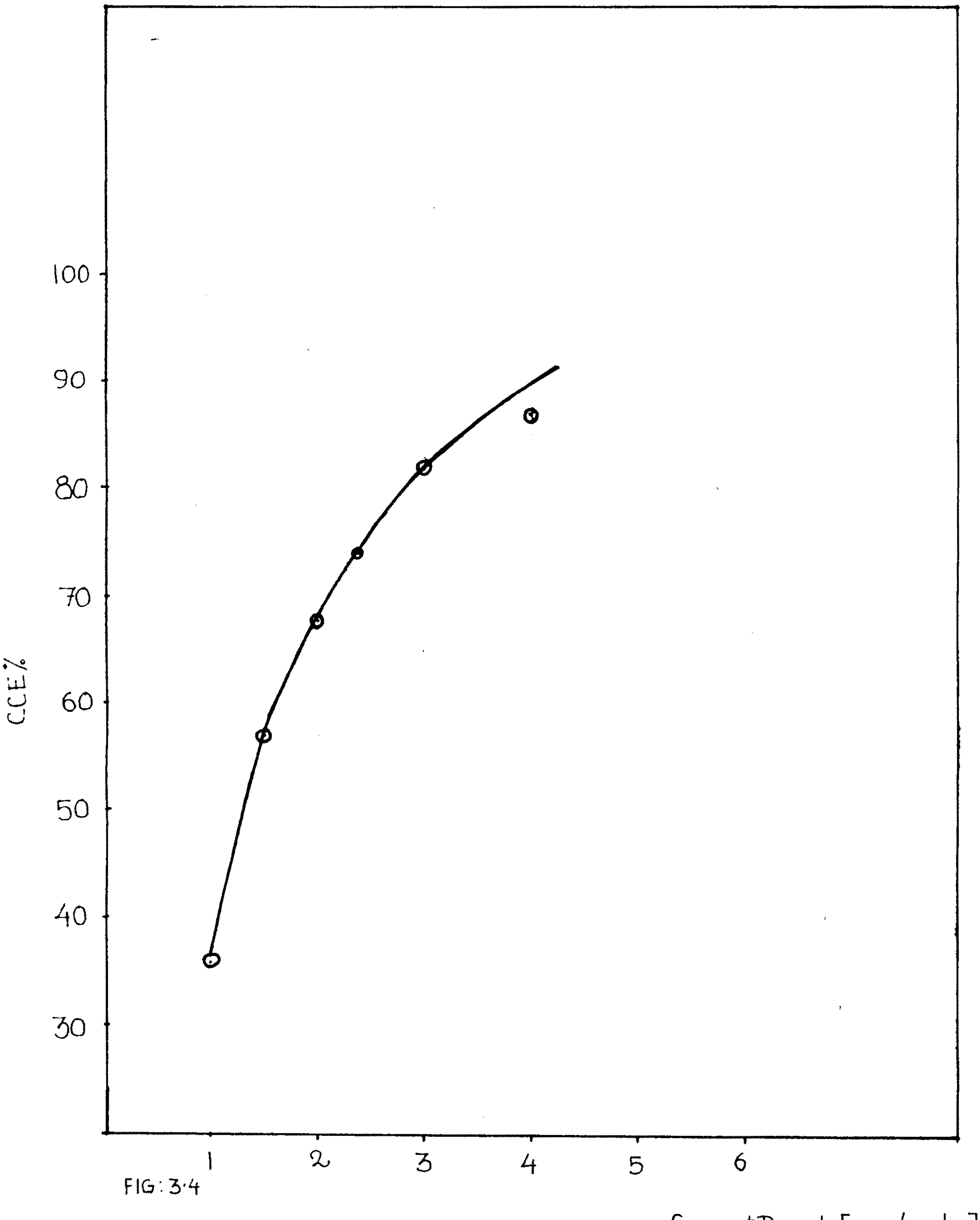


FIG: 3·4

Effect of Current Density on CCE% of Nickel Deposit

TABLE NO.3.5 : The effect of temperature on the metal content and the percentage cathode current efficiency (CCE%) of the Nickel deposit

Nickel Sulphate : 10 gms. per 100 ml. Ammonia : 25 ml per 100 ml.

Boric Acid : 1 gm. per 100 ml Current density : 2.4 amp. per sq.dm.

Duration of Electrolysis : 20 minutes Electrode distance : 4 cms.

Sr. no.	Temp. $\theta^{o}c$	Wt.of copper deposited in coulometer in gms.	Wt. of Nickel deposited in gms.	Percentage CCE	Nature of deposit
1	10	0.060	0.047	84.74	Not uniform
2	20	0.058	0.041	76.47	Good deposit but not uniform
3	30 * ※	0.072	0.038	57.09	Bright, adherent, uniform & smooth deposit.
4	40	0.070	0.032	49.45	Uniform deposit but black at the edges.
5	50	0.064	0.027	45.63	Not satisfactory.

* Optimum condition.

※ Microphotograph - 3

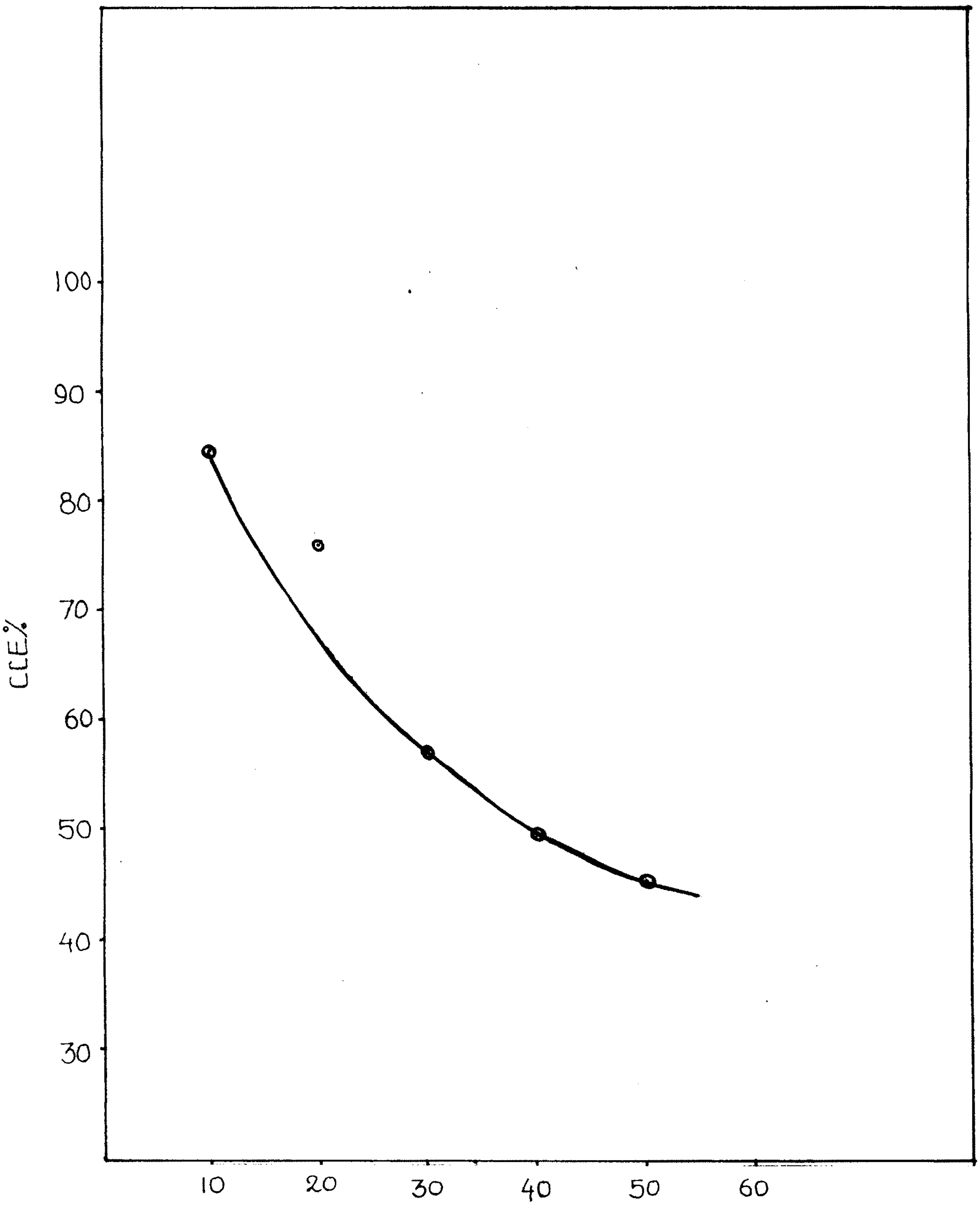


FIG:5

Effect of temparature on CCE% of Nickel Deposit

TABLE NO. : 3.6 The effect of duration of electrolysis on the metal content and the percentage cathode current efficiency (CCE%) of the Nickel deposit.

Nickel sulphate : 10 gms. per 100 ml — Ammonia : 25 ml per 100 ml

Boric Acid : 1 gm per 100 ml — Current density : 2.4 amp. per sq. dm.

Temperature : 30^{o}c — Electrode distance : 4 cms.

Sr. no.	Duration of Electrolysis in mins.	Wt. of copper deposited in coulometer gms.	Wt. of Nickel deposited gms.	Percentage CCE %	Mean	Nature of deposit
1	5	0.025	0.013	56.12		Smooth but dull deposit
2	10	0.021	0.012	61.81		-do-
3	15	0.038	0.023	65.47		slight improvement
4	20 * ⁂	0.037	0.024	70.16		Uniform,bright & Good deposit.
5	25	0.037	0.026	73.1		Smooth & good deposit but black at edges
6	30	0.039	0.027	75.1		-do-

* Optimum condition.

⁂ Microphotograph - 4

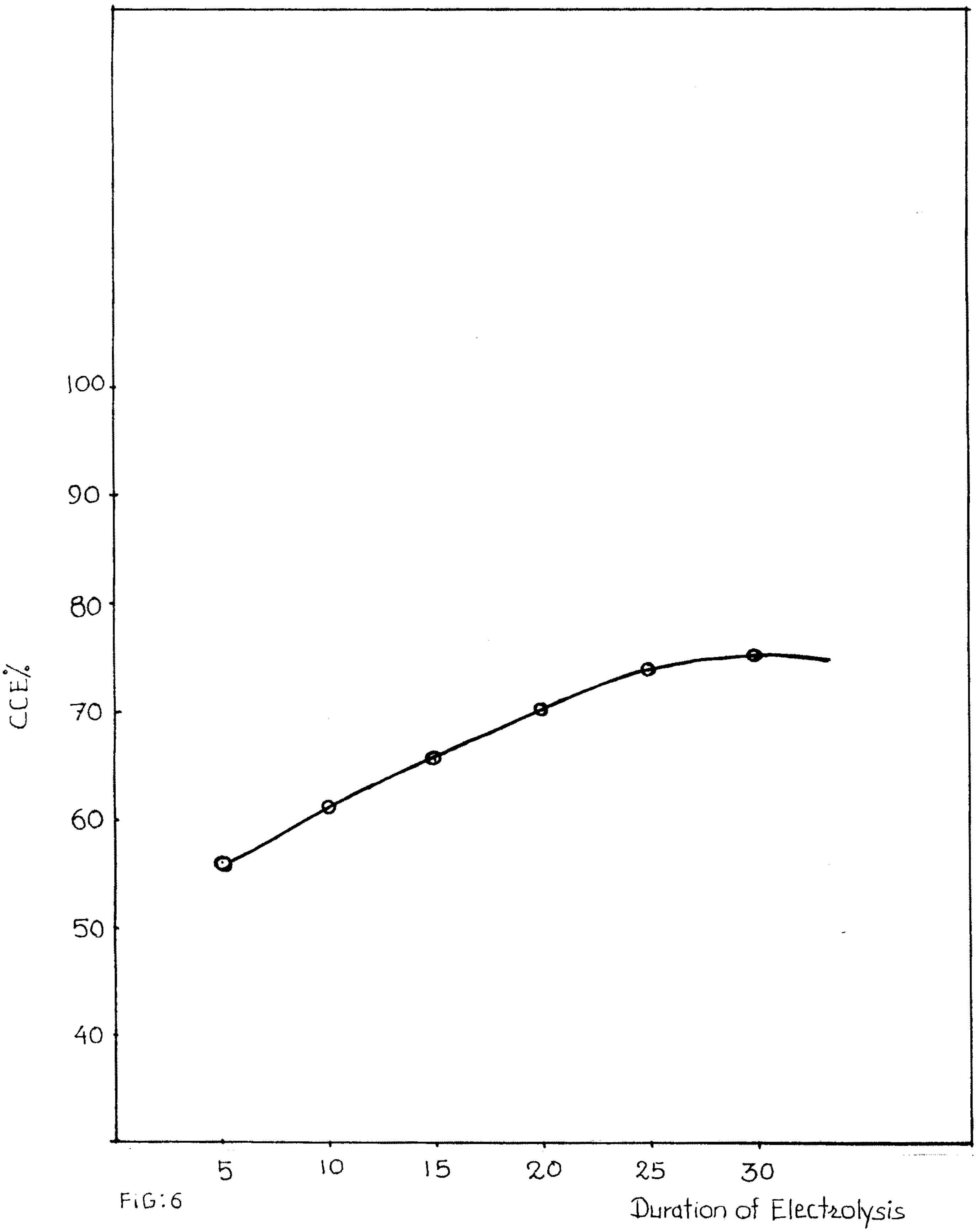


FIG:6

Effect of duration of electrolysis on CCE% of Nickel Deposit

TABLE NO.3.7 : The effect of Electrode distance on the metal content and the percentage cathode current efficiency (CCE %) of the Nickel deposit.

Nickel sulphate : 10 gms. per 100 ml — Ammonia : 25 ml per 100 ml

Boric acid : 1 gm per 100 ml — Current density : 2.4 amp. per sq.dm.

Duration of electrolysis : 20 minutes — Temperature : $30^{o}C$

Sr. no.	Electrode distance cms.	Wt. of copper deposited in coulometer gms.	Wt.of Nickel deposited gms.	Percentage CCE %	Nature of deposit.
1	1	0.045	0.034	81.78	Smooth deposition but blackish
2	2	0.055	0.035	69.07	- do -
3	3	0.032	0.017	57.48	Slight improvement
4	4 *	0.063	0.023	49.62	Bright, good & uniform deposit
5	5	0.067	0.0	46.12	White dull deposit.

* Optimum condition.

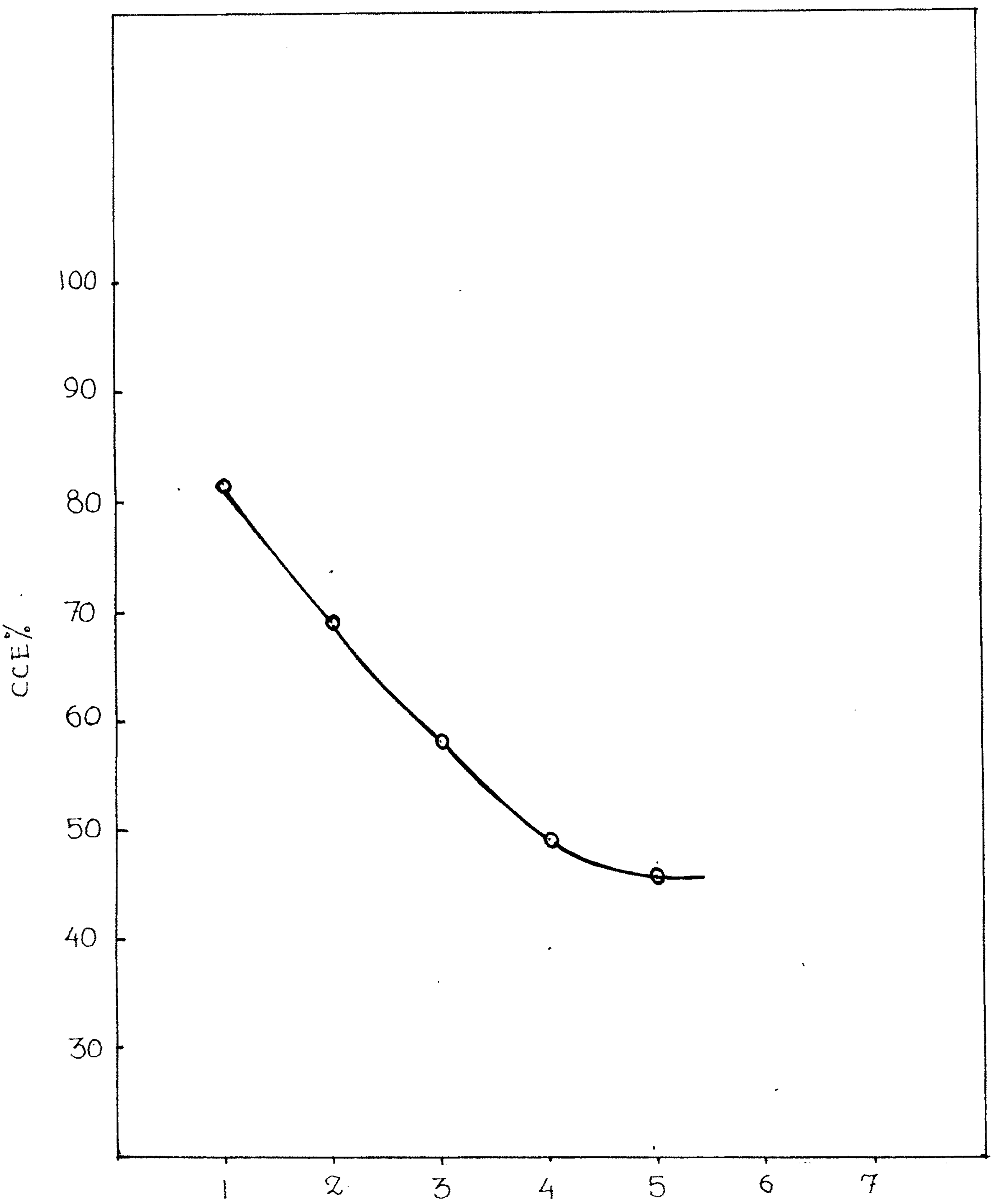


FIG: 7

Effect of electrode distance on CCE% of Nickel Deposit

TABLE NO.3.8 : The effect of addition agents on the metal content and the percentage cathode current efficiency (CCE %) of the Nickel deposit.

Nickel sulphate : 10 gms. per 100 ml

Ammonia : 25 ml per 100 ml

Boric Acid : 1 gm per 100 ml

Current density : 2.4 amp. per sq. dm.

Duration of Electrolysis : 20 minutes

Electrode distance : 4 cm.

Temperature : 30°C

Sr. no.	Addition Agent	Amount per 100 ml gms.	Wt. of copper deposited in coulometer gms.	Wt. of Nickel deposited gms.	Percentage CCE %	Mean	Nature of deposit
1	Agar	0.5	0.075	0.068	98.09		Not satisfactory
2	Gelatine	0.5	0.065	0.059	99.02		Smooth, bright uniform.
3	Gum * ⁂	0.5	0.066	0.048	78.68		Smooth, bright, good
4	Glucose	0.5	0.071	0.056	85.33		Uniform, deposit, Slightly yellowish.
5	Formal dehyde	1 ml	0.074	0.057	83.22		Not satisfactory

⁂ Microphotograph - 5

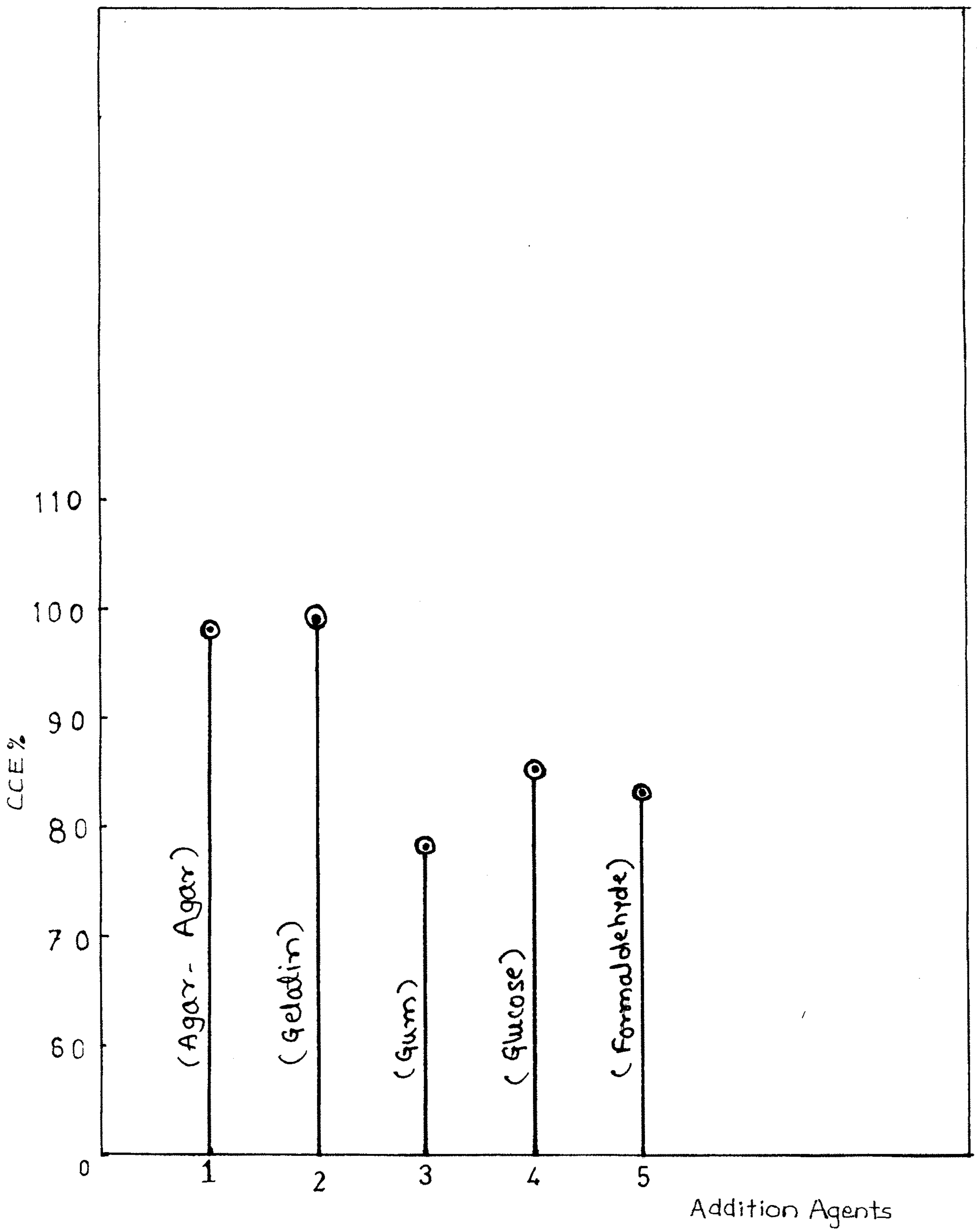
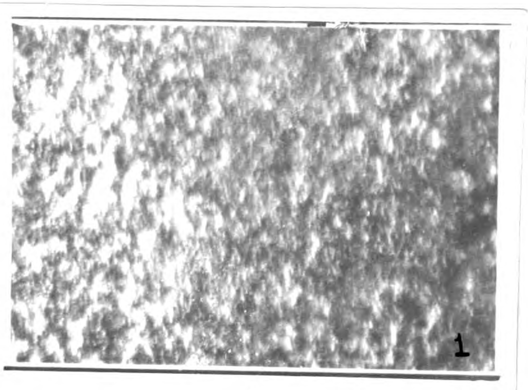
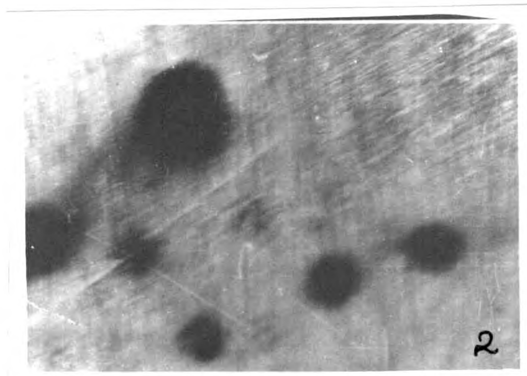


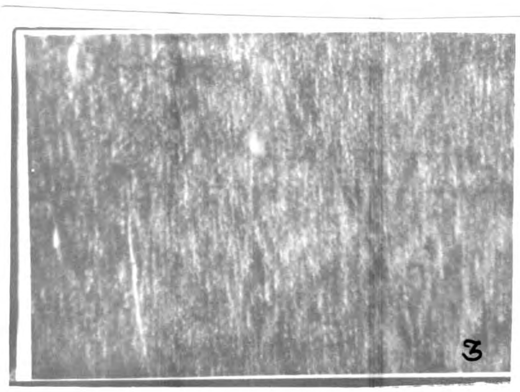
FIG:3·8 Effect of Addition agents on CCE % of Nickel deposit



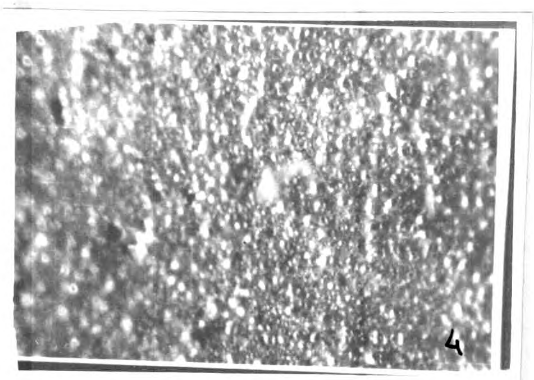
1



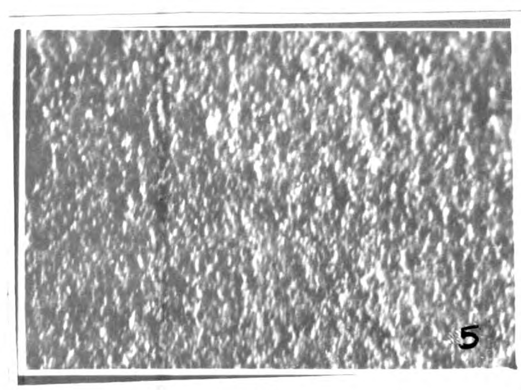
2



3



4



5

[Microphotographs (Nickel)]
1-5

SUMMARY

Electrodeposition of Nickel from Ammonical Bath (Optimum conditions).

The influence of the physico - chemical factor upon the nature and magnitude of the Nickel deposit from Ammonical bath has been shown in the previous table (No. 3.1 to 3.8) and fig (3.1 to 3.8). The ranges over which the parameters were studied and the optimum conditions arrived at by experiments are summerised below :

Parameters studied and Range	Optimum Condition.
1. Composition of the bath.	
a) Conc. of $NiSO_4$, 5-30 gms. per 100 ml. of the solution.	- 10 gms per 100 ml of the solution.
b) Concn. of Ammonia, 5-40 ml per 100 ml of the solution.	- 25 ml per 100 ml of the solution.
c) Concn. of Boric acid, 1-5 gm per 100 ml of the solution.	- 1 gm. per 100 ml of the solution.
2. Current deruity - 1-4 amps per sq. dm	- 2.4 amps. per sq. dm.
3. Temperature 10^0c - 50^0c	- 30^0c
4. Duration of Electrolysis 5-30 minutes.	- 20 minutes.
5. Electrode distance 1 - 5 cms.	- 4 cms.

3.3 : Results and discussion for Nickel :
(Table 3.1 - 3.8)

The platting variables had a marked effect on the quality and composition of the deposits and also on the CCE. The effects of different variables are explained as below :

1. Composition of Bath:

a) Effect of Nickel sulphate concentration :

(Table - 3.1 and Fig. No. 3.1)

Effect of Nickel sulphate concentration was studied between 5 and 30 gms. per 100 ml. of the solution. Dull, spongy, non-adherent as well as uniform, smooth, bright and good depositions were obtained at different concentrations. At low concentration dull, non adherent & black deposits were obtained. This indicates that neither too low or high concentration of Nickel sulphate was suitable for uniform, bright, smooth, good quality depostion. It was noticeable that, as the concentration of Nickel sulphate increases, at the same time deposit also increases. The cathodic current efficiency (CCE) was also increased with increase in the concentration of Nickel sulphate (i.e. from 41.9 to 84.3 at 5 gms to 30 gms). The optimum condition for the concentration of Nickel sulphate was 10 gms. per 100 ml of Nickel sulphate, which gives uniform, bright, and adherent deposition of Nickel.

b) Effect of concentration of Ammonia :
(Table No. 3.2 and Fig. No. 3.2)

The bath used for the deposition of Nickel was Ammonical. Here, ammonia was introduced to the bath as a solvent. The amount of Ammonia has been varied from 5 ml to 40 ml. per 100 ml. For low concentration of Ammonia it gives dull deposit, while at high concentration it gives spatchy deposit. The amount of Nickel sulphate was same for over all concentration. As the concentration of ammonia increases the deposition and CCE increased. The optimum condition was obtained at 25 ml of Ammonia per 100 ml.

c) Effect of concentration of Boric Acid :
(Table No. 3.3 and Fig. 3.3)

Boric acid has no marked effect on the Nickel deposit and also on CCE % with increase in concentration of Boric acid, the CCE % was found to increase slightly. At low concentration of Boric acid, the deposits were uniform, bright smooth and good. However at higher concentration of Boric acid, the depositions were dull, patchy and blackish at the edges. The optimum condition for Boric Acid concentration was 1 gm per 100 ml.

4) Effect of Current density :
(Table No. 3.4 and Fig. 3.4)

The deposits of Nickel were studied in the range of current densities from 1 amp/sq.dm to 4.0 amp/sq. dm. In the lower region of current density (1 amp/ sq. dm) the deposits were not satisfactory but with increase in current density up to 2.4 amp/sq.dm, uniform, smooth, bright and adherent deposits were obtained. Above this current density, the deposits were not satisfactory. They are blackish at the edges. This is always observed at high C.D. due to rapid depletion of the metal ions from the cathode. However, it was observed that as the current density increases, CCE also increases. The optimum condition for current density was found to be 2.4 amp per sq.dm., which gives bright, adherent, uniform depotion.

5) Effect of Temperature
(Table No.3.5 and fig. no.3.5)

In general anincrease in temperature, decreases the polarisation of the more noble metals relatively more than the polarisation of the less nobel metals and causes an increase in the crystal size. The temperature range was studied between 10°c to 50°c under optimum conditions of both composition, and current density. At very low temperature deposits obtained were not uniform. However by increasing the temperature, good deposits were obtained. The influence of temperature is caused by greater solubility and dissociation of the metal salt. At high temperature the mobility of the metal ions increases and there is decrease in viscosity of the solution. The depositions obtained at temperature greater than 30°c. were with black edges. At high temperature 50°c dull white i.e. unsatisfactory deposits were obtained. With increasing the temperature, the Nickel content in deposit decreases hence CCE% as also decrease with increasing temperature.

6) Effect of duration of Electrolysis :
(Table No.3.6 and Fig. No.3.6)

Duration of electrolysis varied from 5 to 30 minutes, under optimum conditions. With increasing the duration of electrolysis, the Nickel content in the deposit was increased from 0.013 gms to 0.027 gm. and CCE% was also increased from 56.12% to 75.1%. Therefore with increase in duration, the CCE% increases upto 70.1% rapidly and then slightly, and finally it remains constant.

At optimum condition i.e. 15 minutes, the deposit obtained was slightly improved but at 20 minutes the deposit was very superior, it was uniform and bright. At 25 minutes and 30 minutes i.e. at longer times, the deposits were with black edges. So the optimum condition was that of 20 minutes.

7) Effect of variation of Electrode distance :
(Table No.3.7 and Fig. No.3.7)

The distance between the electrode i.e. Anode and cathode was varied between 1.0 and 5.0 cm. It was observed that, the deposit as well as the CCE% were changed appricieably. At minimum electrode distance the deposit was smooth but blackish, as the distance between the electrodes was increased, there was slight improvement in the quality of deposit. At electrode distance of 4 cm.the deposit was observed to be bright, good and uniform. At maximum electrode distance the deposit was dull.

The optimum condition was that of 4 Cm.

8) Effect of Addition agents :
(Table No.3.8 and Fig.No.3.8)

It is well known that even small quantities of certain substances added to a depositing, solution markedly influence the structure of the deposit. The presence of very small amounts of colloidal matter, or of certain organic compounds, often results in the production of a smooth, fine-grained and microcrystalline deposit. These colloidal matters are called as addition agent , which can be well defined as substances which, added to deposition baths in traces to produce a change in the charactor of the deposit. Minute quantities of the addition agents are sufficient to cause a profound change in the form of the deposit, an excess of the substance may give loose and powdery or britle deposits. Among the materials used as addition agents the following may be mentioned; gelatine, agar, glue, various gums, rubber, rasein, sugars, camphor, alkaloids, dye stuffs, rubber; the action of any particular substance is often specific and depends on the nature of the metal and the electrolyte.

The addition agents are generally surface active substances and they are probably adsorbed on the crystal nuclei, thus preventing the growth. The deposits obtained in the presence of an addition agent have been found to contain a certain proportion of the latter, in agreement with the view that the added substance is adsorbed.

The addition agents listed in Table 8, were introduced singly to the bath under optimum conditions and the effect was studied, Agar-Agar, gelatine, Gum, Glucose and formaldehyde were introduced to the deposition bath. However deposits were not satisfactory in presence of Agar-Agar & formaldehyde. The deposits in presence of gelatine,gum have been found to be smooth, bright and good.

Nickel generally forms smooth deposits in sulfate or chloride bath even in the absence of addition agents. A gelatinous or colloidal form, can cause the deposit to become smooth and fine grained.